

GRAVIMETRIC AND VISCOELASTIC
INVESTIGATIONS OF ELECTROACTIVE FILMS

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Gravimetric and Viscoelastic Investigation of Electroactive Films

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Gravimetric and viscoelastic studies of thin electroactive polymer films and self-assembled monolayers were carried out using (non)-electrochemical techniques; notably cyclic voltammetry, EQCM and crystal impedance. Mobile species dynamics accompanying film redox switching due to thermodynamic and electroneutrality constraints were theoretically modeled and experimentally determined.

In a novel approach, 3D visual models of solvent and ion transfers under mixed control of thermodynamic and kinetic conditions were described. For the identification of change in behaviour at partial conversion during film redox transformations, flux ratio representations were introduced. Applications of the theoretical models to polyaniline data in EQCM experiments revealed that film solvent population was in equilibrium on the experimental timescale but showed thermodynamic non-ideality. Mass and charge responses of polyaniline gravimetric data were described by a mechanism in which electroneutrality maintenance was satisfied by a mixed transfer of proton and anion.

Adsorption/desorption mechanisms of dendrimer on flavin-functionalised surfaces were gravimetrically determined. The energetics and isotherm models of the adsorption/desorption process were investigated. Frumkin model was found to best fit to the experimental data and site-site interaction parameter was extracted.

Viscoelastic investigations of polyaniline in electrochemical systems were studied. The effects of different anions on film rheological properties during deposition and redox cycling were explored. Shear moduli data were extracted as functions of potential, temperature and timescale using TSM resonator. In an unprecedented manner, macroscopic viscoelastic properties of polyaniline films were described at a molecular level using WLF, Rouse-Zimm, and Activation models. The “time-temperature superposition” principle was applied and the master relaxation curve was constructed. In correlation between solvent content and film structural dynamics, the energetics of solvation were calculated. From thermal dependent viscoelastic responses of the film, glass transition temperature, thermal expansion coefficient and fractional free volume of polyaniline were determined.

Memorandum

Work presented in this thesis is original except where reference or acknowledgement has been made. The project was carried out in the department of chemistry, University of Leicester between January 2003 and April 2007. The method of study used throughout this work was part time. The thesis is based on the following publications:

List of Publications:

1. A. R. Hillman, M. A. Mohamoud, S. Bruckenstein, “*Modelling Mobile Species Dynamics within Electroactive Films under Mixed Thermodynamic and Kinetic Control*”, *Electroanalysis*, 17 (2005) 1421.
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3. M. A. Mohamoud, A. R. Hillman, “*Viscoelastic Phenomena During Electrochemical Deposition of Polyaniline Films*”, *J. Solid State Electrochem.* (2007), in press.
4. M. A. Mohamoud, A. R. Hillman, “*The Effect of Anion Identity on the Viscoelastic Properties of Polyaniline Films during Electrochemical Film Deposition and Redox Cycling*”, *Electrochimica Acta*, (2007), in press.
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Chapter One

Introduction

1.1 Overview

In this thesis, the characterisation of surface modification of conventional electrodes with organic functional materials is the central topic investigated. In modern interfacial electrochemical research, conventional electrodes (e.g. Au, Pt, GC and Ag) have widespread use in many disciplines (e.g. batteries, electroanalytical) but lack specificity and selectivity. With a surface modification, however, one can effectively control and tailor the structure and properties of electrode surfaces at will [1, 2]. This novel approach has enabled electrochemists to design new types of electrodes with a variety of materials which have the desired characteristics and properties. The first generation of modified electrodes, mostly monolayers, was reported by Murray and co-workers in 1975 [3-10]. Since then the research on modified electrode activities has extensively taken diverse directions (mostly polymers) in both theoretical and practical aspects [11-13].

This new class of electrodes (so-called modified electrodes) differ from the conventional inert electrodes in various respects [14, 15]; (i) a thin layer of a foreign material is immobilised on the electrode surface via which a greater control of the electrode surface characteristics and reactivity can be achieved, (ii) the coating of the electrode surface with these materials prohibits direct contact between the bare underlying electrode and the bathing solution in such a manner that any electrochemical reaction will take place in/at the adsorbed layer, (iii) and hence the physicochemical properties of the modifying layer dictate the desired structural and chemo-physical properties of the resultant modified electrode. Therefore, a careful choice of the modifier can enable one to tune the selectivity, reactivity and specificity of the modified electrode properties [14, 15].

In general, the type of modifying layers often employed for surface modification of electrodes can be grouped into three main categories [14]; (i) inorganic thin films such as clays, zeolites and other microcrystalline-structured materials, (ii) self-assembled monolayers such as thiols and sulfides/disulfides used as chemisorption agents for the derivatisation of gold and other electrode surfaces [16, 17], and (iii) various types of multilayer polymer films such as polyaniline, polypyrrole, polythiophene and poly(vinylferrocene) [18]. The research carried out in this thesis is primarily concerned with the latter two categories; among these, the polymer modified electrodes are of the prime interest.

1.2 Self-Assembled Monolayer Modified Electrodes (SAM-ME)

The simplest form of electrode surface modification can be achieved by using functionalised organic materials that spontaneously adsorb (self-organise) on bare electrode surfaces. Through chemisorption, these materials form thin monolayer films immobilised on electrode surfaces known as “self-assembled monolayers (SAMs)” (see Fig. 1.1). Most widely studied systems of SAMs include alkanethiolates on gold electrodes (through Au-S interaction) [19-21], silanes on hydroxyl terminated surfaces (e.g., Al/Al₂O₃, ITO, PtO) [22] and organic acids or bifunctional amphiphiles on metal or metal oxide surfaces [23-26].

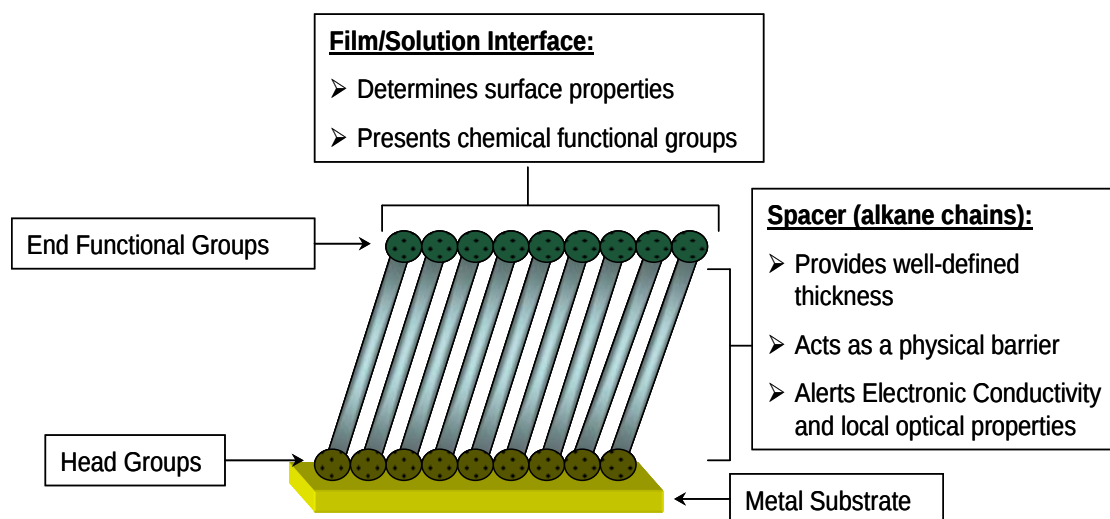


Fig. 1.1: schematic representation of Self-Assembled Monolayer Modified Electrodes

The immobilisation process of SAMs on electrodes can often be achieved by simply immersing the electrode to be modified in a solution of the monolayer species (typically at a millimolar concentration) for over 24 h period [19, 21]. The kinetics of

the SAM adsorption goes through two-step process [27, 28]. In the initial step a fast growth of the SAMs (80-90 % of the final value of thickness) occurs within the first 2-3 minutes. This is followed by a slower step in which film thickness and wettability approach an equilibrium value in an approximate timescale of 10 – 20 h [21]. The structure (packing and order) and the properties of SAMs are influenced by many factors such as the chain length, the functionality of the end group, nature of the solvent, immersion time and the surface morphology of the underlying substrate (electrode).

The novelty of SAMs lies with the ability to control the end-group functionalities in order to form chemically or biologically reactive layers [2]. This can bring about specific purpose-built devices for various potential applications (e.g., biological sensors). Another useful aspect of SAMs is the ease of preparation of mixed SAMs that can offer compositional and topographical variations in the film architecture and can also minimise steric hindrance effects [14].

In this thesis project, we used mixed SAMs of flavin disulfide and butyl disulfide for the purpose of studying “lock and key” mechanism of DAP-dendrimer adsorption and its subsequent desorption (via the action of the small molecule, thymine). The energetics of adsorption/desorption and various isotherms of the system will be explored in chapter 9.

1.3 Polymer Modified Electrodes (PME)

The surface modification of electrodes with polymeric materials was first reported by Merz and Bard using poly(vinylferrocene) [13] and Miller and van de Mark working on poly(4-nitrostyrene) [12]. Since then a flood of publications from other research groups has rapidly spread on the subject of polymer modified electrodes with the use of diverse materials.

Quite generally, polymer modified electrodes have significant advantages over the bare or monolayer modified electrodes in many practical aspects. In polymer modified electrodes, the reaction occurs in a 3D zone rather than 2D interfaces in contrast to bare and monolayer modified electrodes [18]. This permits a far greater

species flux into the bulk of the polymer films attached to the electrode surfaces (see Fig. 1.2). As a result, the electrochemical signals from charging of films containing multiple monolayers of redox sites are larger and easier to detect and study [14]. In addition, polymer modified electrodes are chemically more stable and can survive larger numbers of oxidation state turnovers than do monolayer films [14].

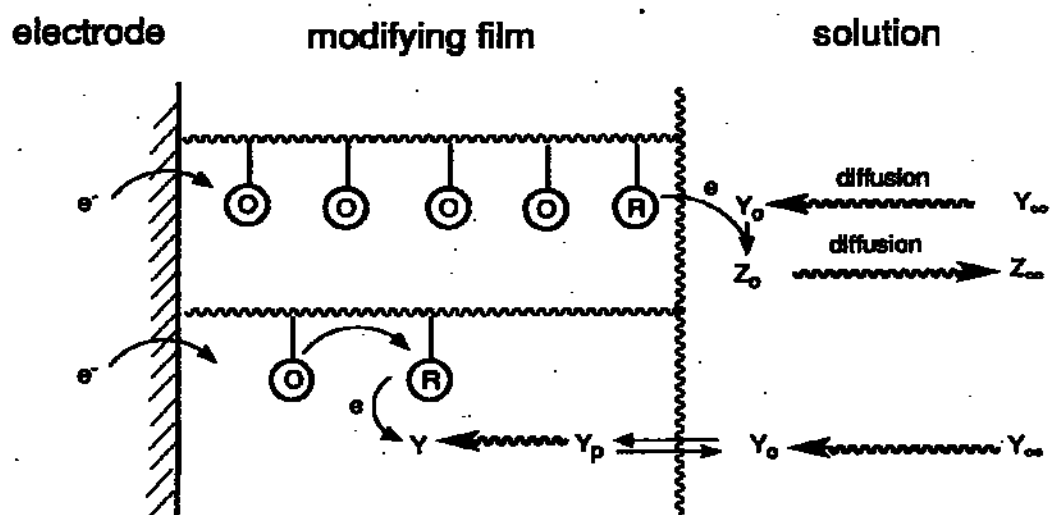


Fig. 1.2: schematic representation of polymer modified electrode. At the polymer/electrode interface, there is an electron exchange due to potential perturbation and at film/solution interface, ion and solvent transfers occur due to electroneutrality and activity constraints. Y and Z represent electroactive species getting oxidised/reduced and the subscript "p" denotes species diffusing in the bulk of the polymers.

1.3.1 Types of Electroactive Polymers and Redox Switching

Based on their structure and (electro)chemical properties, the polymeric materials used as electrode surface modifiers can be subdivided into three general categories: redox polymers, ion-exchange and co-ordination polymers, and conjugated polymers (also known as conducting polymers) [14, 15, 18, 29]. Redox and conducting polymers are themselves electroactive and transport electrons via discrete redox centres covalently bound to polymer chain backbones or within their polymer chains, respectively [14, 18]. In contrast, ion-exchange and co-ordination polymers are not electroactive themselves, but can incorporate electroactive guest molecules [14].

In redox polymer systems, the pendant discrete redox centres function as essentially independent entities [1]. Electron transport within redox polymers occurs via a

hopping-type mechanism [30-34] involving sequential self-exchange between neighbouring groups; the reduced half of the redox couple simply gives its electron to an oxidised counterpart in close proximity (see Fig. 1.2). In cases where redox centres are not rigidly bound to the polymer matrix, it is the physical diffusion of redox centres that provides a mechanistic basis for charge propagation within the surface-confirmed film [35]. Good examples of redox polymers are poly(vinylferrocene) and poly(xylylviologen). For the latter, the redox site is an integral part of the polymer chain compared to poly(vinylferrocene) [1].

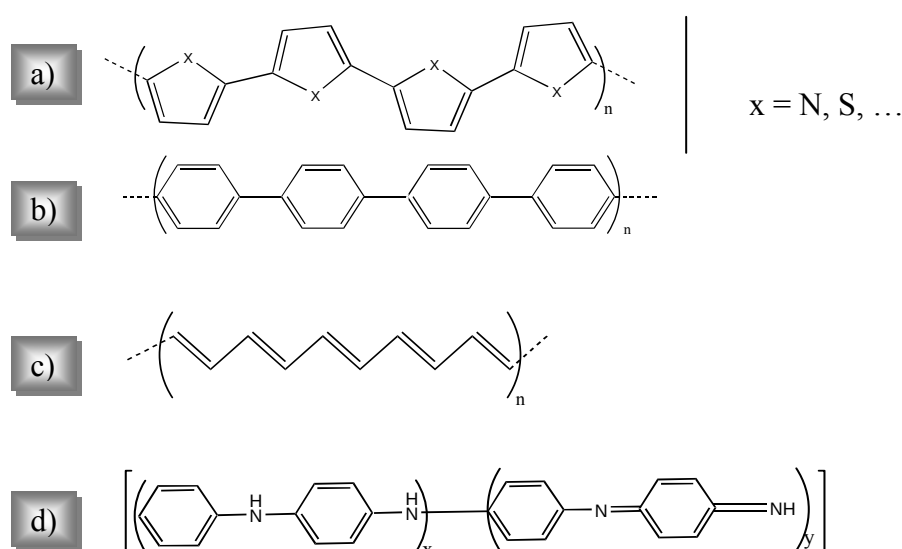


Fig. 1.3: Examples of conducting polymers. a) polypyrrole or polythiophene according to the heterocyclic element represented by the letter x. b) poly(para-phenylene). c) polyethylene, and d) polyaniline where x and y stand for the stoichiometric coefficients of the alternating benzinoid and quinoid units of polyaniline. n, in all polymers, denotes the polymerisation degree.

In conducting polymer systems, however, the charge propagation proceeds via a different mechanism (cf. redox polymers). Basically, all conducting polymers possess a conjugated backbone with a large degree of π -electron delocalisation [35-37]; the cationic sites (polarons/bipolarons, also known as holes) created upon oxidation are delocalised along the spine of polymer chains. It is, therefore, this π -bond delocalisation in conducting polymers that causes the charge propagation and electron transport within polymer chains – dubbed as electron tunnelling (cf. hopping-type

mechanism in redox polymers) [35-37]. Examples of well-known conducting polymers are given in Fig. 1.3.

Upon the application of potential to the polymer modified electrode, an electron exchange occurs at the electrode/polymer interface [38-41]. This process is followed by an ion and neutral species (i.e., solvent/salt) transfer across polymer/electrolyte solution boundary in order to satisfy electroneutrality and thermodynamic activity constraints, respectively [42-45]. A detailed description of theoretical and experimental aspects associated with the mechanistic (kinetic) and equilibrium (thermodynamic) aspects of mobile species transfer will be discussed in chapter 4.

1.3.2 Viscoelastic Nature of Electroactive Films

The viscoelastic nature of thin electroactive films is frequently under-explored. In electrochemical investigations, gravimetric studies of film composition are performed using acoustic-wave based devices (Electrochemical Quartz Crystal Microbalance, EQCM). In these studies acoustically thin (rigid) films are required; the aspects of the EQCM technique will be discussed in section 1.5.2.1 (for more details, refer to chapter two, section 2.3). However, polymer films not-rigidly coupled to the electrode surface (acoustically thick films) will undergo an acoustic deformation across the film. In other words, the upper part of the film will not synchronously move with the underlying electrode and will be subject to attenuation and phase delay [1, 46]. This has the implication of inapplicability of the device as a gravimetric probe.

The origins of the viscoelastic behaviour of thin films are still under study. Polymer film compositional dynamics of mobile species (ion/solvent) transfer accompanying the redox switching of electroactive films are acknowledged to trigger a change in films structural conformation (matrix dynamics) and/or reconfiguration (internal rearrangement) [38, 47-49]. Practically, the understanding of the viscoelastic phenomenon plays a vital role for the optimisation of the device performance based on polymer modified electrodes [50, 51]. Viscoelastic and structure-composition properties of electroactive polymer films will be dealt with in chapters 6-8. In a novel approach, the fundamental processes underpinning the macroscopic behaviour of polymer film dynamics are presented in great detail in chapter 8. In this chapter,

viscoelastic signatures influenced by solvent penetration (plasticization effect), temperature and timescale (frequency) on the mechanical properties of electroactive films are extensively detailed. Depending on these control parameters, the polymer chains may be glassy (frozen) or rubbery (mobile).

Thin films, whose mechanical properties are under investigation, can be deposited on piezoelectric devices; the device used here was an AT-cut quartz crystal. For the determination of acoustic-wave surface mechanical impedance of thin films (of thickness, $h_f < 1 \mu\text{m}$), the composite system of the piezoelectric device and the film is generically represented as an electrical equivalent circuit [52-54]. The principles and the theoretical aspects of these devices will be discussed in chapter 2 in detail. With the use of the simple lumped element model – generally known as Butterworth-van-Dike equivalent model (BvD) [55-58], the shear modulus components as a quantitative measurement of film's rheological properties can be determined [51, 59, 60]. Shear modulus components can be extracted from the admittance spectra of the system using Crystal Impedance Analysis Technique.

For the first time, we were able to apply – in this research project - viscoelastic theoretical models, describing the functional variation of film mechanical properties with timescale (cf. frequency), temperature and potential, to electroactive thin films represented here by polyaniline films (see chapter 8). The models considered were Williams-Landel-Ferry (WLF), Rouse-Zimm and activation models which were initially developed for bulk polymers [61-63]. These models address – at a molecular level interpretation – the viscoelastic behaviour of films associated with the polymer spine, free volume and/or side chain dynamics [49, 50]. Furthermore, the principle of time-temperature correspondence [63-66] was used to construct stress master relaxation curve of polyaniline films (and of polythiophene derivative films by other members of Hillman's research group [48-51]). The shift factors of individual thermally activated viscoelastic responses extracted from the master curve were subsequently used to determine the glass transitional temperature, fractional free volume and the solvation energetics of the system (for further details, refer to chapter 8).

1.3.3 Polyaniline

Polyaniline is one of most important conducting films extensively studied for the last three to four decades [45, 67-69]. It has attracted the interest of different electrochemical research groups for its stability (both in low and elevated temperatures), easy preparation (both chemically and electrochemically), cost-effective and reasonable conductivity [70-76]. Polyaniline exists in various forms with different doping level and oxidation degree of which have been called “aniline black”, “nigraniline”, “emeraldine”, “pernigraniline” and “leucoemeraldine” [72, 77]. The green partially oxidised form (emeraldine) is only the conducting form of polyaniline which can then easily be converted to either the fully oxidised form (pernigraniline – non-conducting) or to the fully reduced form (leucoemeraldine – also non-conducting) [72]. Because of this complexity, polyaniline shows a variety of complicated electrochemical and physical behaviours; this has led different research groups - working on several basic aspects, e.g., polymerisation, conductivity, degradation, etc. - to put forward contradicting and divergent views on understanding the intrinsic properties of polyaniline film [72].

Despite the high volume of literature publications on many aspects of polyaniline (> 7,000 papers and articles appeared since 1990), there are still many questions that remain to be addressed. Examples of on-going active investigations are the study of the electropolymerisation mechanism [67, 78], co-polymerisation with other conducting polymers [79-81], degradation (cf. growth rate) mechanism [82-84], redox transformation of polyaniline nanotubes [85, 86] and the behaviour of polyaniline-gold nanoparticle [87, 88] and/or carbon nanotube composites [89-91].

In this research project, polyaniline is one of the conducting polymers studied in great detail. The areas of interest here are the structure-composition relationship and the dynamics of mobile species population changes accompanying film redox switching. As indicated above (section 1.3.2), the viscoelastic behaviour of thin polyaniline films in electrochemical systems has been explored for the first time (refer to chapters 6 and 7). Coupled electron/ion and solvent transfer fluxes across electrode/film/solution interfaces have been elucidated in a new way using novel theoretical models (see chapter 4).

1.4 Preparation Methods of PME

Polymer growth and deposition on electrode surfaces can be performed using a variety of routes. The simplest method of polymer immobilisation on electrode surfaces is dip-coating of the bare electrode into the solution of the polymer followed by solvent evaporation [15, 92]. One of the limitations associated with this method is that the amount of material to be coated on the electrode is difficult to control; the use of accurately measured volume of the solution may solve this problem. Spin-coating is another useful method for polymer coating on the electrode surfaces [92, 93]. This can be carried out by the application of a drop of the solution onto the electrode surface followed by spinning to evaporate solvent.

However, the route most widely preferred is the electrochemical deposition of polymer films on electrodes from the solutions of corresponding monomers (mainly on the order of 0.01-0.1 molar concentration) [94]. The advantage this method has over its variants is its cheapness, time-effective and less laboriousness. In order to achieve films of desired properties, many parameters need to be effectively controlled in the electrosynthesis process of polymer modified electrodes. The variables to be optimised include: the type of solvent, monomer/background electrolyte concentration and the mode of electrochemical preparation (potentiostatic, potentiodynamic, coulstatic/ampereometric, etc.). Though all of these variables are known to determine the overall physico-chemical properties of the resultant polymer modified electrode, the mode of oxidation has been shown to have a profound effect on the structure and the morphology of the polymer film [38, 71, 94-96]. The film thickness and the surface coverage of the polymer can also be controlled via careful choice of the experimental timescale, charge density, number of cycles (for cyclic voltammetry, see below) and monomer concentration.

The mechanism of electrodeposition of polymers is subject to a number of factors. The most significant factors include the nature of solvent, background electrode, pH, temperature, electrode material, monomer structure and the electrochemical control function employed for the polymer growth [36, 97]. The initial step of the polymer electrosynthesis starts with the formation of a radical cation (removal of an electron from the monomer, see Fig. 1.4) upon oxidation (at $E = 0.9$ V for polyaniline, for

example). Since then the process propagates by coupling of two radical cations followed by loss of protons and formation of dimers and oligomers. And finally, the process continues to a situation where intermediate oligomers become insoluble in the solution (due to chain length) and eventually deposit on the electrode surface (see Fig.1.4).

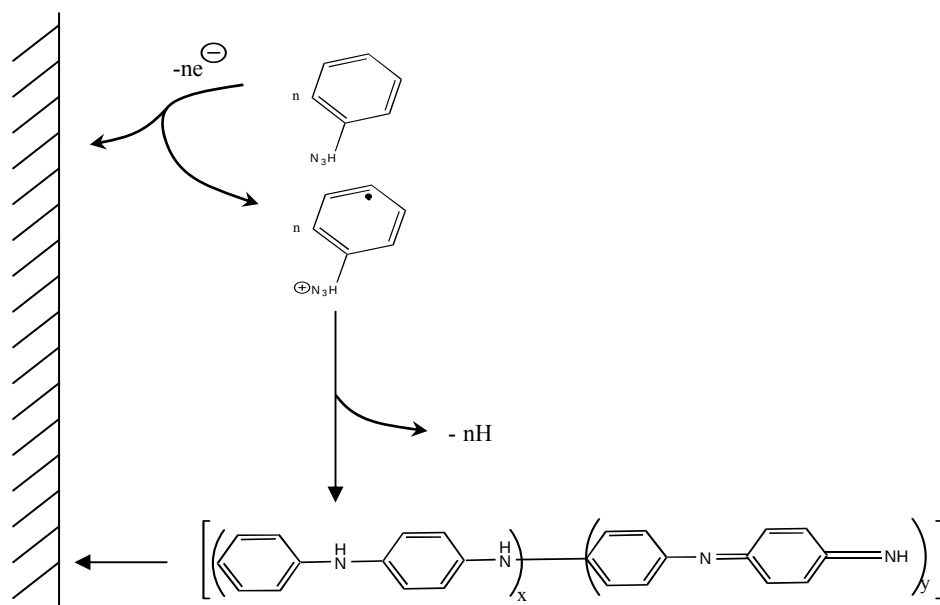


Fig. 1.4: Schematic representation of the mechanism of electrochemical polymerisation of polymers. In this figure, polyaniline was used as an example, but other polymers also take similar routes.

1.5 Characterisation Techniques of PME

Characterisation of polymer modified electrodes (PME) is an essential practice for understanding the underpinning concepts of film structure-composition and interfacial properties at electrode/film and film/solution boundaries [14, 18]. The electrochemical, optical, rheological and morphological properties of electroactive polymer films need to be explored in depth. Great interest was given in this thesis to the correlation between a film's structural dynamics and the modulation of the film's mobile species composition; for permselective films, mobile species represent ions and solvent. The mechanism of the coupled electron/ion and solvent transfers across the interfaces has also been studied using both theoretical and experimental methods.

There are a number of techniques which provide complementary information on different aspects of the system under investigation. Electrochemical techniques, for example, are powerful tools for driving the redox transformation of electroactive films and can provide useful information on kinetic and thermodynamic parameters of the system; diffusion, conductivity/resistivity, electrostatic interaction of the redox centres, mobile species fluxes, heterogeneous rate constants and equilibrium constants are such examples. However, electrochemical techniques alone can not answer all of the questions required to address for the characterisation of polymer modified electrodes. Furthermore, these techniques can not give information related to structural and spatial separation of redox sites; these aspects require the use of other physical probe techniques (see below). Another limitation with electrochemical techniques is their blindness to neutral and solvent species in solution or within polymer layers. Therefore, the use of other *in situ* (*ex situ*) non-electrochemical techniques coupled with electrochemical experiments is necessary for proper understanding of the system under scrutiny. Such examples of non-electrochemical techniques can be spectroscopic, e.g., Uv/vis, IR/Raman, XPS (structural/compositional information), surface imaging, e.g., AFM, STM (morphological information/surface topology) and acoustic wave resonators, EQCM, Crystal Impedance Analysis (structural and compositional dynamics). In the following sections, a number of these techniques will be concisely reviewed.

1.5.1 Electrochemical Techniques

Electrochemical techniques are widely used for the electrosynthesis and the subsequent characterisation of the resultant films. With these techniques, one can effectively monitor the growth and degradation mechanisms of films during deposition as well as films response to their ambient environment during probing conditions.

1.5.1.1 Cyclic Voltammetry

As the name implies, this technique employs ramping the potential linearly back and forth between two pre-set points, E_1 and E_2 at a steady scan rate, v/Vs^{-1} . The potential cycling procedure is repeated two or more times and the current response monitored continuously [98-103]. Cyclic voltammetry has received enormous popularity among electrochemists in that obtaining the CV of a new electrochemical system is often the

first experiment performed [99, 102, 103]. This powerful technique provides invaluable information about the properties and the characteristics of electrochemical processes. It is very useful for the elucidation of surface reaction mechanisms, particularly with respect to the reaction intermediates by simply controlling the potential scan rate. In this introductory review, we focus on the interpretational aspects of this technique; more theoretical and experimental aspects will be discussed later in chapter 2.

For the characterisation of electroactive films, the kinetics of the system are controlled via the rate constant (as a function of potential polarisation) and the scan rate (i.e. experimental timescale). This plays a vital role in determining whether all the electroactive (redox) sites within the film are oxidised (reduced) during the voltammetric scan. The strategy is to compare the time constant for the charge transport in the film, $\tau = h_f^2/D$ (where h_f is film thickness and D is the diffusion coefficient associated with charge propagation) with the timescale parameter for the experimental scan rate, $t = RT/nFv$ (where v is the scan rate and the rest have their usual meaning) [15]. If $t \ll \tau$, only a small fraction of the redox active sites will have a chance to get oxidised or reduced within the experimental timescale [15]. As a result of this, the voltammetric current wave will appear diffusional in nature. On the other hand, if $t \gg \tau$, the entire population of film redox sites will be oxidised or reduced within the observational timescale and a monolayer-type voltammogram (diffusionless) will be obtained [15]. The overall population of film redox sites can then be calculated from the area under voltammetric peaks according to Faraday's law.

At typically low scan rates, $v < 10 \text{ mV s}^{-1}$, the system is at equilibrium and thermodynamic parameters, such as formal potential, E° , can be evaluated [102, 103]. In this regard, the shape of the voltammogram gives an insight into the reversibility of the system and/or the electrostatic repulsive/attractive forces between the redox centres of the films [102, 104-110]. For example, symmetrical peak currents (i.e. small separation between peak potentials, ΔE_p) with scan rate are characteristic for surface-confined films. Ideally, the value of half height peak width, $\Delta E_{1/2}$, is estimated to be ca. 90 mV at 25 °C for one electron transfer process [105].

The broadening of symmetrical peak shapes has been related to repulsive interactions between the electroactive sites [104, 105], differences in the spatial distribution of redox centres [106, 107] and to the distribution of electroactive groups with different local E° values within films [108]. Asymmetric voltammetric peak shapes may result from a number of factors; the presence of side reactions are thought to be main factors (kinetic effects that give qualitative and diagnostic information) [99, 102, 103, 111]. The difference in surface activities of film's two redox states (oxidised and reduced) may also lead to asymmetric voltammograms [106, 109, 110]. From the knowledge of peak current, peak potential and peak width, one can extract a wealth of physically meaningful information; such examples include diffusion coefficients, equilibrium constants for mobile species transfer and number of electrons involved in the redox transformation of electroactive films [99, 100, 102, 103]. The details of these aspects are beyond this brief review and can be found in the conventional electrochemistry texts.

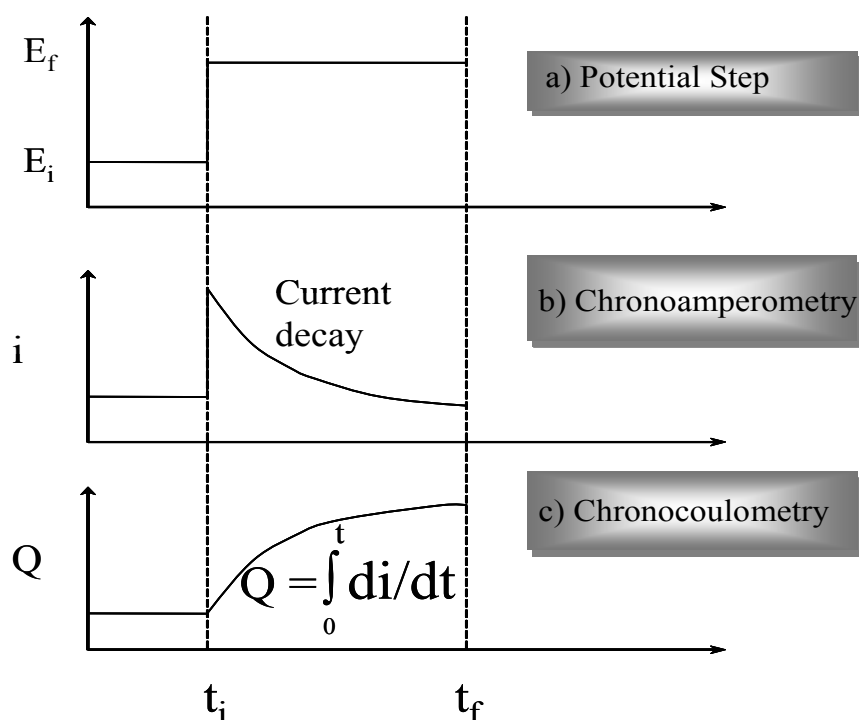


Fig. 1.5. Schematic representation of potential step experiment signals. a) Stepping potential (controlled) from E_i to E_f against time. b) Chronoamperometry (differential response) and c) chronocoulometry (integral response).

1.5.1.2 Potential Step

In potential step experiments, the potential of the working electrode is instantaneously jumped from an initial value, E_i , where no chemical reaction occurs at the electrode surface to a final value, E_f , where the reaction of interest takes place (see Fig.1.5a). The current (chronoamperometry, Fig.1.5b) or charge (chronocoulometry, Fig.1.5c) response is plotted against time. In terms of interpretation, chronoamperometry gives the rate of reaction while chronocoulometry (the integral form of chronoamperometry) monitors the extent of reaction [15, 99, 102].

At short times, the reactants at the metal/film interface are rapidly consumed [101, 112]. In such a case, the charge propagation through the film – rather than the interfacial kinetics – is the rate limiting step. This means current-time relationship obeys the Cottrell equation (refer to chapter two for more details) where i vs $t^{-1/2}$ gives a straight line; hence, the diffusion coefficient can be obtained from gradient of the plot.

For polymer modified electrodes, the diffusion coefficient may represent a range of physical processes [18]. For examples, intrinsic electron exchange rate, physical motion of redox centres or other mobile species within the film contribute into the physical significance of the diffusion coefficient; here, mobile species mean the coupled electron/counter-ion and solvent necessary to maintain electroneutrality and activity equilibrium constraints. These processes can be distinguished through the functional dependence of diffusion coefficient, D , on particular variables [15]: site-site separation within polymer chains, the size and charge of counter-ions, temperature, film's solvent population and the ionic strength of the electrolyte solution. Similar to the arguments presented above for diffusion-controlled systems (section 1.5.1.1), if the electroactive species is free to diffuse through the matrix of polymer chains (controlling the rate of charge transport), then the diffusion coefficient, D , of the system is assigned for the migration of redox active species within the film [15]. In this case, D is analogous to the diffusion coefficient of electroactive species in an electrolyte solution. On the other hand, if the charge propagation within the films occurs via electron hopping (as it is the case in redox polymers), then the diffusion coefficient, D , may be related to the rate of electron

hopping process, $D \sim kc\lambda^2$ (where $k/M^{-1}s^{-1}$, is the rate constant, c/M ($M = \text{mol nm}^{-3}$) is the redox site concentration and λ/nm (ca. 1 nm) is the jump distance [113, 114].

Furthermore, potential step experiments are complementary to cyclic voltammetry through which one can establish strong link between the electrochemical responses and the physical characteristics of polymer modified electrodes. In potential step experiments, the diffusion coefficient of the system is determined; in cyclic voltammetry experiments time constant of charge propagation (determined via the diffusion coefficient) and experimental timescale compared (via the variation of scan rate).

1.5.1.3 AC Impedance Analysis

In this technique, an oscillating potential perturbation, $E(\omega)$, with small amplitude ($\sim 5 \text{ mV}$) is applied to the system and the a. c. current response, $i(\omega)$, is recorded. For the system characterisation, suitable equivalent electrical circuits are used to represent polymer/electrode interface and the components of the electrolyte solution [15, 99, 115]; a combination of resistors and capacitors – connected in either parallel or series – is chosen as system models. In this experiment, Randle's equivalent circuit (Fig. 1.6, panel b) is commonly used for the representation of an electrochemical reaction occurring at electrode surfaces [115-117]. Resistors represent either charge transfer resistance, R_{ct} , of the system reflecting the kinetics of charge (electron) transfer or the uncompensated background electrolyte IR drop and capacitors represent the double layer capacitance arising from the electrified electrode/electrolyte interface.

In practical terms, the impedance, $Z(\omega)/\Omega = E(\omega)/i(\omega)$, of the system (a complex quantity containing both magnitude and phase information) is measured over a wide range of angular frequency, $\omega/\text{rad s}^{-1}$. For the acquisition of system parameters, experimental results are fitted against the theoretically calculated values of the equivalent circuit components. Analogous to the scan rate in cyclic voltammetry, the variation in frequency of the sinusoidal perturbation controls the experimental timescale. As a result of this, the electrochemical and physical characteristics of the system vary with the control of angular frequency, $\omega/\text{rad s}^{-1}$; these phenomena are observed from the change in amplitude and/or the phase shift of the response.

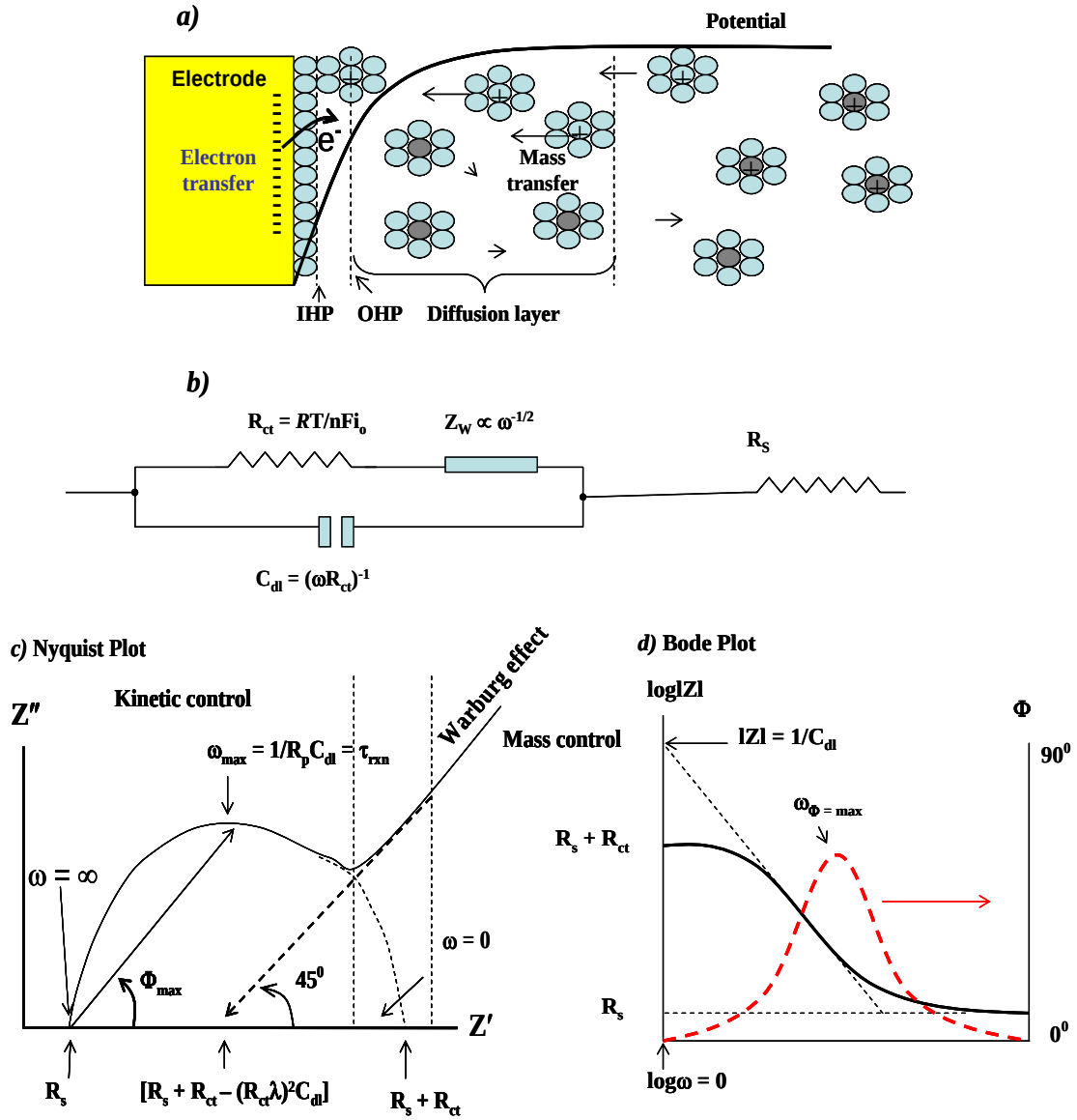


Fig. 1.6: Schematic representation of an electrochemical system, the corresponding equivalent electrical circuit and modes of data representation; a) simple electrochemical interface of electrified electrode (typically metal) and adjacent electrolyte solution. In this representation, double capacitive, diffusion and mass transport zones are clearly labelled; b) Randle's equivalent circuit comprised of a combination of resistance and capacitance electrical components representing the dissipative and charge storage characteristics of the system. For details of the components and their representation, refer to the text; c) Nyquist plot in which all major characteristic features are labelled and defined. The Warburg impedance due to the mass transfer is defined as $Z_w = \lambda / \sqrt{2\omega}$ where $\lambda = k_f / \sqrt{D_{Ox}} + k_b / \sqrt{D_{Red}}$, D_{Ox} and D_{Red} are diffusion coefficients for the redox species; d) Bode representation in which all the characteristic features of the model are defined and labelled as well.

In terms of data interpretation, the imaginary component, $Z''(\omega)$, of the impedance is often plotted against the real component, $Z'(\omega)$; a characteristic semi-circle is formed depending on the nature of the electrochemical reaction. This representation is known as Nyquist or Agrand diagram (Fig. 1.6, panel c). From the characteristic features of the plot, one can extract useful information of the system [99, 115, 117]. For example, the charge transfer resistance, R_{ct} , of the system can easily be obtained from the width of the semi-circle (see the Nyquist plot); $R_{ct} = RT / nFi_o$ where R here is the universal gas constant and F is Faraday. The electrochemical rate constant, k_o , can be calculated from exchange current, i_o , (through the charge transfer resistance); $k_o = i_o / nFAC^\infty$, where C^∞ is the bulk concentration of reactants. The interfacial double layer capacitance, C_{dl} can be evaluated from the maximum frequency; $C_{dl} = (\omega_{max} R_{ct})^{-1}$. The diffusion coefficient, $D_{Ox/Red}$, of redox species can be found from the gradient of Warburg impedance (a rising spine that develops at very low frequencies with characteristic phase angle of 45°); Warburg impedance, $Z_w = \lambda / \sqrt{2\omega}$, (where the Warburg coefficient, $\lambda = k_f / \sqrt{D_{Ox}} + k_b / \sqrt{D_{Red}}$) is observed as a result of mobile species mass transport. Using a. c. impedance spectroscopy, the conductivity, corrosion protection, mobile species activities of polymer modified electrodes can be studied [117-119].

1.5.2 Non-Electrochemical Techniques

As indicated earlier, electrochemical procedures alone – though powerful - cannot provide all the necessary information needed for the comprehensive understanding of fundamental aspects related with polymer modified electrodes. Electrochemical control functions (i-V-t) can give comprehensive insight of the overall dynamics of the system, but can provide little information about the mechanism of electrochemical reaction and the accompanying electroinactive species (solvent and/or neutral entities). Recently, electrochemists have used other in situ non-electrochemical techniques coupled with electrochemical experiments of which most common of these techniques include: thickness shear mode resonators, spectroscopic/reflectivity and surface imaging probes. With the combination of these techniques, wealth information of structural, morphological, rheological and electrochemical properties

of electroactive polymer systems can be appraised. In the following sections, a brief review of these non-electrochemical techniques will be presented.

1.5.2.1 Electrochemical Quartz Crystal Microbalance (EQCM)

The electrochemical quartz crystal microbalance (EQCM) also known as a thickness shear mode resonator (STM) is an extremely sensitive device for the investigation of composition and viscoelastic properties of polymer modified electrodes [1, 47, 52, 55, 57, 58]. In this thesis project, this technique is predominantly used in great extent; the basic principles and instrumentation of the technique will be detailed in chapter 2.

In principle, the technique is based upon the converse piezoelectric property of the quartz crystal. By the application of an a. c. potential across the thickness of especially cut crystal (with respect to the angle and orientation of the crystallographic axis, see section 2.3), the quartz crystal undergoes surface mechanical deformation. As a result, an acoustic wave is propagated into the medium immediately adjacent to the piezoelectric element [1, 47]. The commonly used cut is an AT-cut crystals vibrating in the thickness shear mode (TSM) where the greatest amplitude of the lateral oscillation occurs at the resonant frequency of the crystal.

For polymer modified electrodes, EQCM devices are used as an *in situ* interfacial probe. The device response, through the interaction of the acoustic wave with the adjoining medium, is determined by the composition and the viscoelastic properties of the surface-attached materials and the surrounding medium in which the EQCM is immersed [1, 120, 121]. If the polymer film immobilised on the electrode surface is sufficiently rigid (termed as “acoustically thin”, i.e. no further acoustic deformation across the film), the EQCM device functions as a gravimetric probe capable of detecting mass changes at nano-scale ranges [53, 122-124].

In principle, changes in the surface mass (ΔM) lead to a decrease in the resonant frequency (Δf) of the oscillating quartz crystal. In this case, the ion and solvent composition of thin polymer films can be determined through the combination of the change in resonant frequency (Δf) of quartz crystals and the coupled electrochemical

response functions (current/charge); this provides the underlying mechanistic information related with ion and solvent transfers across polymer/solution interface.

On the other hand, if the polymer films on electrode surface are thicker and/or softer (termed “acoustically thick”, i.e. acoustic wave attenuation develops across the film), the EQCM device operates as a viscoelastic probe responding primarily to the film structural dynamics. In this case, film mechanical properties, quantified via shear modulus (storage and loss moduli), can be extracted; the shear modulus values of polymer films are sensitive to several control functions. With the control of temperature, experimental timescale (through higher harmonics of the resonant frequency), and film composition, a full insight of film structural dynamics can be gained. Useful parameters in terms of application and material processing may be glass transition temperature, film fractional free-volume and local polymer chain relaxation time constants.

Historically, G. Z. Sauerbrey [125] was first to describe the quantitative relationship between the change in resonant frequency and the mass load on the crystal surface. Subsequently, the application of *in situ* quartz crystal microbalance (QCM) with electrochemical systems was reported by Bruckenstein and Shay [126, 127] and Nomura and Iijima [128]. Later on, theoretical and experimental procedures for the determination of viscoelastic properties of polymer films through the application of equivalent electrical models were advanced by Martin and co-workers [52, 57, 58].

1.5.2.2 Spectroscopic Techniques

Atomic and molecular level information related to the structural changes of polymer modified electrodes as a direct response to electrochemical stimuli can be studied through the application of the conventional spectroscopic techniques. The most common are UV/vis absorbance, IR and photoelectron spectroscopies. With the help of these techniques, one can examine the nature of redox entities deliberately introduced onto the electrode surface – just like “normal” chemistry. In the following sections, we review the significance of these techniques to the characterisation of polymer modified electrodes.

i – UV/visible Spectroscopy

UV/visible spectroscopy is the most widely used *in situ* spectroscopy technique coupled with electrochemical systems [18, 99, 115]. This technique probes HOMO/LUMO, i.e. energy levels, from/to which electron exchanges of electrochemical reactions occur. The basic principle operation of this technique lies upon the measurement of the amount of light transmitted/absorbed by the materials on the electrode surface. With this kind of experiment on polymer modified electrodes, the substrate electrode must be optically transparent. In practical terms, tin oxide (TO) or indium doped tin oxide (ITO) electrodes on glass substrates are employed; these electrodes are commercially available and quite transparent over the entire visible spectrum [129].

Nevertheless, most electrode materials are not transparent and this technical limitation can be overcome by using reflectance mode methods [15]. The reflectance, R , can simply be obtained as the ratio of the intensity of reflected light (from the electrode surface) to that of incident light. The idea is that if there are light absorbing species (chromophores) on the electrode surface, the reflectance, R , gets attenuated. The data acquired can be processed by evaluating the measured reflectance, R , against the reflectance of a conveniently defined standard, R_0 [15]; R_0 can be the reflectance of the bare electrode (uncoated) or the reflectance at some reference potential, E_{ref} . Analogous to the absorption spectrum, the reflectance spectrum (R/R_0) can be plotted vs wavelength or energy.

With the application of UV/visible spectroscopy, the dynamics of mobile species population of electroactive polymers – during potential cycling - can be appraised. The appearance or absence of additional absorption bands (not present before the potential perturbation) are monitored and used as fingerprints for the electro-generated species [115]. Through the Beer-Lambert law, the mole ratio of the reduced and oxidised forms of the electroactive species within the film may be observed with good precision.

In addition to the traditional spectroelectrochemistry, a new approach of combining UV/visible and potentiodynamic experiments has proved to be useful for the characterisation of conducting polymers [94, 130, 131]. In this approach, the

absorbance at a given wavelength is observed as the potential is cycled. With this technique, the n and E° values corresponding to the production of polarons and bipolarons can be found [94]. Plotting the differential form of the absorbance as a function of potential produces a signal that looks much like the cyclic voltammogram. Correlation between the cyclic voltammogram and the differential cycloabsorbance can give significant information on the early stages of polymer formation on electrode surfaces. Johnson and Park [130] used this technique for the investigation of polyaniline growth mechanism on Pt electrode.

ii – Infrared Spectroscopy (IR)

IR spectroscopy is used to provide specific information on both molecular identity and orientation at electrode surfaces [132-134]. In this technique, vibrational motions, kinetics and other microstructural features related with polymer modified electrodes are probed. The application of IR radiation to the system excites characteristic vibrations from which the structure of the polymer chains and the nature of redox species present within the polymer can be deduced.

Similar to UV/visible spectroscopy, there are some difficulties associated with the use of IR technique [115]. These limitations arise in two main areas: the overall sensitivity of IR is lower (i.e. intrinsic) compared to UV/visible spectroscopy and fouling signals arise due to the sensitivity of IR to the medium of interaction (local environment); the latter refers to the strong absorption bands of solvents (such as water) in the region of IR electromagnetic radiation. The effect of these limitations can be reduced by the use of the IR technique in a differential mode; this is called electrochemically modulated infrared spectroscopy (EMIRS) [115]. In this operational setup, the reflected light from an electrode contained in a thin layer cell is detected; the data acquired provides useful information about the species close to or adsorbed on the electrode surface. For the elimination of the effect of solvent or the bulk solution, the spectroscopic signal is carefully correlated with the potential pulse. This is performed by switching the electrode potential between a value at which no electrode reaction occurs and a potential that drives the desired electrochemical reaction. As a result of this, the spectroscopic signal due to the species of interest fluctuates with a frequency identical to that of the potential pulse (termed “lock-in

detection” of the optical signal) [135]. In this case, the effect of solvent or bulk solution contribution to the signal remains constant [136]. Therefore, the use of EMIRS proves to be effective for discriminating between electrogenerated species at or close to electrode surfaces and other IR active species in the bathing solution (fouling species), i.e. constraining the detection signal to the materials of interest (product of the electrode reaction).

iii – Raman Scattering Spectroscopy

This technique is complementary to IR spectroscopy and reveals useful information on the backbone structure of polymer modified electrodes [137]. Basically, the technique relies upon inelastic scattering of light (cf. Rayleigh scattering) due to the interaction of the incident excitation beam with the vibrational energy levels (electric dipole) of molecules; in other words, the energies of the incident and scattered photons are different. The observation of “*Raman Effect*” (very small fraction, 1 in 10^7 of the incident beam) depends on the energy of the incident radiation; UV/visible light is usually the incident radiation used, but it can be near IR. Furthermore, for the molecule to be Raman active (cf. IR active), there must a change in the polarizability of the electron cloud (cf. a change in dipole moments for IR) in association with vibrational motions.

In general, Raman scattering spectroscopy is particularly useful for the characterisation of polymer modified electrodes and has a number of distinct advantages over its variant, IR spectroscopy [138]. In terms of instrumentation, both mid and far infrared spectral regions can be accessed in Raman spectroscopy with the same instrumental setup; in IR spectroscopy, these regions typically require separate optics. In contrast to IR (see above), the effect of solvent or bulk solution does not severely interfere the signal from the electrode surface due to its weak *Raman Effect*. More importantly, in Raman spectroscopy, the chain length in polymers (conjugation length in conducting polymers) can be determined through the change in polarisation in chemical bonds; an effect not available in IR experiments [94]. The relationship between the chain length and the change in resonant frequency of Raman scattering was found to be inverse, i.e. resonance occurs at progressively lower frequencies with the increase of chain length (conjugation length) [94].

However, there are some limitations that reduce the applicability of this technique. The signal observed from the surface of modified electrodes may be weak, particularly for monolayers. This problem can be minimised via surface enhancement, known as the surface enhanced Raman scattering (SERS) effect. With this approach, the amplification of the signal from three to six orders of magnitude can be achieved [139-141].

1.5.2.3 Surface Imaging Techniques

Topographic (surface mapping) and morphological features of polymers immobilised on electrode surfaces can be studied with imaging probe techniques. With these techniques, it is possible to correlate growth mechanism and local structural changes of polymers with preparation conditions [142, 143]. Through *in situ* surface imaging, changes in film thickness - during deposition – can be detected on the order of a few nanometer [143]. We focus on the most two common imaging probes used for the characterisation of polymer modified electrodes: scanning tunnelling microscopy (STM) and atomic force microscopy (AFM).

i – Scanning Tunnelling Microscopy (STM)

STM surface imaging is used to give a 3D atomic-scale surface mapping. In principle, the technique is based on the existence of tunnelling current between a sharp tip (~ 1 nm in diameter) and the surface of the sample to be imaged [99]. Experimentally, the topography of sample surfaces can be recorded, in a three dimensional way, through monitoring the tunnelling current induced by the overlap of the electronic wavefunctions of the tip (~ single atom point) and the sample surface.

One of the limitations of this technique is that the surface to be probed must be electronically conductive. As a result, STM is particularly suited for the morphological investigations of redox and conducting polymers on electrode surfaces [68, 144-147].

ii – Atomic Force Microscopy (AFM)

In terms of application, AFM is similar to STM providing atomic-scale surface mapping probe. In this technique, unlike the STM, the operation relies upon the attractive or repulsive interatomic or intermolecular forces between the probe tip and

the sample surface [15, 99]. In AFM, the sharp probe tip (in a form of whisker made up of silicon carbide, not metal as in STM) is mounted on a cantilever supported by a spring (Fig. 1.7). The interatomic forces experienced by the tip as it tracks across the surface cause the spring supporting the cantilever to deflect; the movement of the spring deflection is then recorded via a laser beam reflected from an attached mirror. In most cases, the tip-to-sample distance is maintained via feedback mechanism to avoid the risk of the tip colliding with the sample surface; a piezoelectric tube capable of moving the sample in z-direction for maintaining constant force and x-y directions (lateral shifting) for sample scanning is used as a sample mount [148-151]. Therefore, the surface image of the sample, in AFM experiments, is simply a plot of the tip deflections (because of the attractive/repulsive interatomic forces, in the z-direction) against lateral shifting on the sample surface (x-y directions).

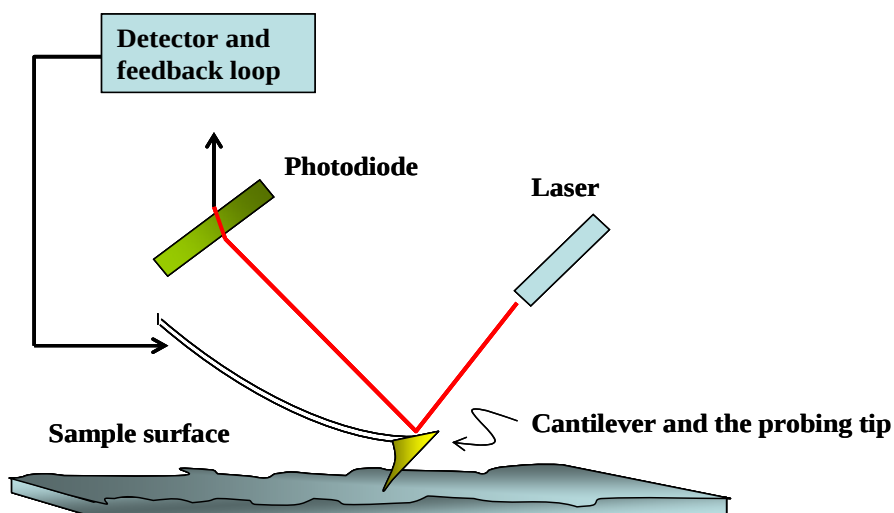


Fig. 1. 7: Schematic representation of AFM; modified and adapted from Refs [150, 151]

Both imaging techniques (STM and AFM) can be performed *in situ* and combined with electrochemical experiments. AFM, however, has an advantage over STM in that the sample surface can be insulating or conducting [152, 153]; in STM as indicated earlier the target surface must be conducting for this is necessary to the tunnelling current on which the technique is based (cf. interatomic forces in AFM). Nevertheless, both techniques are complementary to each other; in addition to the morphological data that can be obtained from AFM imaging, compositional data can also be extracted from STM experiment [154, 155].

1.6 Applications of Polymer Modified Electrodes

In recent years, modified electrodes have become of significant interest to electrochemists and material scientists. This is primarily because of their useful properties and potential applications they have in the commercial market place [156, 157]. These potential applications include many fast growing areas of which examples are: electrochemical synthesis [18, 158], energy conversion and storage devices [159, 160], electrochromic displays [161], (bio)-sensors [162, 163] and corrosion inhibition [164-166]. Quite generally, the merits of all these applications are based upon the redox transformations of the polymer modified electrodes. These redox transformations are brought about by the injection/removal of charge as a direct result of electrochemical control functions and the accompanying compositional and structural changes.

In electrochromic display devices, the concept of electrochromism actually depends upon the ability of the polymer film to change colour with the change of the film's redox state [94]. In sensors and electrocatalysis, the polymer film acts as a host that mediates electron exchange between the underlying electrode and the electroactive species in the adjacent solution [94]. The role of the polymer modified, in these applications, is therefore to enhance the sensitivity and selectivity of electrochemical detection for a variety of target analytes [94]. In corrosion inhibition, the objective may be one of two things: i) the suppression of all electrochemical reactions with the underlying electrode which can be achieved by the formation of a coherent insulating polymeric film and/or ii) simply the suppression of corrosion without impeding the redox reactions mediated through polymer/solution interfaces [18]. Either may be the objective, the application should rely on the redox conversion of electroactive film deposited on the electrode surface.

Despite the technological and commercial promise of polymer modified electrodes, there are yet some practical challenges that still lie ahead and demand further investigation. The correlation between film composition and structural dynamics is not so far fully understood [1, 48, 49, 51]. Main concerns are shown in the instability, relatively short charge storage lifetime and low electronic conductivity of most polymers employed. So far, the best conducting polymers have conductivities on the

order of $10^{-6} \text{ S cm}^{-1}$ [167]; this lies in the range of metallic-insulator transition. Many of these problems relate to morphological defects in the polymer chains, doping processes, charge transport mechanism and polymer chain lengths. The good news, however, may be that conducting polymers based on doped polyaniline and polypyrrole demonstrate the stability required for commercial applications [168]

The incorporation of the conducting polymers with gold nanoparticles [87, 88, 169] and carbon nanotubes [170-172] may bring about dramatic improvements in both of the modified sensitivity and selectivity towards target species. First attempts to form nanostructures of conducting polymers (through templating) are just emerging [173]. Investigators expect these nanoscale materials to have greater conductivities than their bulk counterparts and be used in nanoscale electronics [170].

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Chapter Two

General Theory – Underpinning Aspects

2.1 Overview

In sections 1.5.1 and 1.5.2.1, some useful electrochemical and acoustic wave techniques were summarised. In this chapter, we present the general theory underpinning the research carried out in this thesis. The fundamentals of electrochemical and acoustic wave device techniques used for the polymer film preparation and characterisation will be discussed in detail. In-depth analysis of theoretical and interpretational models developed for film compositional and structural dynamics are described in chapters 4-8. Cyclic voltammetry and electrochemical quartz crystal microbalance, EQCM, (in a hybrid combination) were the techniques used throughout thesis.

2.2 Basic Concepts of Electrochemistry

Electrochemistry can be defined as the study of chemical reactions driven by the application of electrical control functions (potential/current) across the electrode (typically, but not necessarily metallic)/solution interface [1]. In polymer modified electrodes, there are two or more interfaces; at electrode/polymer interface electron exchange occurs (ion-blocking) whereas at polymer/solution interface ion/solvent transfer takes place (electron-blocking). In conventional electrochemistry, the typical electrochemical reaction at the surface of the electrode can be represented in the following equation:



where Red and Ox represent the reduced and oxidised forms of the electroactive species, respectively. For this reaction (electron transfer at the electrode/solution interface) to continue, a fresh supply of reactants and the rapid removal of products are required [2]; this process necessitates a continuous electron transfer and mobile species mass transport. In general, the overall redox conversion occurs in the three steps described in Fig. 2.1. Understanding the mechanism (mode of transport and exchange) of both electron transfer and the accompanying mass transport is therefore vital for the extraction of kinetic information related with electrode dynamics.

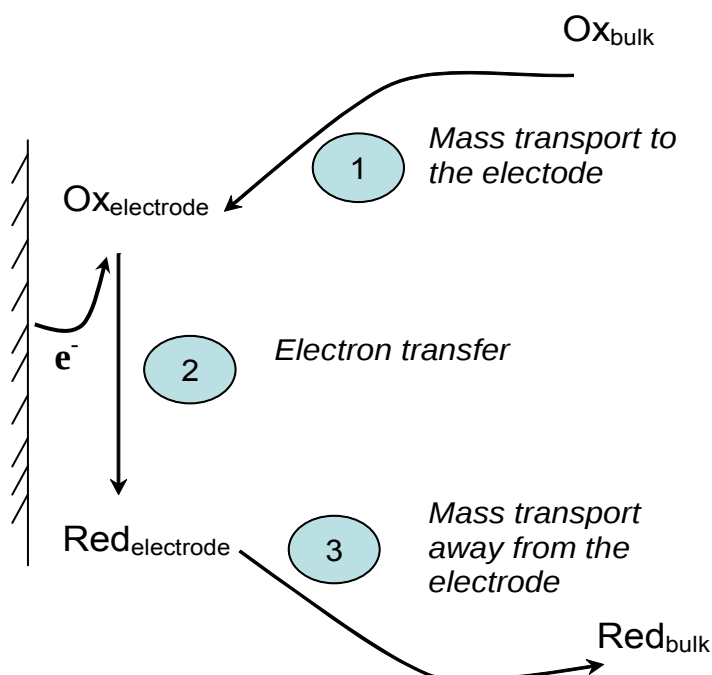


Fig. 2.1: Schematic representation of electron transfer (step 2) and mass transport (steps 1 and 3) following the redox conversion of electrochemical reactions.

For the polymer modified electrode, the redox centres are surface confined, and there is no need for the redox-active sites to be part of mass transport processes. Instead, when the redox-active sites within the polymer undergo *internal* electrochemical conversion, the electroneutrality process is satisfied by an *external* co and/or counter-ion exchanges across polymer/solution interface. Below, we discuss the various modes of mass transport for electroneutrality-driven ions to or from the electrode surface.

2.2.1 Mass Transport

In Fig. 2.1, the mechanism of mobile species dynamics occurs in the following three steps: reactant molecules need to be transported from the bulk solution into the electrode surface; electron exchange takes place right at the electrode surface; and in parallel to this, reaction products formed at the electrode surface should be removed away from the reaction site (electrode surface). This type of movement (steps 1 and 3) in the electrochemical cell is known as “mass transport” and necessary – as indicated earlier – for the electrochemical reaction to proceed.

Of the three steps discussed in Fig. 2.1, the overall rate of electrochemical reaction (Eq. 2.1) is controlled by the slowest process of either the kinetics of electron exchange, step 2, or the dynamics of mass transport, steps 1 and 3 [1, 2]. In chapter 4, we describe novel theoretical models for the coupled electron/ion and solvent transfers across film/electrode and solution interfaces. Three scenarios will be advanced in relation to the nature of control conditions; kinetic, thermodynamic or mixed conditions.

With regard to electron transfer, the kinetics of the system can experimentally be controlled via the electrode potential. The relationship between the variation of electrode potential and electron transfer kinetics is exponential [1]; this leads to the electron transfer rate varying substantially as a result of simply changing the electrode potential by a relatively small increment. For rapid electrochemical reaction, i.e. fast electron transfer, mass transport is the rate limiting [1]. On the other hand, for very slow electrochemical reaction, i.e. slow electron transfer, the study of electron kinetics is more important - for a successful data interpretation - than the observation of mass transport.

Mobile species transport can proceed by three different modes, depending on experimental conditions [1-5]: diffusion, convection and migration. These aspects will be the subject of discussion in the following sections.

2.2.1.1 Diffusion

Diffusion can be defined as the spontaneous movement of chemical species (at a molecular level) due to a concentration gradient until a uniform distribution of the

chemical species is reached through the system [1-5]. This process is indeed an integral part of electrode reactions [2]; the consumption of Ox at or near the electrode surface will result in concentration gradient with respect to the bulk solution, and hence a mass transport should occur via diffusion.

The rate of transport by diffusion can be quantified by using Fick's general laws (first and/or the second) or Cottrell equation (see section 2.2.2.1), based on a specific electrochemical technique.

2.2.1.2 Migration

Migration is the movement of charged particles under the influence of a potential gradient (cf. concentration gradient in diffusion process); this happens in the vicinity of electrode/solution interface [1-5]. In most electrochemical reactions, the effect of migration is kept to a minimum by the use of concentrated background electrolyte.

The role of the background electrolyte is to reduce the field strength on the target species (except very near the electrode surface, < 10 nm) [3]. In other words, it is the ions of the supporting electrolyte that migrate and respond to the electrostatic force created by the potential polarisation of the electrode.

2.2.1.3 Convection

Unlike the diffusion process, convection involves the bulk movement (cf. chemical species movement) of the solution; this is sometimes called “hydrodynamic mass transport”. There are two phenomena associated with convection [1-5]: the first is a “*forced convection*” which can be performed either by i) mechanical stirring of solution, ii) rotating the electrode or iii) letting the solution flow through the electrochemical cell, and the second is a “*natural convection*” in which chemical species movements are caused by the thermal and/or density variations within the solution. The effect of convection is very small at short experimental timescale in quiescent solution and can be ignored.

2.2.2 Electrochemical Techniques

A myriad of electrochemical techniques are studied in the traditional texts of the subject. Among these techniques, cyclic voltammetry (and/or its corresponding

coulometry, integrated variant) is the method used in this research project for both polymer deposition and characterisation. Below, the basic principles of the technique are reviewed in a more interpretational way.

2.2.2.1 Cyclic Voltammetry

In section 1.5.1.1, the fundamental features of cyclic voltammetry were explained. In this section, the mathematical and theoretical aspects that govern the characteristic features of the techniques will be discussed.

Commonly, voltammetric experiments are carried out in stationary solutions [1]. The mass transport to and from the electrode surface, then relies upon diffusion process (see section 2.2.1.1). The flux of species following the electrode reaction (Eq.2.1) is defined by Fick's second law [1-5]:

$$\frac{\partial[Ox]}{\partial t} = D_{Ox} \left(\frac{\partial^2[Ox]}{\partial x^2} \right) \quad (2.2)$$

where $\partial[Ox]/\partial t$ is the flux of the oxidised species, $\partial[Ox]/\partial x$ is the concentration gradient of the Ox species with respect to the distance, x , these species should travel to the electrode surface, and D_{Ox} is the diffusion coefficient. Using Einstein equation, the depletion (diffusion) layer thickness, Δx , can be found through the relationship:

$$\Delta x = (\pi Dt)^{1/2} \quad (2.3)$$

For the polymer modified electrode (the core subject of this thesis), the mobile species movement - following the charge propagation within the film – is another form of mass transport process by means of diffusion; note the redox centres themselves may be considered as fixed points. This may depend on the balance between the time constant of a film's redox transformation, $\tau = l^2/D$ (l being film thickness) and the timescale, t , of particular experiments (see section 1.5.1.1).

In cyclic voltammetry, the scan rate controls the experimental timescale. The potential of the electrode at any point (as a function of time) can be expressed as:

$$E(t) = E_i + vt \quad (2.4)$$

where E_i is the initial potential, and v is the scan rate (see the schematic representation in Fig. 2.2).

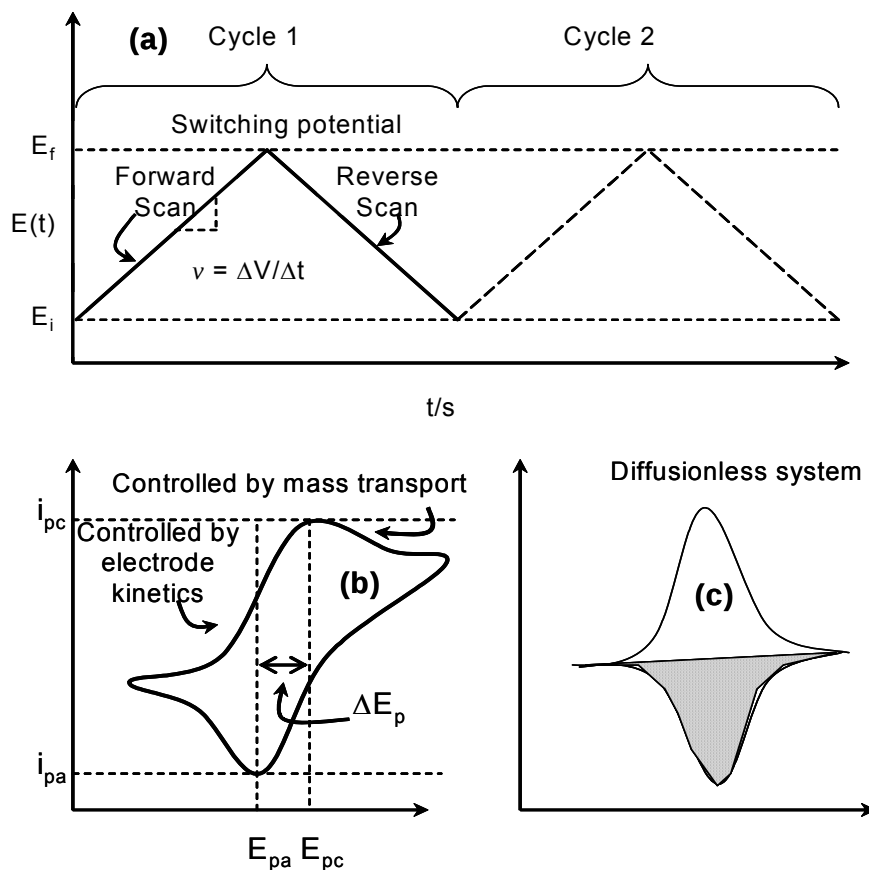


Fig. 2.2: schematic representation of typical cyclic voltammetry experiments based on Eq.2.1; a) the triangular waveform of cyclic voltammetry with respect to time; b) cyclic voltammogram of electroactive species in solution (under diffusion control); and c) voltammogram expected from surface-bound electroactive films (diffusionless system).

In this experiment, the data is recorded as a current response against the cycled potential, and hence, the term “cyclic voltammetry”. In panel *b* of Fig. 2.2, the current response goes through a maximum peak. The behaviour of the system is initially controlled prior to the peak maximum by the kinetics of the heterogeneous electron transfer across the electrode/solution interface (i.e. heterogeneous rate constant, k_e) [1, 2]. After the peak maximum, the current response flows under the

influence of the concentration gradient of the redox couple (i.e. under diffusion control, D).

Quantitatively, the value of peak current, i_p , (at 25 °C) for the diffusion controlled (*reversible*) systems can be calculated using Randles-Sevcik equation [1-5]:

$$|i_p| = 2.69 \times 10^5 AC^\infty (n^3 Dv)^{1/2} \quad (2.5)$$

where n is the number of electrons transferred, A is the electrode area, D is the diffusion coefficient of the redox species, C^∞ is the bulk concentration of the redox species, and v is the scan rate for the cyclic voltammetry experiment. According to Eq. 2.5, the peak current is proportional to the square root of the scan rate ($i_p \propto v^{1/2}$).

Unlike diffusion controlled systems, the surface-confined electroactive species show the type of the voltammogram depicted in panel *c* of Fig. 2.2. In this redox conversion system, electroactive species are bound to the electrode surface (no diffusion from the bulk solution required) and the peak current can - ideally - be obtained by:

$$|i_p| = (n^2 F^2 v A \Gamma) / 4RT \quad (2.6)$$

where Γ is the surface coverage of the redox species (the population of which can be evaluated from the area under the peak curve) and the rest have their usual meanings. Here the peak current is related to v , but not to $v^{1/2}$ as in the diffusion-controlled systems [4]. Eq. 2.6 applies when thin films show Langmuir behaviour, i.e. no site-site interaction. Under non-ideal conditions, diffusion-like response is observed due to the repulsive/interactive forces of polymer redox-active sites.

In potentiodynamic experiments, the thermodynamic and kinetic information of the system can be inferred from a number of characteristic features in the i - E curve. Moreover, the shape, width, and the position of peak currents (e.g. i_p , E_p , ΔE_p , see panels *b* and *c* of Fig. 2.2) and how these features vary with the scan rate can be decisive on the condition under which the system is controlled. The shape of the

voltammogram is an indicative of reversibility/irreversibility of electrochemical reaction at the electrode surface; the terms “*reversible and irreversible*”, here, refer to whether the electrode kinetics (electron transfer) is fast (slow) relative to the mass transport of the redox species [2, 3]. If the electron transfer across electrode/solution interface is rapid and the accompanying redox process remains in equilibrium throughout the potential cycle, the system is said to be electrochemically reversible. In this case, the ratio of the surface concentration of Ox/Red couple obeys the value required by the Nernst Equation at each point of the potential scan:

$$E = E^o + \frac{RT}{nF} \ln \left(\frac{[Ox]_o}{[Red]_o} \right) \quad (2.7)$$

where E is the applied potential, E^o , $[Ox]_o$ and $[Red]_o$ are the formal potential and surface concentrations of redox couple, respectively, and the rest have their usual meaning.

In addition, one should note that the reversibility (irreversibility) behaviour of the system depends on the relative values of the heterogeneous rate constant, k_e , of the electron transfer and the potential scan rate, v ; practically, what is more important is the ratio of the two parameters, k_e/v or in other words, the normalisation of the rate constant with the experimental scan rate. If the value of k_e/v is sufficiently very small, i.e. either the rate constant, k_e , is very small (slow electron transfer) or the scan rate, v , is relatively very high (in other words, the mass transport does not have enough time to keep pace with electrode dynamics), the above Nernst equation (Eq. 2.7) cannot be maintained and the system is said to be “*irreversible*” or under kinetic control.

I – Thermodynamic Control Condition

When the normalised parameter, k_e/v , of the electrochemical reaction is sufficiently large, the system is reversible and under thermodynamic control (i.e. within particular experimental timescales). In a cyclic voltammetry experiment, characteristic features are observed in i - E profiles for electrochemically reversible processes are:

- ▶▶ The peak potential separation, $\Delta E_p = E_{pa} - E_{pc}$ (see Fig. 2.2, panel *b*) has the value of $0.058/n$ V at 25 °C for all scan rates. Under thermodynamic control, the peak potential and separation are both independent of the scan rate though slightly influenced by the switching potential and the cycle number [3]. With the knowledge of the peak potential width, the number of electrons, n , involved in the electrochemical reaction can then be calculated.
- ▶▶ The formal reduction potential, E^0 , of the redox couple can be obtained from the mean value of peak potentials: $E^0 = (E_{pa} + E_{pc})/2$ provided the transfer coefficient, $\alpha = 0.5$; a parameter that measures the potential dependence of the electron transfer rate constant.
- ▶▶ The values of anodic, i_{pa} , and cathodic, i_{pc} , peak currents have the same magnitude, i.e. $i_{pa}/i_{pc} \approx 1$ for $D_{Ox} = D_{Re}$. Reproducible curves are often obtained after a number of cycles (due to settling-down effects), and this equation should strictly be considered beyond the first scan [3].

II – Kinetic Control

Conversely, when the value of the normalised parameter, k_e/v , is small (cf. large in the above condition), the electrochemical system is under kinetic control. This is due to either slow electron transfer (i.e. small k_e vs fast mass transport) or very slow mass transport (i.e. very high scan rate vs fast electron exchange). In other words, the electrochemical reaction is either irreversible in terms of electron transfer or the equilibrium condition has not yet been reached within the particular experimental timescale in terms of mass transport for the redox couple. The following diagnostic tests can be noted when the system is under kinetic control:

- ▶▶ The peak width, ΔE_p , increases above that of the reversible process, i.e. $\Delta E_p > 0.058/n$ V. In this condition, the peak width is a function of both the heterogeneous rate constant, k_e , and the potential scan rate, v [2, 3]; the variation of the peak width with the scan rate may, therefore, be useful for estimating the value of the rate constant for electron transfer at electrode/solution interface. Further to this, the peak separation might be influenced by the IR drop across the solution, and this effect should be at best minimised; ideally eliminated [4, 5].

- The transfer coefficient, α (a parameter that measures the potential dependence of the electron transfer rate constant [6] with a typical values of $0.3 < \alpha < 0.7$) and the number of electrons, n , involved in the electrode reaction can be acquired from the difference between the peak potential, E_p , (either cathodic or anodic) and the half peak potential, $E_{p,1/2}$ [6] by:

$$E_p - E_{p,1/2} = 0.048 / \alpha n \quad (2.8)$$

Alternatively, the two variables (α and n) can be evaluated by taking the difference of peak potentials from i-E curves recorded at two different scan rates [2, 7]:

$$E_{p,2} - E_{p,1} = \left(\frac{RT}{\alpha n F} \right) \ln \left(\frac{v_1}{v_2} \right)^{1/2} \quad (2.9)$$

where $E_{p,2}$ and $E_{p,1}$ are the peak potentials of cyclic voltammograms taken at the scan rates, v_2 and v_1 , respectively, the rest have their normal meanings.

III – Limitations of Cyclic Voltammetry

Alongside the widespread advantages of cyclic voltammetry over most other electrochemical techniques, there are a number of limitations associated with this powerful technique. First, the coupled effects of the slow processes for electrode dynamics and an accompanying chemical reaction can be mixed responses (difficult to separate) in cyclic voltammetry experiments. Under this circumstance, the heterogeneous rate constant of the electron transfer may be calculated using simulation studies [8]. Exploring the effect of the variation of i_{pa}/i_{pc} ratio with the scan rate can also give an insight into the rate of the chemical reaction [8]. Second, in potentiodynamic experiments, there is a background charging current with a magnitude of vC_{dl} throughout, where v is the scan rate and C_{dl} is the double layer capacitance at electrode/solution interface. As a result of this background current (non-Faradaic), the detection limit of the current response (Faradaic) is restricted to about 10^{-5} M [3, 8]. The detection limit of the current response can be improved via the increase of the scan rate, which in turn leads to the increase of peak current (defined by Eqs. 2.5 and 2.6). However, increasing the scan rate compromises the

signal to noise ratio, i.e. peak current to charging current; this is due to the direct relationship of the charging current to the scan rate, $i_c \propto v$ (cf. $i_p \propto v^{1/2}$) [3, 8]. This limitation sets the upper value of the scan rate that can be used in cyclic voltammetry experiments.

The effect of the background current on the measured signal (Faradaic current) can be significantly reduced using a differential method [3]. In this method, simultaneous potential scans are performed on two matched electrodes; one electrode is immersed in a solution containing the target species and the other electrode in a blank electrolyte. The results of the two electrode responses are then subtracted eliminating the effect of the background current. This method relies on the reproducibility of electrode responses.

In general, all electrochemical techniques – including cyclic voltammetry – share common aspects. For example, these techniques are blind to electroinactive species (i.e. solvents, important for determining the composition of polymer modified electrodes), and do not give information on interfacial structure. Combining electrochemical techniques with other in situ techniques is the appropriate step forward for solving out these problems.

2.3 Thickness Shear Mode (TSM) Resonator

The thickness shear mode (TSM) resonator, also known as quartz crystal microbalance, is a powerful technique used as both a gravimetric sensor and/or material properties probe [9-19]. The functioning of the technique is based on an electric excitation of a piezoelectric quartz crystal. Understanding the basic principles of the technique is crucial for the work carried out in this research. Moreover, the theoretical aspects underlying the practical operations of the TSM resonator will be discussed in the following sections.

2.3.1 Piezoelectric Quartz Crystal

Materials that produce an electrical potential when mechanically stressed are said to be “piezoelectric”; from a Greek work “piezein” that means “to press” [10, 20]. This effect is called the “direct piezoelectric effect”. Conversely, applying an electrical

potential across the piezoelectric material creates a corresponding mechanical deformation. This effect is also known as the “converse piezoelectric effect”. This property is related to the dipole moments and the internal arrangements of atoms in the crystalline lattice (asymmetric centre). Many naturally occurring crystals show this effect of which the quartz crystal is the most import and popular.

For quartz crystals, different piezoids (modes of oscillation) are produced depending on the cutting angle with respect to the crystallographic axis of the single crystal [10, 12, 20]. The most common cut used is the AT cut due to its stability, zero temperature coefficient, and availability at reasonable low cost [10, 12, 14]. In AT-type of a cut, the desired part of the crystal is sliced from a large single crystal of α -quartz at an angle of $35^\circ 15'$ with respect to z-axis (see Fig.2.3).

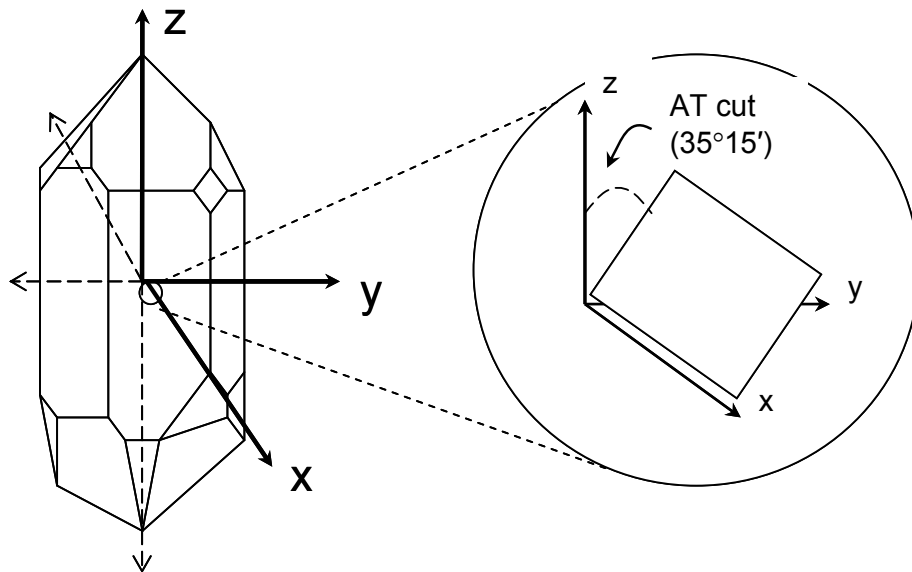


Fig. 2.3: Schematic representations of AT-cut α -quartz crystal.

2.3.2 Quartz Crystal Microbalance

Quartz crystal microbalance (QCM) is an acoustic wave device based on the *piezoelectric* property of the AT-cut α -quartz crystal. In this technique, two metal electrodes (typically, Au or Pt) are placed on the opposite sides of a thin wafer of the crystal (Fig. 2.4, panel b). The application of an oscillating potential to the AT-cut crystal drives the crystal mechanical vibration in a shear mode resonance (i.e.

displacement parallel to quartz crystal surfaces, see Fig. 2.4, panel a) [9, 10, 13, 16, 20]. At the natural mechanical resonance of the piezoelectric crystal, a standing acoustic wave propagates across the crystal thickness with the maximum displacement (antinodes) occurring at the crystal faces and a node (i.e. stationary points) existing at the centre of the crystal (see Fig. 2.4) [12, 14, 20, 21].

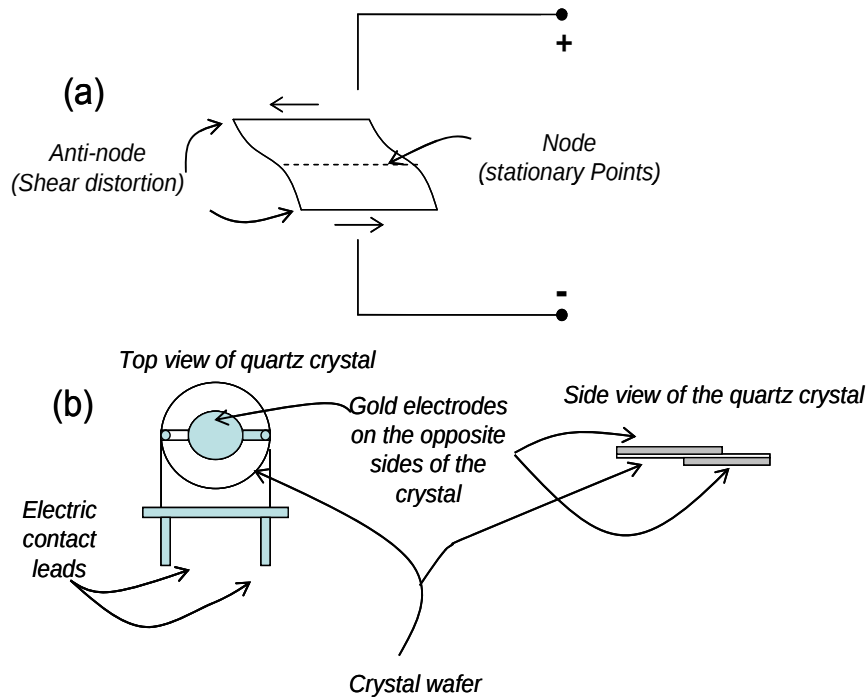


Fig. 2.4: schematic representation of AT-cut α -quartz crystal: a) an exaggerated view of crystal vibrating in shear mode with maximum displacement at crystal faces and a central node; b) top and side views of a crystal with two Au electrodes on opposite sides.

The fundamental frequency, f_o , of the crystal resonance is inversely proportional to the thickness of the crystal slice [9-12, 14]. Crystal resonance occurs when the crystal thickness, h_q , corresponds to an odd multiple of half the wavelength of the propagating acoustic wave [9-11] as defined by:

$$h_q = \frac{1}{2} N \lambda = \frac{1}{2} N \left(\frac{v_s}{f_o} \right) \quad (2.10)$$

where h_q is the thickness of the crystal wafer, λ is the acoustic wavelength, v_s is the shear wave velocity, N is an odd integer ($N = 1, 3, 5, \dots$) and f_o is the fundamental resonant frequency of the crystal oscillation. In mechanical physics, the shear wave

velocity (a material property) can be found from the intrinsic values of crystal shear modulus, μ_q ($\mu_q = 2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$) and the crystal density, ρ_q ($\rho_q = 2.648 \text{ g cm}^{-3}$):

$$v_s = \left(\frac{\mu_q}{\rho_q} \right)^{1/2} \quad (2.11)$$

Inserting Eq.2.11 into Eq.2.10, we get:

$$h_q = \frac{1}{2} \frac{N}{f_o} \left(\frac{\mu_q}{\rho_q} \right)^{1/2} = \frac{N}{f_o} (1.7 \text{ nm/s}) \quad (2.12)$$

Eq. 2.12 establishes a direct relationship between the crystal thickness and the fundamental resonant frequency of the crystal. Most measurements in QCM experiments are performed at fundamental frequencies of 5 and 10 MHz corresponding to $h_q \equiv 0.0334$ and 0.0167 cm , respectively for AT-cut crystals [9, 10]. Eq. 2.12 also implies that using very thin crystals can result in higher resonant frequencies; however, handling very thin crystals (fragile) is practically difficult (sensitivity vs robustness). An alternative solution to this problem can be the excitation of the crystal resonance at higher harmonic frequencies (through the control of the applied alternating potential) instead of reducing the crystal thickness.

2.3.2.1 Mass-Frequency Relationship

Eqs. 2.10 and 2.12 define the inverse relationship between the crystal thickness, h_q , and the fundamental resonant frequency, f_o , of the crystal oscillation. It is straightforward to show that the increase in crystal thickness (as a result of mass accumulation) will lead to a decrease in the resonant frequency; this means that changes in frequency, Δf , result from changes in the crystal thickness. Mathematically, this relationship can be expressed as follows:

$$\frac{\Delta f}{f_o} = - \frac{\Delta h}{h_q} \quad (2.13)$$

where the negative sign indicates the opposite directions of change between the thickness-frequency changes. With the knowledge of the density, ρ_q , and the piezoelectric active area, A_p , of the crystal, the change in thickness, Δh , in Eq.2.13 (due to mass deposition on the crystal surface) can be converted into the corresponding mass:

$$\Delta h = \frac{\Delta m}{A_p \rho_q} \quad (2.14)$$

Substitution of Eq. 2.14 into Eq. 2.13, gives a direct relationship between the frequency change, Δf , and the mass uptake, Δm on the crystal surface:

$$\frac{\Delta f}{f_o} = - \frac{\Delta m}{h_q A_p \rho_q} \quad (2.15)$$

Now, combining Eqs. 2.12 and 2.15 we get:

$$\frac{\Delta f}{f_o} = - \frac{2 f_o}{N} \frac{\Delta m}{A_p \rho_q} \left(\frac{\mu_q}{\rho_q} \right)^{\frac{1}{2}} \quad (2.16)$$

Using algebraic rearrangement with a further simplification of Eq.2.16, we obtain the well-known basic Sauerbrey Equation:

$$\Delta f = - \frac{2 f_o^2 / N}{(\mu_q \rho_q)^{1/2}} \frac{\Delta m}{A_p} \quad (2.17)$$

Eq.2.17 is frequently abbreviated to:

$$\Delta f = -C_1 \Delta m \quad (2.18)$$

where $C_1 = 2.26 \times 10^8 \text{ Hz cm}^2 \text{ g}^{-1}$ represents the combination of quartz and crystal constants as defined earlier, and $N = 1$ for the fundamental resonant frequency of 10

MHz AT-cut crystal. One of the practical advantages of the QCM is that there is no need for a prior calibration of the device as the areal mass sensitivity of the crystal is a precisely known quantity [11]. Eq. 2.18 shows that a frequency change of 1 Hz, for 10 MHz crystal, corresponds to a mass change of ca. 1 ng; this can give access to sub-nanomole population changes on the electrode surfaces.

2.3.2.2 Electrochemical Quartz Crystal Microbalance (EQCM)

QCM experiments are often used in combination with electrochemical techniques. In this case, the device is dubbed “*Electrochemical Quartz Crystal Microbalance*” (EQCM). In these experiments, one of the two electrodes deposited on the crystal faces is employed as the working electrode and exposed to liquid medium. Under these conditions, the resonant frequency shift of the QCM does not only depend on the mass load, but also on the density and viscosity of contacting liquid [22-28]. Incorporation of this effect into the Sauerbrey equation gives [23, 24, 28]:

$$\Delta f = -f_o^{3/2} \left(\frac{\rho_L \eta_L}{\pi \rho_q \mu_q} \right)^{1/2} \quad (2.19)$$

where $\rho_L \eta_L$ is the product of density and viscosity of the liquid. Under ideal conditions, the shift in frequency caused by this product, $\rho_L \eta_L$, (due to the viscous coupling of the QCM to the liquid media) is found to be constant during the course of the experiment, i.e. contributions from this product can be ignored [29]. Consequently, the Sauerbrey equation still remains applicable in electrochemical experiments. Polymer films encountered in electrochemical investigations are, however, commonly viscoelastic in nature and their contribution to the behaviour of the QCM device should not be ignored. Viscoelastic effects on the electromechanical behaviour of thickness shear mode resonators will be discussed in section 2.2.3.3.

Combination of Faraday’s law with the Sauerbrey equation is of great practical importance in terms of determining the composition of thin polymers immobilised on electrode surfaces during redox cycling. The correlation of $Q-\Delta f$ data for film electrodeposition can also yield the effective molar mass of the monomer [16, 30, 31]. With the same combination, one can separate solvent population from the ions

exchanged under the influence of electrochemical control conditions [31]. For more details, one should refer to chapter 5.

2.3.2.3 Limitations of (E)QCM Experiments

Despite the powerful utilisation of (E)QCM as a very sensitive gravimetric sensor at a nanoscale level, there are a number of drawbacks associated with the use of this technique. Firstly, the linearity of Δf - Δm relationship, as defined by the Sauerbrey equation (Eqs. 2.17 and 2.18), fails at higher mass loads [9, 12]. This becomes apparent when the change in frequency, Δf , exceeds 2% of the initial value of fundamental resonant frequency, f_o [12, 14]; for the 10 MHz crystal, this corresponds to a frequency shift of ~ 200 kHz, i.e. ca. 1 mg cm^{-2} of surface mass accumulation.

The sensitivity of QCM frequency shift can be improved up to 40% of the initial resonant frequency (cf. 2%) by using a method known as “Z-match” [14, 20, 32]. In this method, the acoustic impedance, Z_f , of the mass load (foreign film layer) on the electrode surface should be known and matched to the acoustic impedance of the unperturbed quartz crystal, Z_q as defined by:

$$\tan\left(\pi \frac{f_t}{f_o}\right) = -\frac{Z_f}{Z_q} \tan\left(2\pi f_t \frac{\Delta m}{(\mu_f \rho_f)^{1/2}}\right) \quad (2.20)$$

where Z_f , μ_f , ρ_f are the acoustic impedance, shear modulus, and density of the foreign layer (mass load), Z_q is the acoustic impedance of the quartz crystal, and f_t is the resonant frequency of the crystal at time t . In practice, this method is not often used because of the very limited knowledge of the acoustic impedance of the foreign mass load. For further discussions, the reader is advised to consult with the cited references above; this is beyond the scope of this thesis.

For the (E)QCM to be valid as a gravimetric probe for the study of the composition (ion/solvent) of thin polymer films, the material on the surface of the electrode should be rigid and not experience significant shear deformation. If the material deposited on the electrode surface is viscoelastic in nature, crystal admittance analysis should be

used. This is a variant of the EQCM technique in which the electrical admittance of the crystal is recorded as a function of frequency in the vicinity of crystal resonance.

2.3.2.4 Crystal Admittance Analysis

This technique, also known as “Crystal Impedance Analysis” is very sensitive for discriminating viscoelastic and gravimetric regimes of polymer films deposited on electrode surfaces [9, 14, 15, 22, 29]. In principle, the admittance (the quotient of the current response and the applied potential, $Y = I/V$) of the film as a function of frequency near the crystal resonance is acquired using a network analyser (see chapter 3).

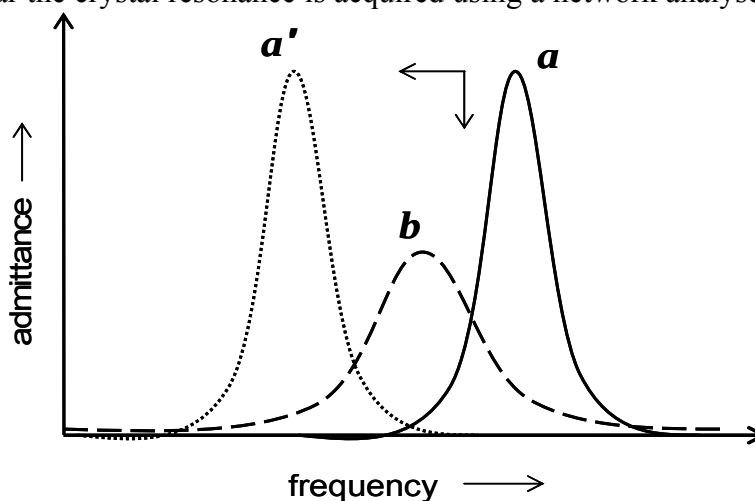


Fig. 2.5: Schematic representation of typical admittance spectra as a function of frequency in the proximity of crystal resonance; spectrum *a* represents the reference spectrum, usually a bare electrode in solution before film deposition; spectrum *a'* indicates a rigid film or mass layer deposited on the crystal (lateral negative shift of resonant frequency) and spectrum *b* represents a viscoelastic film which causes both lateral negative shifting of resonant frequency and damping of peak admittance.

Fig. 2.5 shows a schematic representation of typical admittance spectra of rigid film (spectrum *a'*) and a viscoelastic film (spectrum *b*) deposited on electrode surfaces. At crystal resonance, the electrical admittance, Y/mS , of the crystal goes through a maximum peak (minimum impedance, $Z = 1/Y$). Qualitatively, the shape and the position of the admittance peak are diagnostic of the physical properties of the film attached to the crystal surface.

For a rigid film (termed “*acoustically thin*”), the peak admittance shifts to lower frequency without a change in shape (no peak damping). In this case, the EQCM can be used as a gravimetric probe and the Sauerbrey equation is used to quantify the mass change. For a viscoelastic film (termed “*acoustically thick*”), both a change in position and shape of the peak admittance occurs (spectrum *b* of Fig. 2.5), i.e. a lateral negative shift of resonant frequency and a broadening in width and a decrease in height of the peak admittance (*peak damping*). In this case, the resonant frequency shift is not a function of mass change alone, but also reflects the viscoelastic properties of the material. Through electrical equivalent circuit models, the physical parameters pertaining to the mechanical properties of the polymer films can be extracted with good precision. Furthermore, the shear modulus components of the polymer – as a quantitative representation of film’s viscoelastic properties - can be calculated from the measured electrical impedance (admittance) of the composite system (quartz crystal/film); for details see chapters 6 and 7. In the following sections, the background theory of the electrical equivalent circuit models used for the polymer film characterisation will be briefly outlined.

2.3.2.4.1 Electrical Equivalent Circuits

Viscoelastic properties of polymer films deposited on a TSM resonator can be characterised via an electromechanical modelling representation [14, 17, 20, 28]. Basically, the oscillating surface of the TSM resonator interacts mechanically with the overlying film [9, 12, 14, 15]. This surface mechanical interaction of the crystal/film composite is reflected in the electrical properties of quartz crystal [12, 14, 15, 24, 33]; this is due to the piezoelectric property of the crystal quantified by the electromechanical coupling factor, $K^2 = 7.74 \times 10^{-3}$, of the quartz crystal. The effect of a deposited polymer film (whether rigid or viscoelastic) on the crystal response, then, depends on the mechanical impedance (the quotient of the surface stress driving the motion and particle velocity, the motion) contributed by the film layer. Therefore, the mechanical properties of the film can be directly extracted from the electrical response (expressed as either admittance or impedance) of the TSM resonator [15, 28, 29, 33, 34].

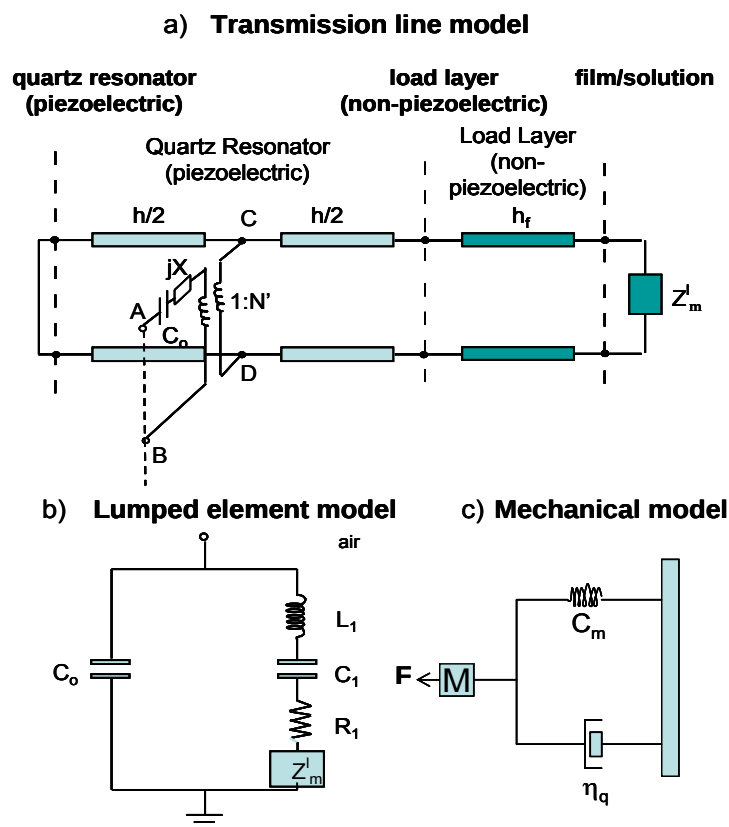


Fig. 2.6: Electrical equivalent circuits; a) transmission line model, also known as Mason model; b) lumped element model, also known as Butterworth van Dyke (BvD) model; c) a mechanical model consisting of a mass attached to a spring and a dashpot. The electrical components and their physical meaning in representation of the TSM resonator are explained in the text.

In crystal admittance (impedance) analysis, it is common practice to represent the mechanically oscillating system (crystal/film composite) by an electrical equivalent circuit in which a combination of resistors (R), capacitors (C), and inductors (L) is used to mimic the physical components of the system [9, 14, 28, 35-38]. Resistors represent energy loss due to viscosity, capacitors represent energy storage due to elasticity, and inductors represent inertial mass contributed by the mass upload. In addition, the voltage represents the shear stress while the current represents the particle velocity.

Analogously, the TSM resonator can be represented by a mechanical model consisting of a mass, M , attached to a spring with a compliance C_m (equivalent to $1/k$ where k is Hook's constant) and a dashpot with a viscous friction η_q (see Fig. 2.6, panel c) [14,

39]. The functional similarity of both equivalent electrical and mechanical models appears in equations of motion [14]:

$$M \left(d^2x/dt^2 \right) + \eta_q \left(dx/dt \right) + (1/C_m) x = F \quad 2.21a$$

$$L \left(d^2q/dt^2 \right) + R \left(dq/dt \right) + (1/C) q = V \quad 2.21b$$

where x is the surface displacement of the TSM resonator. The equations (2.21a and 2.21b) are equivalent through the electromechanical coupling coefficient, K , by $F = KV$.

In general, there are two electrical equivalent circuits in common usage for the representation of TSM resonators [9, 40, 41]; the transmission line model (TLM), also known as a Mason model and lumped element model (LEM), also referred as a Butterworth van Dyke (BvD) model – see Fig. 2.6.

In the transmission line model (TLM) as shown in panel *a* of Fig. 2.6, the two crystal faces are represented by two acoustic ports (marked as C and D) which are, in turn, connected by a transmission line to two electrical ports (marked as A and B) via a transformer; the number of turns N' is proportional to the quartz electromechanical coupling factor, K^2 . In TSM resonator applications, one face of the crystal is exposed to air. this is indicated by an electrical short in the TLM model, signifying zero impedance (i.e. stress-free). However, the other crystal face carrying the load (the film and the electrolyte solution) is represented by a surface load mechanical impedance, Z_m^1 .

The complex electrical input impedance, Z , for the TSM resonator with the loaded film (as described by TLM model in panel *a* of Fig. 2.6) can be found by [18, 35, 41]:

$$Z = Z_{AB} = \frac{1}{j\omega C_o} + jX + \frac{1}{(N')^2} Z_{CD} \quad (2.22a)$$

$$= \frac{1}{j\omega C_o} \left[1 - \frac{K^2}{\varphi_q} \frac{2 \tan(\varphi_q/2) - j\zeta}{1 - j\zeta \cot(\varphi_q)} \right] \quad (2.22b)$$

In Eq. 22a, Z_{CD} is the acoustic impedance at C-D, C_o is static capacitance due to the electrodes on opposite sides of the crystal, X is electrical reactance (imaginary part of the electrical complex impedance), N' is the transformer turns ratio, and $\omega = 2\pi f$ is the angular frequency (oscillation frequency). In Eq.22b, K^2 is the complex electromechanical coupling factor, ϕ_q is the complex acoustic wave shift across the crystal, $\zeta = Z_m^l/Z_q$, is the ratio of the surface load mechanical impedance, Z_m^l and the quartz characteristic impedance, $Z_q = (\rho_q \mu_q)^{1/2}$, where ρ_q and μ_q are the crystal density and crystal shear modulus, respectively, and $j = (-1)^{1/2}$ is the complex number.

Eq. 2.22 comprises a combination of two electrical impedances [9, 18, 34, 38]: a static capacitance, C_o , arising from the two metal electrodes (and the holding mounts), as defined above, in parallel with a motional impedance, Z_m , due to the piezoelectrically induced mechanical resonance of the crystal (with the non-piezoelectric film/electrolyte load on the crystal surface). Moreover, Eq. 2.22 can be expressed as:

$$Z = (j\omega C_o + 1/Z_m)^{-1} \quad (2.23)$$

After a little algebraic rearrangement of Eq. 2.22b in terms of the motional impedance, Z_m , in Eq. 2.23, we get:

$$Z_m = \frac{1}{j\omega C_o} \left[\frac{1 - j\zeta \cot(\phi_q)}{\frac{K^2}{\phi_q} (2 \tan(\phi_q/2) - j\zeta)} - 1 \right] \quad (2.24)$$

which can be expanded as [15, 29, 41]:

$$Z_m = \frac{1}{j\omega C_o} \left[\frac{\phi_q}{2K^2 \tan(\phi_q/2)} - 1 \right] + \frac{\phi_q \zeta}{4K^2 \omega C_o} \left[1 - \frac{j\zeta}{2 \tan(\phi_q/2)} \right]^{-1} \quad (2.25a)$$

$$= Z_1 + Z_2 \quad (2.25b)$$

In Eq.2.25b, Z_1 describes the motional impedance of the unperturbed quartz crystal resonator (i.e. without surface load), and Z_2 describes the added motional impedance arising from the surface load (i.e. film and/or electrolyte).

I - Unperturbed Crystal Resonator

From Eq. 2.25a, the motional impedance associated with the unloaded crystal resonator, Z_1 is given by [15, 22, 34, 41]:

$$Z_1 = \frac{1}{j\omega C_o} \left[\frac{\varphi_q / K^2}{2 \tan(\varphi_q / 2)} - 1 \right] \quad (2.26)$$

The tangent function in Eq. 2.26 can be approximated as shown in Eq. 2.27 near the quartz crystal resonance, i.e. the acoustic wave phase shift, $\text{Re}(\varphi_q) \cong N\pi$, where N ($N = 1, 3, 5, \dots$) is the harmonic number of the resonant frequency of the TSM resonator [15, 34].

$$\tan\left(\frac{\varphi_q}{2}\right) \cong \frac{4\varphi_q}{(N\pi)^2 - \varphi_q^2} \quad (2.27)$$

Substituting Eq.2.27 into Eq.2.26, we obtain:

$$Z_1 \cong \frac{1}{j\omega C_o} \left[\frac{(N\pi)^2 - \varphi_q^2}{8K^2} - 1 \right] \quad (2.28)$$

Correlating the motional impedance, Z_1 , of the unperturbed crystal and the corresponding physical quantities of the piezoelectric quartz crystal, Eq. 2.28 expands into [15, 34]:

$$Z_1 \cong \left(\frac{\omega^2 h_q^2 \rho_q \eta_q}{8K^2 C_o \mu_q} \right) + j\omega \left(\frac{h_q^2 \rho_q}{8K^2 C_o \mu_q} \right) + \frac{1}{j\omega} \left(\frac{(N\pi)^2 - 8K^2}{8K^2 C_o} \right) \quad (2.29)$$

where the definitions of the acoustic wave phase shift, φ_q , across the crystal, the complex shear modulus of the crystal, μ_q , are defined as follows:

$$\varphi_q = \omega h_q \sqrt{\frac{\rho_q}{\mu_q}} \quad (2.30a)$$

$$\mu_q = \mu_{q,o} + j\omega\eta_q \quad (2.30b)$$

where $\mu_{q,o}$ is the shear stiffness of the quartz crystal and η_q is the effective quartz viscosity. Since the quartz losses are very small, the approximations [34]: $|\mu_q| \cong \mu_{q,o}$ and $\omega\eta_q \ll \mu_{q,o}$ are also used in Eq. 2.29.

In the lumped element model, i.e. Butterworth van Dyke model, as shown in panel b of Fig. 2.6, a combination of series-connected resistor, inductor and capacitor in parallel with a static capacitor is used to represent the mechanical resonance of the TSM resonator. For the unperturbed crystal, the motional impedance of BvD model can be found by [18, 34, 37]:

$$Z_1 = R_1 + j\omega L_1 + \frac{1}{j\omega C_1} \quad (2.31a)$$

$$= R_1 + jX_1 \quad (2.31b)$$

where R_1 , L_1 , and C_1 are the resistance, inductance, and capacitance of the unperturbed crystal, respectively and X_1 is the reactive (imaginary) part of the impedance; $X_1 = (\omega L_1 - 1/\omega C_1)$. Near crystal resonance, Eq. 2.31 has the same frequency dependence as Eq. 2.29, i.e. $\omega = \omega_s$, where $\omega_s = 2\pi f_s$ and f_s is the series resonant frequency. In fact, series resonance occurs when the reactive part of the series impedance in Eq. 2.31 is zero. Comparison of Eq. 2.31a and Eq. 2.29, gives the values of the circuit elements for the unperturbed resonator as follows [34, 41]:

$$C_1 = \frac{8K^2 C_o}{(N\pi)^2 - 8K^2} \quad (2.32a)$$

$$L_1 = \frac{h_q^2 \rho_q}{8K^2 C_o \mu_q} \quad (2.32b)$$

$$R_1 = \frac{\omega_s^2 h_q^2 \rho_q \eta_q}{8K^2 C_o \mu_q} \quad (2.32c)$$

From the above values of the circuit elements, one can identify the series resonant frequency, ω_s , as [15, 34]:

$$\omega_s = \left(\frac{1}{L_1 C_1} \right)^{1/2} = \frac{N\pi}{h_q} \sqrt{\frac{\mu_q}{\rho_q}} \sqrt{1 - \frac{8K^2}{(N\pi)^2}} \quad (2.33)$$

Following the approximations made near crystal resonance, deviations between the resonant frequencies (determined empirically) of the full transmission-line characterisation and lumped element models are very small ($\sim 5\text{ppm}$); thus, the BvD model can be used to describe the unperturbed crystal resonator in all practical sensor applications [9, 15, 17, 22].

II - Surface Loaded TSM resonator

From Eq. 2.25a, the motional impedance associated with the surface load (film/electrolyte) is given by [18, 22, 34, 35]:

$$Z_2 = \frac{1}{\omega C_o} \frac{\varphi_q \zeta}{4K^2} \left[1 - \frac{j\zeta}{2 \tan(\varphi_q/2)} \right]^{-1} \quad (2.34)$$

When the surface load impedance, Z_m^l , is very small, the second term in brackets of Eq. 2.34 is much less than one, and Eq. 2.34 reduces to Eq. 2.35 using the same approximations as in Eqs. 2.27, 2.32 and 2.33 near crystal mechanical resonance:

$$Z_2 = \frac{N\pi}{\omega C_o} \frac{\zeta}{4K^2} \approx \frac{N\pi}{4K^2 \omega_s C_o} \left(\frac{Z_m^l}{Z_q} \right) = R_2 + jX_2 \quad (2.35)$$

where R_2 and X_2 are the real and imaginary components of motional impedance for the surface load; for the non-piezoelectric surface load, $X_2 = \omega L_2$. Theoretically, BvD responses of the surface-loaded TSM resonator match within 1% error of those of

transmission line model provided $Z_m^l \ll 0.2Z_q$ [15, 36, 37, 41]. This requirement is satisfied in most situations and in all those studied in this work.

In electrochemical applications, there are three primary surface types on the TSM resonator (see Fig. 2.7); an ideal mass layer, a Newtonian fluid and a viscoelastic film. In the following sections, the surface mechanical impedance, Z_m^l will be related to the physical parameters of the above-mentioned different surface loads.

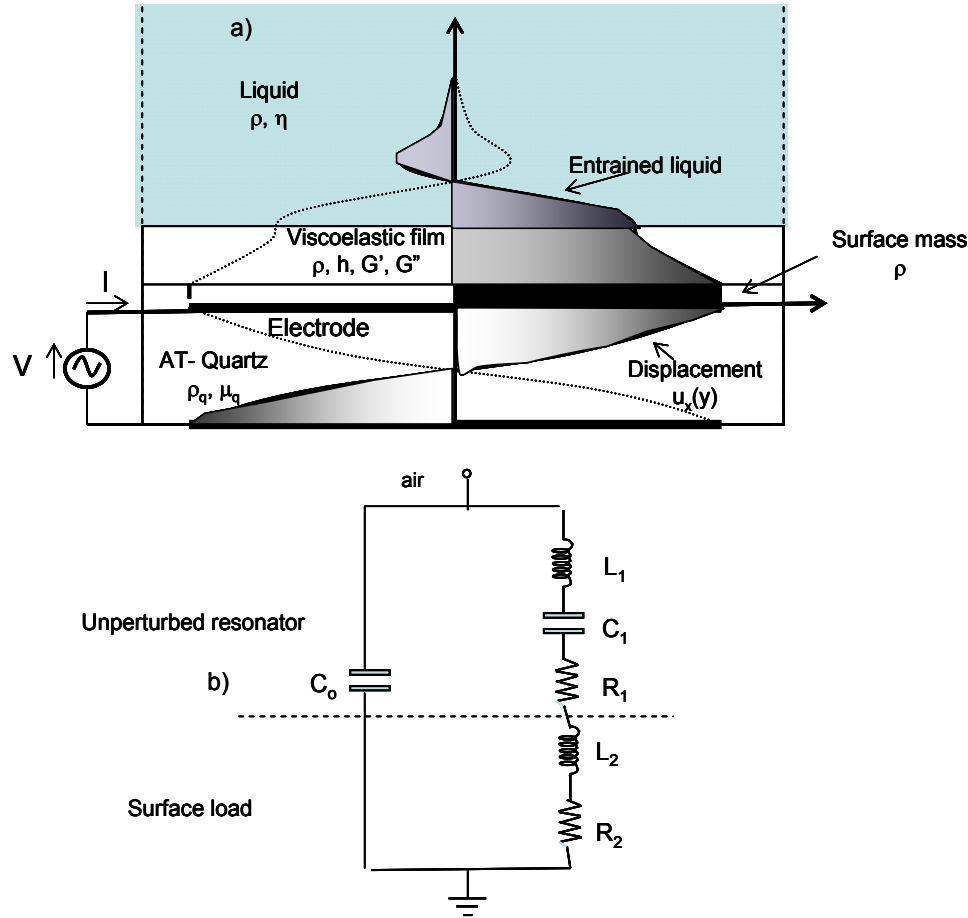


Fig. 2.7: Cross-sectional view of TSM resonator with a surface load of rigid mass, finite viscoelastic film and electrolyte liquid (panel a) and the corresponding modified BvD electrical equivalent model for the system (panel b); in panel b, the load impedance is broken into motional inductance, L_2 and resistance, R_2 .

III - Ideal mass layer

A sufficiently thin layer deposited on the crystal surface (Fig. 2.7) can be considered as an ideal mass layer. The rigidly coupled mass layer moves synchronously with the crystal, i.e. the propagating acoustic wave across the crystal undergoes a negligible

attenuation and phase shift, and the surface mechanical impedance, Z_m^l , contributed by this mass layer is [17, 35-37]:

$$Z_m^l = Z_{iml} = j\omega\rho_m \quad (2.36)$$

where ρ_m is the mass per unit area (the product of thickness and density) of the layer. Combining Eq.2.35 and 2.36, the motional impedance elements, R_2 and L_2 , due to the ideal mass layer are [15, 29, 41, 42]:

$$R_2 = 0 \quad (2.37a)$$

$$X_2 = \frac{N\pi}{4K^2\omega_s C_o} \frac{\omega\rho_m}{Z_q} \quad (2.37b)$$

From Eq. 2.37a-b, it is apparent that there is no power dissipation (R_2) associated with the ideal mass layer, but only energy storage (X_2) arising from kinetic energy of the mass layer [15, 42]. In other words, the energy storage is proportional to the areal mass, ρ_m , and results in a decrease in the resonant frequency without dissipative effect on the resonator admittance (see Fig. 2.5 above); this is in agreement with the Sauerbrey equation (Eq. 2.17).

IV - Semi-Infinite Newtonian Fluid

A Newtonian fluid on the TSM resonator is viscously coupled to the crystal surface by the shear motion of the resonator [23, 24, 43]. The shear stress of the entrained fluid (see Fig. 2.7, panel *a*) is related to the gradient of fluid velocity via the viscosity. Through the solution of the Navier-Stokes equation for the in-plane shear oscillation of the plane-parallel fluid flow, the surface mechanical impedance, Z_m^l , contributed by the semi-infinite Newtonian fluid can be obtained by [15, 34, 37, 41, 42]:

$$Z_m^l = Z_l = (1 + j) \left(\frac{\omega\rho_L\eta_L}{2} \right)^{1/2} \quad (2.38)$$

Combining Eq.2.38 with Eq.2.35, the motional impedance elements associated with the semi-infinite Newtonian fluid are found by:

$$R_2 = \omega L_2 = \frac{N\pi}{4K^2 \omega_s C_o Z_q} \left(\frac{\omega \rho_L \eta_L}{2} \right)^{1/2} \quad (2.39)$$

Eq. 2.39 shows that the power dissipation (R_2) and energy storage (L_2) components (related to the power radiation into the contacting liquid and the kinetic energy of the entrained liquid, respectively) are equivalent, and both are proportional to $(\rho_L \eta_L)^{1/2}$.

V - Viscoelastic Film

A TSM resonator loaded with a viscoelastic film (see Fig. 2.7, panel *a*), unlike the ideal mass layer, launches a shear acoustic wave across the film which in turn undergoes significant attenuation and phase shift [34, 37, 41]. The surface mechanical impedance, Z_m^l , of a finite viscoelastic film is [15, 18, 41, 44]:

$$Z_m^l = Z_f = (G \rho_f)^{1/2} \tanh(\gamma h_f) \quad (2.40)$$

where ρ_f and h_f are the density and the thickness of the viscoelastic film; $\gamma = j\omega(\rho_f/G)^{1/2}$ is the complex acoustic propagation constant determined by solving the equation of motion associated with the shear displacement profile of the film, and $G = G' + jG''$ is the complex shear modulus of the film. The hyperbolic tangent term in Eq. 2.40, describes the nature of wave interference between acoustic waves generated and reflected at the resonator/film and film/air interfaces, respectively. In the finite viscoelastic film, the film thickness, h_f , is much smaller than the decay length, $\delta = 1/\gamma$ (reciprocal of the wave propagation constant), of the acoustic wave propagating across the film. On the other hand, when the acoustic decay length, δ , is much smaller than the film thickness, h_f , the viscoelastic film behaves as though semi-infinite, and the surface mechanical impedance, Z_f , associated with the film (with the assumption of $\tanh(x) \rightarrow 1$, for $x \rightarrow \infty$) is:

$$Z_f = (G \rho_f)^{1/2} \quad (2.41)$$

Eq.2.41 reveals that the surface mechanical impedance contributed by the semi-infinite film is independent of the film thickness, h_f .

In the case of a thin rigid film, i.e. $G \rightarrow G'$, Eq. 2.40 reduces to Eq. 2.36 (with the assumption of $\tanh(x) \rightarrow x$, for $x \rightarrow 0$); this means that the rigid film behaves as an ideal mass layer and Sauerbrey equation (Eq. 2.17) holds for the data interpretation. Conversely, if the film shows very high viscous behaviour, i.e. $G \rightarrow jG'' = j\omega\eta$, Eq. 2.40 reduces to Eq. 2.38, i.e. the film exhibits liquid-like behaviour.

In electrochemical experiments, the most commonly encountered case is a finite viscoelastic film exposed to a Newtonian electrolyte solution (Fig. 2.7). The surface mechanical impedance, Z_m^l , arising from this composite is not equal to the sum of the characteristic individual impedances of the film (Eq. 2.40) and fluid (Eq. 2.38). This is due to the acoustic phase shift across the non-rigid film ($\varphi = \gamma h_f$), and the acoustic wave interference effects at the film/fluid interface [9, 34, 41]. In this case, Z_m^l of the composite is found by [15, 34, 41]:

$$Z_m^l = Z_f \left[\frac{Z_L + Z_f \tanh(\gamma h_f)}{Z_f + Z_L \tanh(\gamma h_f)} \right] \quad (2.42)$$

where Z_f and Z_L are the characteristic mechanical impedances of the viscoelastic film (defined by Eq. 2.40 and Eq. 2.41) and Newtonian fluid (defined by Eq. 2.38), respectively. With a simple inspection, one can easily discern that when $Z_L = 0$, i.e. no fluid on top of the film, Eq. 2.42 reduces to Eq. 2.40.

For polymer films deposited on crystal surfaces, the amount of material trapped due to the surface roughness is regarded as a thin ideal mass layer and Eq. 2.42 is modified as:

$$Z_m^l = j\omega\rho_s + Z_f \left[\frac{Z_L + Z_f \tanh(\gamma h_f)}{Z_f + Z_L \tanh(\gamma h_f)} \right] \quad (2.43)$$

2.4 Viscoelasticity of Polymer Films

The term “viscoelasticity” refers to materials that exhibit both viscous (liquid-like) and elastic (solid-like) properties. In general, polymer films show viscoelastic behaviour when they are mechanically perturbed due to segmental chain motions. The ability of the system to restore its original configuration (structural memory) depends on both the characteristic relaxation time (the time necessary for the system to forget the original configuration it had prior to perturbation) and the timescale of the experiment (perturbation) [45].

In liquids (viscous materials), the structural memory of the system is very short at molecular level and as a consequence, the molecular reorganisation occurs very rapidly. The mean characteristic relaxation time of liquids is very small [45-48]. In solids (elastic materials), on the other hand, the structural relaxation (molecular reorganisation) at the molecular level is extremely low. Therefore, the difference between solid (elastic) and liquid (viscous) is not based on an absolute distinction between different classes of materials [45]. However, a material to be defined as solid or liquid depends on the subjective comparison of the relaxation time of the system and the time of observation [45, 46]. For example, a liquid (e.g. water) behaves as solid at very high dynamic frequencies (short times) and a solid (e.g. ice) behaves as a fluid at very low frequencies (very long timescale).

In the following subsections, viscoelastic responses of polymer films to mechanical perturbation and/or temperature variation are discussed. In addition, detailed interpretation of polymer viscoelastic behaviour at the molecular level will be presented using theoretical models. Though the theoretical models discussed here were originally designed for bulk polymers, the novelty here lies with the application of these models to thin polymer films immobilised on electrode surfaces.

2.4.1 The Principle of Time-Temperature Superposition

The viscoelastic responses of polymer films are dependent on the temperature and the timescale ($t = 1/f = 2\pi/\omega$) of particular experiments [47, 49-55]. At long times, relative to the film’s characteristic stress relaxation time, τ , the viscoelastic film is soft (liquid-like material). [48, 52-54, 56]. Conversely, at very short times, the film

becomes progressively stiffer going through a transition between glassy and rubbery like regions (see Fig. 2.8). The transition region is experimentally unpredictable and may occur over a considerably long time. Consequently, the timescale of particular experiments often provide a very restricted observational “window” of the polymer stress relaxation process. It is not practical to run a single experiment for days and months (let alone years) to observe this unpredictable transition phenomenon.

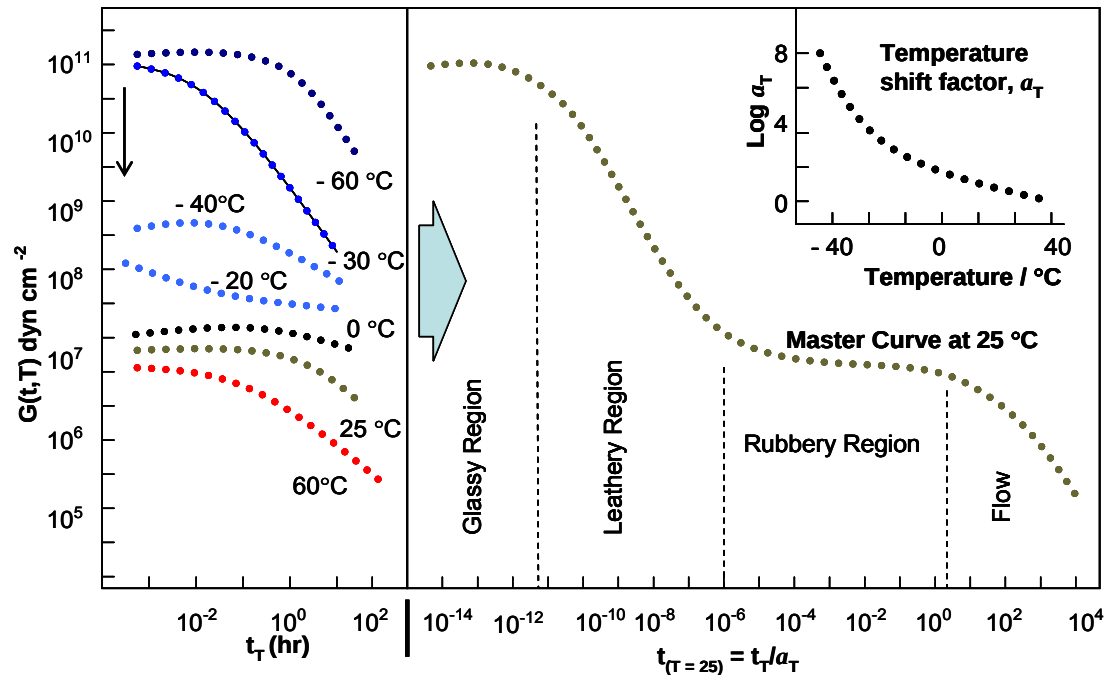


Fig. 2.8: schematic representation of time-temperature superposition for the shear modulus, $G(t,T)$, data of a viscoelastic film. On the left, the figure exhibits the experimentally measured shear modulus data, $G(t,T)$, as a function of time at given isotherms. On the right, the master curve is plotted; the superposition of the horizontally shifted isothermal data at an arbitrary reference temperature. The inset figure is the plot of temperature shift factors as a function of temperature. Refer to the main text for more details.

Alongside the timescale effect, the polymer relaxation process is highly temperature dependent through the change in film viscosity and the thermal energy of polymer chain vibrational motions that arise from temperature variation. Thus, the viscoelastic measurements of a wider “window” of effective timescales can be accessed via temperature variation at different experimental timescales.

Since the relaxation process of viscoelastic films is a function of both timescale and temperature, there is a general correspondence between the time (frequency) and the temperature dependences of viscoelastic films, i.e. a polymer film with rubbery characteristics under certain conditions may appear to be glassy at lower temperatures or shorter experimental timescales (higher frequencies). This is usually described as the “*time-temperature correspondence principle*” [45, 48-56]. This approach is well-developed and commonly applied to the characterisation of bulk polymers, but not thin films. For the first time, we have applied the “*time-temperature equivalence principle*” to thin surface-bound polymer films under electrochemical control experiments – the novelty here. In our experiments, we used a TSM resonator operating in higher harmonic modes (10 – 110 MHz) under electrochemical potential and temperature control conditions.

This principle makes possible the display on a single curve (known as a “*master curve*”) of the material behaviour over a much broader range of time (frequency) that can be measured at a single temperature or feasible experimental timescale. Basically, shear modulus data, $G(t,T)$, measured at different temperatures are plotted on common logarithmic time (frequency) scale (see Fig. 2.8). The isothermal curves are shifted horizontally with respect to an arbitrary reference temperature, T_0 , so that the curves superimpose at points of the same gradient (i.e. have similar habit) producing a single “*master curve*” covering the whole relaxation timescale (see Fig. 2.8). For a perfect superposition, a slight vertical shift is also required due to the material softening effect of temperature [45, 48-50]. One of the characteristic parameters of this principle is the so-called “*shift factor*, a_T ” which is the logarithmic horizontal displacement necessary to superimpose individual isotherms at T on the dynamic viscoelastic data measured at the arbitrary reference temperature, T_0 [45, 48, 50, 56]. This parameter “*shift factor*” is used as a gauge for the temperature dependence of material’s viscoelastic manifestations.

Practically, one should note that if $T > T_0$, then $a_T < 1$ and if $T < T_0$, $a_T > 1$; the consequence is that if the temperature of the system is varied, a corresponding time (frequency) of the polymer mechanical relaxation can be found at which the dynamic viscoelastic responses will be the same. In other words, the temperature variation is effectively accelerating or retarding dominant viscoelastic processes. Observably,

isotherms measured at high temperatures reflect the responses of viscoelastic data associated with long experimental timescales (low frequencies). In addition, mechanical excitations associated with relatively short times (higher frequencies) are detected at temperatures close to the glass transition temperature, T_g , a temperature below which the mobility of polymer chains is practically frozen.

The relaxation function, due to the time-temperature superimposition principle, will be of the form [45, 50, 51, 56]:

$$G(t, T) = G\left(\frac{t}{a_T(T)}, T_o\right) \text{ or } G(\omega, T) = G(a_T \omega, T_o) \quad (2.44)$$

where T_o is the reference temperature and $a_T(T)$ is the temperature shift factor obtained from the master curve. The term $t/a_T(T)$ is sometimes called the “reduced time” and gives the full-scale observational time-dependent window of the relaxation process if one would perform the experiment at the arbitrary reference temperature, T_o . In the common case, the mechanical properties of viscoelastic films depend on the ratio (τ/t or $\omega\tau$) of the films characteristic relaxation time, τ (temperature dependent variable), and the observational timescale, t . With the knowledge of the temperature dependence of τ , the values of the shift factors, a_T , can be predicted. Conversely, if the shift factors are determined (via the construction of the master curve), one can get an insight into the underlying physicochemical processes and the energetics of the system (see chapter 8).

In fact, the principle of time (frequency)-temperature superposition will fail if all viscoelastic responses (relaxation processes) of the material do not have the same temperature dependences [45, 49, 54, 56]. In other words, the shift factors, a_T , should be same for all viscoelastic functions (within the precision of the experiment), i.e. for both $G'(t, T)$ and $G''(t, T)$. For example, if the material undergoes a phase transformation in the temperature range of interest or if the dominant relaxation mechanism is not thermally activated, the principle will not hold.

The physical significance of the time (frequency)-temperature correspondence principle can be addressed through the application of well-established models: Activation Model, Williams-Landel-Ferry model and Rouse-Zimm model. With the use of these models, one can effectively interpret macroscopic viscoelastic responses in terms of the underlying molecular level physicochemical processes.

2.4.2 Activation Model

The activation model is developed to describe the side-chain motions of branched polymers [52-54]. The thermal activation enthalpy, ΔH_a , associated with the shrinking or stretching behaviour of the polymer side-chains (due to the temperature variation) can be calculated from the experimentally determined shift factors, a_T by [45, 48, 56]:

$$\Delta H_a = 2.303R \frac{\partial \log a_T(T)}{\partial (1/T)} \quad (2.45)$$

where $R = 8.32 \text{ J mol}^{-1} \text{ K}^{-1}$ is the gas constant. The activation enthalpy, ΔH_a , can be extracted from the gradient of Arrhenius-type plot of Eq. 2.45.

2.4.3 Williams-Landel-Ferry (WLF) Model

WLF model is developed to describe viscoelastic responses on the basis of the long-range backbone motions of polymer chains. In this model, the stress relaxation processes are interpreted via shift factors in terms of material parameters for viscoelastic polymers as follows [45, 47, 49-51, 55]:

$$\log a_T = \frac{-C_1(T - T_o)}{C_2 + T - T_o} \quad (2.46)$$

where T_o is the arbitrary reference temperature, and C_1 and C_2 are material-specific constants. When the reference temperature is set to be the glass transition temperature T_g , many viscoelastic polymers have nearly “universal” values for $C_1 = 17.4$ and $C_2 = 51.6$. In terms of the theoretical rationalisation of the WLF model, we need to consider the semi-empirical Doolittle equation [45, 48]:

$$\ln \eta = \ln A + B \left(\frac{1}{f} - 1 \right) \quad (2.47)$$

where η is the viscosity, f ($f = V_f/V$, where V_f and V are free volume and total volume, respectively) is the fractional free volume (unoccupied space) of the system, and A and B are constants.

Above the glass transition temperature, the fractional free volume, $f = V_f/V$, increases linearly with temperature by [45, 48]:

$$f = f_g + \alpha_T(T - T_g) \quad (2.48)$$

where f is the fractional free volume at T , any temperature above T_g , f_g is the fractional free volume at T_g , and α_T is the thermal coefficient of the fractional free volume above T_g . Inserting Eq. 2.48 into Eq. 2.47, the Doolittle equation becomes:

$$\ln \eta(T) = \ln A + B \left(\frac{1}{f_g + \alpha_T(T - T_g)} - 1 \right) \text{ at } T > T_g \quad (2.49)$$

and at T_g :

$$\ln \eta(T_g) = \ln A + B \left(\frac{1}{f_g} - 1 \right) \quad (2.50)$$

Subtracting Eq. 2.50 from Eq. 2.49 yields:

$$\ln \frac{\eta(T)}{\eta(T_g)} = B \left(\frac{1}{f_g + \alpha_T(T - T_g)} - \frac{1}{f_g} \right) \quad (2.51)$$

With a little algebraic rearrangement, Eq.2.51 simplifies to a form identical to the WLF equation:

$$\log \frac{\eta(T)}{\eta(T_g)} = \log a_T = -\frac{B}{2.303 f_g} \left(\frac{T - T_g}{(f_g / \alpha_T) + T - T_g} \right) \quad (2.52)$$

where $C_1 = B/2.303f_g$ and $C_2 = f_g/\alpha_T$. From Eq.2.52, one can recognise that WLF equation is simply a short-hand form of the empirical Doolittle equation. The glass transition temperature T_g , fractional free volume at T_g , and the thermal expansion coefficient, α_T , above T_g are all useful parameters for polymer technology and can be determined from the master relaxation curve.

2.4.4 Rouse-Zimm Model

The Rouse-Zimm model describes viscoelastic responses of polymers in viscous medium on the basis of multiple relaxation times and partial moduli associated with each relaxation time [45, 48, 56]. The model considers a polymer film containing N chains per unit volume (cm^{-3}) in which each chain is also subdivided into z sub-molecular units. The characteristic relaxation time, τ_p , of each sub-molecular polymer chain perturbation can be found by [45, 48, 52, 56, 57]:

$$\tau_p = \frac{6\eta}{Nk_B T \pi^2 p^2} \quad (2.53)$$

where η represents the viscosity of the medium in which chains are present, $p = 1 \dots z$ and $Nk_B T$ is modulus associated with each relaxation time; k_B is the Boltzmann constant and Eq. 2.53 can also be derived from the Stokes-Einstein relationship ($\tau = l^2/D = k_B T / 6\pi\eta a$ with $N = a^{-3}$). Based on the Maxwell-Wiechert mechanical model (a combination of parallel sets of a serially connected dashpot and a spring, see panel c of Fig. 2.6), the dynamic real, $G'(\omega)$, and imaginary, $G''(\omega)$, shear moduli of the polymer relaxation process can be found, respectively, by [45, 48, 56]:

$$G'(\omega) = Nk_B T \sum_{p=1}^z \frac{\omega^2 \tau_p^2}{1 + \omega^2 \tau_p^2} \quad (2.54a)$$

$$G''(\omega) = Nk_B T \sum_{p=1}^z \frac{\omega \tau_p}{1 + \omega^2 \tau_p^2} \quad (2.54b)$$

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Chapter Three

Experimental

3.1 Overview

In this chapter, the experimental work in terms of materials, instrumentation, procedures and the methodologies adopted for data interpretation is described. The major experimental performance carried out in this thesis was the deposition and characterisation of conducting polyaniline films in both gravimetric and viscoelastic terms. Flavin derivative SAMs used as surface-bound receptors for 2,6-diamidopyridine (DAP) dendrimer and their characteristic isotherms were also thoroughly investigated. Electrochemical, (E)QCM and crystal admittance analysis were the techniques employed.

3.2 Instrumentation

3.2.1 Crystal Preparation

Quartz crystals used in this project were described in sections 2.3.1 and 2.3.2 of chapter 2. In terms of the surface finish, the 10 MHz AT-cut quartz crystals were of two types: polished (smooth) and unpolished (rough) crystals. The thin wafer (~ 0.2 mm of thickness) of the 10 MHz quartz crystals has the surface finish of $5\text{ }\mu\text{m}$ for the rough crystals and $< 2\text{ }\mu\text{m}$ for the smooth crystals. The unpolished crystals were used for the deposition of Flavin derivative SAMs and the subsequent characterisation of the monolayer with DAP-dendrimer. With regard to polymer films (here, polyaniline) two types of experiments were performed; gravimetric investigations of thin polyaniline film composition and viscoelastic studies of thick polyaniline viscoelastic responses. In both cases, polished crystals were used to minimise the effect of mass trapping in the surface features of the crystal. The thickness of the gold electrodes on opposite sides of the crystals is $\sim 90\text{ nm}$ and the piezoelectric and electrochemical

active areas of the crystal are 0.21 and 0.23 cm², respectively. In all experiments, the crystals were used as supplied by the International Crystal Manufacturing (ICM) Co. Ltd., Oklahoma, USA.

3.2.2 Electrochemical Measurements

In all electrochemical experiments conducted, the standard three-electrode cell was used as depicted in Fig.3.1. The reference electrode used was a home-constructed saturated calomel (SC) electrode since all electrochemical measurements were made in aqueous solutions.

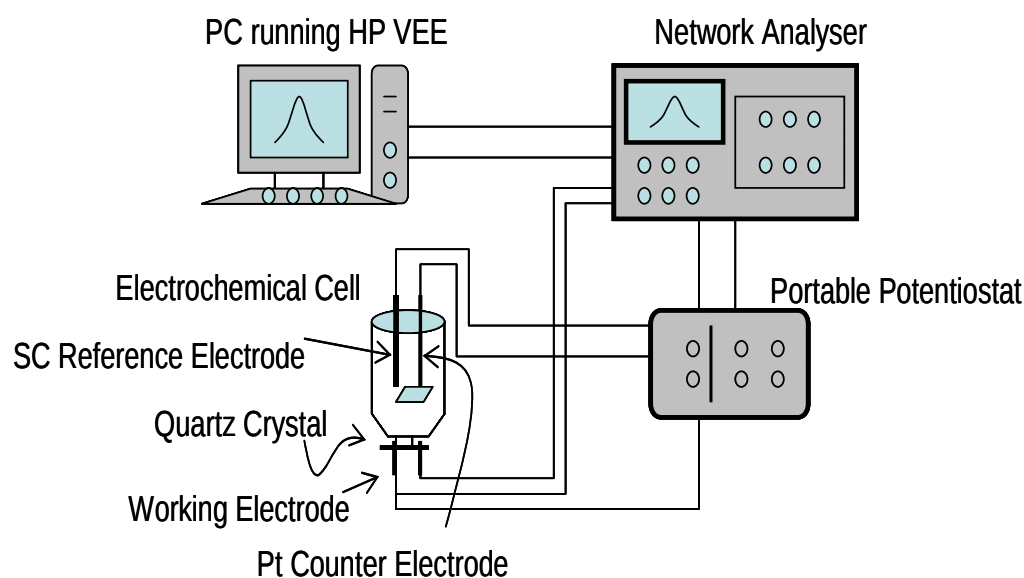


Fig. 3.1: Schematic representation of combined electrochemical system and a network analyser. All of the components of prime interest are labelled. One of the gold electrodes on the crystal surface was exposed to the solution and used as the working electrode. This electrode should be connected to the ground lead of the coaxial cable connecting the crystal to the network analyser to avoid the electrical noise arising from the interaction between the DC potential (driving the electrochemical reaction) from the potentiostat and the a. c. potential (driving the piezoelectric effect) from the network analyser.

The counter electrode was a Pt gauze. The working electrode was one of the Au electrodes on the crystal surface; this requires one of the crystal faces to be exposed to the electrochemical solution. For this purpose, the crystal was mounted at the bottom of the electrochemical cell (see Fig. 3.1) with a non-corrosive silicone sealant (Dow-

Corning 3145 RTV). A fine film of the sealant (silicone rubber glue) should be used to avoid the reduction of crystal sensitivity. Excessive use of the glue on the crystal may put an extra mechanical stress that may result in significant damping of the crystal resonant oscillation; this leads to the malfunctioning of the device. The electrolyte solution was not allowed to leak into the other side of the crystal to prevent capacitive shunting and a subsequent loss of oscillation [1]. After the adhesion, the crystal was normally allowed to dry for ca. 24 h.

A manual portable potentiostat was used to drive the electrochemical reaction from which the range of potentials, the sensitivity of current response (through the variation of resistance), and the scan rate of all experiments were controlled. Electrochemical measurements were performed at different temperatures for particular experiments. Gravimetric experiments were carried out at room temperature (ca. 19 ± 2 °C). In contrast, for the investigation of viscoelastic properties of polyaniline films, the temperature was varied over the range: $5 \leq T/^\circ\text{C} \leq 60$ using a thermostat bath capable of controlling temperature to ± 1 °C (see chapter 8).

3.2.3 Data Acquisition

During polymer electrochemical deposition, crystal admittance spectra were collected for two purposes: the qualitative determination of the conformity of thin films to the “*acoustically thin*” condition and the quantitative study of viscoelastic properties of “*acoustically thick films*”. All admittance data were acquired in the vicinity of the fundamental mode (10 MHz) and at higher harmonics (30-110 MHz); higher harmonics used here are the odd integer multiples of the fundamental frequency. Data acquisition were achieved by using a Hewlett Packard HP8751A network analyser connected to a HP8752A transmission/reflection unit via a 50 Ω coaxial cable (see Fig. 3.1) [2-4]. Electrochemical and acoustic wave device data collection were controlled via a computer running the HP VEE program and connected to the network analyser through an HP10833B interface card. The transmission/reflection unit was used to measure the scattering parameter, $S_{11}(f)$, as a function of frequency, f , in the vicinity of the crystal resonance which returns the input electrical impedance, $Z(f)$, of the thickness shear mode resonator as described below [2, 3, 5-7]:

$$Z(f) = Z_o \left(\frac{1 + S_{11}(f)}{1 - S_{11}(f)} \right) \quad (3.1)$$

where $Z_o = 50 \, \Omega$ is the standard impedance of the system for the instrumentation used. Before data collection, the network analyser was calibrated with elements of an open, a short and a load with $50 \, \Omega$ resistance. The input electrical impedance, Z , as defined in Eq. 3.1 is displayed as a complex admittance quantity, $Y(f) = 1/Z(f)$.

3.3 Materials and Procedures

3.3.1 Polyaniline Deposition and Characterisation

Polyaniline films were deposited from 1 M aqueous acidic solutions [HClO_4 (BDH), H_2SO_4 (Aldrich) or HCl (Aldrich)] containing 0.1 M aniline (99+%, Lancaster, Alfa Aesar 99%); all materials were used as received. A fresh sample of solution was used for each polymer deposition.

The films were grown potentiodynamically over the potential range of $-0.2 \leq E/\text{V} \leq 0.9$ at a scan rate of $\nu = 10 \, \text{mV s}^{-1}$. Before the film deposition, initial crystal admittance measurements on the bare crystal in air and in deposition solution were used to acquire crystal and solution parameters, respectively. In doing so, the crystal impedance parameters in air and electrolyte solution parameters (product of viscosity-density) can be extracted; these parameters are used to calibrate subsequent crystal admittance data for film deposition and characterisation. Acoustic admittance spectra were recorded at an interval of 2 s (equivalent to 20 mV potential ramping) with 401 points equally spaced across the selected frequency range.

For gravimetric investigations, a thin polyaniline film was grown by six potential cycles. Effectively controlling the number of deposition cycles enabled us to grow polyaniline films on the electrode surface with the desired film thickness and properties. At the end of the experiment, the electrode was disconnected at $E = -0.2 \, \text{V}$ and removed from the solution. For the characterisation of rigid polyaniline films, three different scan rates were used; $\nu = 5, 10$, and $20 \, \text{mVs}^{-1}$.

For the preparation of acoustically thick films, different deposition media were used and the rate of polyaniline film deposition was found to be dependent upon the type of the particular electrolyte present during deposition [8-11]. Polyaniline films grown in sulphuric acid media showed fast rate of film deposition compared to films deposited in either hydrochloric or perchloric acid solutions. The strategy was to determine materials properties that may differ in different thickness regimes. Consequently, the deposition experiments were terminated after different numbers of potential cycles such that the resultant films were of comparable thickness (i.e. similar polymer coverage). Typically, this was after 20 cycles in HClO_4 , 10 cycles in HCl and 9 cycles in H_2SO_4 , at which point the cell was disconnected at the negative end of a potential cycle ($E = -0.2 \text{ V}$).

Practically, one can extract accurate shear modulus data from admittance spectra where there is sufficient damping ($>10\%$ drop in peak admittance from that for the bare electrode) to distinguish it from the acoustically thin regime, but not so much that the signal:noise ratio is compromised ($> 80\%$ drop in peak admittance) [11-13]. The deposition of viscoelastic polyaniline films satisfied this requirement, a fact that was readily observed visually on screen as the raw spectra were acquired. Expressed in more fundamental terms, this condition corresponds to an acoustic phase shift (φ) greater than 20° [13] (below which the film is regarded as acoustically “thin”) but less than 90° (where complications associated with film resonance arise [14], for more details on film resonance refer to appendix A). The value of φ (for a shear acoustic wave of angular frequency, $\omega = 2\pi f$) across a film of thickness h_f and density ρ_f is related to the viscoelastic properties of the film by [11-13, 15]:

$$\varphi = \gamma h_f = \omega h_f \sqrt{\rho_f} \sqrt{\frac{1 + G'/|G|}{2|G|}} \quad (3.2)$$

where:

$$\sqrt{G} = \left(\frac{|G| + G'}{2} \right)^{1/2} + j \left(\frac{|G| - G'}{2} \right)^{1/2} \quad (3.3)$$

and

$$|G| = \left[(G')^2 + (G'')^2 \right]^{1/2} \quad (3.4)$$

Following deposition, the polyaniline films were rinsed with distilled water and transferred to fresh monomer-free background electrolytes for voltammetric and acoustic characterization (in the range $-0.2 < E/V < 0.5$, spanning the first redox process). Two types of experiment were carried out, one in which the film was characterized using the same acid (anion) solution as for deposition and one in which the acid (anion) was changed.

3.3.2 Data Fitting

The extraction of the physical parameters for the bare AT-cut polished quartz crystal, the semi-infinite Newtonian liquid, and the surface-coated film was performed by fitting the components of lumped element equivalent electrical circuit (Butterworth van Dyke) to the experimental data. For each experiment, the admittance spectrum of the crystal in air and solution was collected prior to the film deposition. This initial measurement gives the surface mechanical impedance associated with the mounted bare crystal and the adjoining liquid. Typically, the peak admittance of the bare crystal is ca. 100-120 mS (0.008-0.01 k Ω), before mounting, and ca. 40-60 mS (0.017-0.025 k Ω) after the crystal is mounted onto the cell. In aqueous solutions, the value of the peak admittance falls to ca. 3-4 mS (0.25-0.33 k Ω). This corresponds to the extracted resistive and inductive components of the solution with the values: 0.27 k Ω and 8.25 mH, respectively. The mass per unit area, ρ_s , associated with the trapped material in the surface roughness of the crystal induces additional surface mechanical impedance, though negligible (see Eq. 3.5). In quantitative terms, the amount of polymer trapped in the surface roughness features of the crystal is very small and equivalent to the effect of the liquid entrapment. The surface mechanical impedance associated with this (polished crystals) is $\sim 70 \text{ g cm}^{-2} \text{ s}^{-1}$ compared to $9 \times 10^5 \text{ g cm}^{-2} \text{ s}^{-1}$ and $8 \times 10^2 \text{ g cm}^{-2} \text{ s}^{-1}$ for bare quartz crystal and bulk solution, respectively. A polymer film of ca. $1.8 \times 10^7 \text{ dyn cm}^{-2}$ shear modulus and a density of ca. 1 g cm^{-3} contributes a surface mechanical impedance of ca. $4.24 \times 10^3 \text{ g cm}^{-2} \text{ s}^{-1}$. Therefore, any variation of surface mechanical impedance with the material in surface features can contribute only ca. 2% to the total film signal.

The values of storage, G' , and loss, G'' , shear moduli of viscoelastic films were calculated by fitting experimental impedance, Z , data with the help of the Maple standard package and the add-in solver tool of Ms Excel software. Eq. 3.5 was used for the extraction of storage and loss shear moduli values.

$$Z = j\omega\rho_s + Z_f \left[\frac{Z_L \cosh(\gamma h_f) + Z_f \sinh(\gamma h_f)}{Z_f \cosh(\gamma h_f) + Z_L \sinh(\gamma h_f)} \right] \quad (3.5)$$

where γ acoustic wave propagation constant as defined in Eq. 3.2.

In all experiments, polyaniline film density of $\rho_f = 1.0 \text{ g cm}^{-3}$ was used. Here, the monomer ($\rho_M = 1.02 \text{ g cm}^{-3}$) and solvent ($\rho_s = 1.0 \text{ g cm}^{-3}$) components have relatively similar densities, so there is negligible uncertainty in film density introduced by variations in film solvation. The value of film thickness was obtained by an optimisation process. In this process, the allowable bounds of film thickness were constrained in three ways. First, a combination of the coulometrically determined molar coverage and the monomer density gives a lower (solvent-free) bound to film thickness, h_f^0 . Second, systematic variation of h_f above h_f^0 reveals a restricted range within which real and positive values of G' are obtained. Simultaneous application of this consideration for G'' results in a narrow range of physically acceptable h_f values. In the context of a single shot dynamic deposition experiment, the above optimisation process cannot be repeated as a function of harmonic number. However, this was done for film redox switching to further tighten the constraint [11, 12].

The values of the shear modulus components were used to calculate the decay length, δ , of the shear acoustic wave in the propagation direction, perpendicular to the interface [2, 5].

$$\delta = \frac{1}{\gamma} = \frac{1}{\omega\sqrt{\rho_f}} \sqrt{\frac{2|G|}{1-G''/|G|}} \quad 3.6$$

The round trip (to the outer film interface and back to the electrode) for the acoustic wave is 4δ [11, 12]. When physically realistic solutions to the shear modulus components are obtainable, the film thickness, h_f , is expected to be more than 0.1δ (finite viscoelastic regime). When acceptable signal:noise ratios are observed in the raw spectra, the film thickness, h_f , is expected to be less than 2δ (semi-infinite viscoelastic regime).

3.3.3 Deposition of Flavin-Functionalised Self-Assembled Monolayers

For the deposition of flavin-functionalised monolayers, a mixed solution containing 1 mM each of flavin disulfide and butyl disulfide was prepared. The solvent used for the deposition of the monolayer and subsequent characterisations was dichloromethane (DCM), CH_2Cl_2 (Fisher Scientific, 99%). Solutions for studying dendrimer adsorption contained 0.051, 0.0691, 0.0923, 0.11 and 0.144 mM DAP (diamidopyridine 16-branch dendrimer). Solutions for removal of surface-bound dendrimer contained 0.95, 3.8, 8.1, 13.8 and 19.5 mM thymine.

The deposition of flavin monolayers was accomplished by exposing the Au electrode of 10 MHz AT-cut quartz crystal to a solution containing both flavin disulfide and butyl disulfide (each 1 mM) for 18-24 h. Gravimetric assays of DAP dendrimer adsorption and thymine-induced desorption were obtained by monitoring the resonant frequent shift and admittance spectra at 30 s time intervals. The measured frequency shifts were converted to areal mass density changes, Δm (g cm^{-2}), using the Sauerbrey equation:

$$\Delta f = -\left(\frac{2}{\rho_q v_q}\right) f_0^2 \frac{\Delta m}{A_p} = C_1 \Delta m \quad (3.7)$$

where $C_1 = -2.26 \times 10^8 \text{ Hz cm}^2 \text{ g}^{-1}$ represents the combination of quartz and crystal constants.

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Chapter Four

Modelling Mobile Species Dynamics within Electroactive Films

4.1 Overview

The applications of electroactive polymer films involve the exchange between the film and its bathing solution of ions, solvent and other neutral species, collectively referred to as “mobile species” [1-9]. The importance of this exchange process is true regardless of whether the application is based upon mediated charge transfer to permeating solution reactant (electrocatalysis or amperometric sensors) or upon changing film properties with redox state (electronic/optical devices or charge storage), as described in section 1.6 (chapter one).

A number of experimental techniques possess the capability to monitor the film populations (or changes thereof) of one or more mobile species. In particular, the electrochemical quartz crystal microbalance (EQCM), ellipsometry and neutron reflectivity, have provided useful information on mobile species transfers and dynamics [3, 4, 6-17]. To complement these experimental approaches, means of modelling and visualizing these redox-driven film population changes are required. In this chapter, the visualisation and mechanistic diagnosis of mobile species transfer processes accompanying the redox switching of electroactive films are modelled. Through the characteristics of this modelling representation, one can show how different behavioural patterns of mobile species transfers may be identified on the basis of experimental data (this will be discussed in chapter 5).

Two constraints apply to the film populations of mobile species at equilibrium and provide driving forces for their interfacial transfer. First, the sum of the ion populations is required to satisfy electroneutrality within the film. This constraint may be satisfied in different ways by combinations of anion and cation transfer in opposite directions. Second, neutral species - notably solvent - must satisfy an activity constraint [1, 2, 5, 9, 10], such that the chemical potential at equilibrium of each species must be the same in the film and solution phases. The timescales on which these constraints are satisfied in a dynamic experiment are generally rather different. Since ions are field-driven, they commonly move faster. The various transfers of these mobile species in response to a change in film redox (charge) state provide a driving force for changes in film structure. In the case of a polymer film, this may be associated with reconfiguration, changes in free volume and/or viscoelastic properties [3, 4, 6-8].

4.2 Background

Theoretical modelling processes of redox switching of electroactive films were largely restricted – in the early stages – to the coupled electron/ion transfer within multilayer films [18-25]. Very little attention was given to the neutral species transfer; the consideration given was mainly qualitative [26]. Previous theoretical studies by Bruckenstein et al. [1, 4, 5, 27, 28] have established the general concept of representing film composition in terms of multidimensional vectors under ideal and non-ideal thermodynamic and kinetic control conditions. In those studies, the consideration was given to thermodynamic and kinetic phenomena in isolation. However, the departures from ideal thermodynamic behaviour of typical chemically modified systems are more likely to occur in combination rather than in isolation.

The novelty here is to combine these individual elements into a more general model for mobile species transfer. In doing so, the vectorial representation of film composition is modelled in a 3D figure for the specific case of “*permselective*” film, i.e. one for which redox switching involves coupled electron/ion transfer and solvent transfer, but no salt transfer. This condition prevails when the concentration of the supporting electrolyte is low (typically, $c < 0.1$ M).

In a recent study by Jackson et al. [5, 29], overall film compositional state was represented by a vector in (E,Q, Λ)-space, where E/V is the potential, Q/C cm⁻² is the film charge density, and Λ /mol cm⁻² represents film populations of one or more neutral species. In the simplest case, Λ represents the film solvent population (Γ_s) for a permselective film. Moreover, the film composition is represented by a 3D vector in (E,Q, Γ_s)-space; the inclusion of other net neutral species such as salt could be included by the extension to vectors (visually, figures) of higher dimensionality [30].

The changes in film solvent population (Γ_s) can directly be followed using the EQCM as a consequence of the generality and simplicity of detection by mass; the expression of model results in terms of mass changes is most readily envisaged. Nevertheless, the methodology described here is applicable to any *in situ* probe of film solvation change. The aim is to calculate surface populations without questioning how these will be determined experimentally. With regard to the EQCM operating under non-rigid (acoustically thick) film conditions, it is important to point out that the present models still apply. In this case, the acoustic wave device simply responds to solvent population indirectly and non-linearly through film shear modulus, rather than directly and linearly through mass.

Under ideal thermodynamic control conditions, the film composition obeys the Nernst equation, and the film solvent content is linearly related to its charge. When non-idealities are introduced into the solvent behaviour (non-linear film solvation with charge state), curvature is seen in the Γ_s -Q projections in (E,Q, Γ_s)-space. Curvature of Γ_s -Q projections is also a feature of kinetically slow solvent transfer. This raises an important issue when diagnosing the origins of curvature in experimental data. The ambiguity can be resolved by exploration of the time domain, a feature we explore in more detail here. Under kinetically controlled conditions, the system is perturbed from the equilibrium state and the mechanistic routes competing to bring the system to a new equilibrium state should be studied.

In previous studies [29, 31], the effect of non-ideal solvation was considered within the (probably unlikely) context that solvation equilibria are rapidly established within the film. Identification of response (Q for electrons/ions and Γ_s for solvent) showing hysteresis during a potential-controlled complete redox cycle was shown to provide identification of the rate limiting elementary step. This immediately raises three limitations of the previous models that are considered in the present work. First and foremost, we recognize that it is unlikely any given system will show complexity in only its thermodynamics *or* its kinetics. Given the high concentration environment of the film, it is an unrealistic expectation that solvation will be ideal, and given the gel—in some case near solid-state like—nature of the film it is unlikely that solvent transfer will be instantaneous. Second, one cannot presume that at least one of ion or solvent transfers will be very rapid. This is self-evidently true of a voltammetric experiment in which the rate constant for electron transfer is varied by several orders of magnitude during the experiment. Thirdly, while it is not too difficult to predict observed behaviour for a tightly defined set of processes with known thermodynamic and kinetic parameters, it can be much more difficult to invert the process starting from experimental data and working back to a mechanism and parameters. An important feature of the present work is that: i) we establish procedures for describing the behaviour of films showing simultaneous thermodynamic and kinetic complexities, ii) identify diagnostics for separating these effects, and iii) explore a more sensitive differential (solvent:ion flux ratio) representation for identifying changes in behaviour at partial conversion during the time course of film redox transformation.

4.3 Theory

4.3.1 The compositional model and overview of approach

The film redox chemistry is represented by:



where O and R , respectively, represent a film redox site in the oxidised and reduced state. For simplicity, we will consider the case that the number of electrons transferred per

redox site, $n = 1$; generalization to other values of n is straightforward. Furthermore, the case of a permselective film (see above) is considered for this redox transformation in response to the most commonly employed electrochemical control function, a cyclic voltammetric sweep (scan rate $v / V s^{-1}$).

Fig. 4.1 illustrates the concept [5] of the visual model. The instantaneous film composition is represented by the vector $\Omega(t)$:

$$\Omega(t) = E(t)i + Q(t)j + \Lambda(t)k \quad (4.2)$$

where i, j, k are the 3D unit vector coefficients for the Q, E , and Λ axes. For the permselective case we consider here, $\Lambda \equiv \Gamma_s$.

For convenience, $Q = 0$ and $\Gamma_s = 0$ are associated with the composition of the fully reduced film. Thus, as the film undergoes oxidation and subsequent reduction, $\Omega(t)$ traces out a path in compositional space that is characteristic of the film's thermodynamic and kinetic characteristics and of the applied electrochemical control function and its associated timescale. Fig. 4.1 illustrates in cartoon form different scenarios of the model we set out to explore in detail. Specifically, it shows as a solid line the (unlikely) result that would be seen for a film whose thermodynamics showed no non-idealities and whose electron, ion and solvent transfer kinetics were arbitrarily rapid. In Fig. 4.1, it is indicated by means of annotation the deviations that one would expect to see as thermodynamic and kinetic complexities are individually introduced. Schematically, the arrows (Fig. 4.1) summarise the *separate* outcomes of these individually introduced thermodynamic (non-ideal) or kinetic complexities. These individual models will be summarized below as a precursor to *combining* them - the primary goal of this study (the more practically realistic scenario).

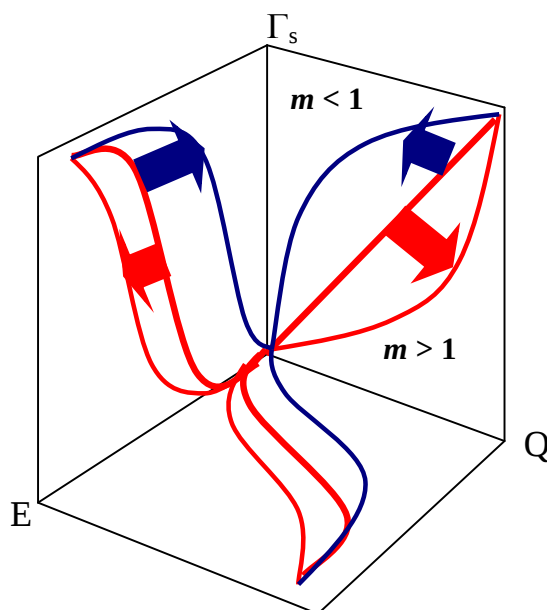


Fig. 4.1: 3D schematic population space representation of solvent population (Γ_s), charge density (Q) and potential (E). For each 2D projection, the central line represents the simplest possible (and physically unlikely) case of rapid kinetics and ideal thermodynamics. The arrows indicate departure from this scenario as a consequence of slow charge transfer (horizontal plane), slow solvent transfer (left hand vertical plane) and non-ideal solvation (right hand vertical plane). For significance of non-ideality parameter, m , see the text below.

4.3.2 Thermodynamic Control

Thermodynamic control of a film containing a population $\Gamma_T/\text{mol cm}^{-2}$ of electroactive sites yields a redox state that responds to the applied potential, E/V , in a Nernstian manner. The charge density associated with this process (Eq. 4.1), $Q/\text{C cm}^{-2}$, is given by Faraday's law:

$$\Gamma = Q/nF \quad (4.3)$$

where F is the Faraday. Under permselective conditions, Eq.4.3 also defines the population of counter-ion, $\Gamma_A/\text{mol cm}^{-2}$, that must transfer in order to satisfy the electroneutrality condition for the film.

Film solvation changes in response to redox switching are expressed through:



where O represents an oxidised site prior to the solvent transfer (i.e. with the equilibrium solvation state of species R) and O_s represents an oxidised state at equilibrium following the transfer of x molecules of solvent, S . One should note that the value of x may - unlike the value of n in Eq. 4.1 - be non-integer. In addition, according to the relative lyophobicity / lyophilicity of species O and R , x may also be negative or positive, i.e. solvent may in principle transfer in either direction. To be more precise, it must be pointed out that x represents the amount of solvent *transferred*, not the *absolute* population of solvent in the film at any state. The forward and reverse rate constants for Eq. 4.4 are denoted k_f and k_b , respectively, and their ratio is the solvation equilibrium constant K_s .

Under thermodynamically ideal conditions, the redox induced population change within the film of solvent, Γ_s , can be expressed via [5]:

$$\Gamma_s = \frac{K_s}{K_s + 1} \frac{yQ}{F} \quad (4.5)$$

where y represents the fraction of the charge density required for the solvent transfer into and out of the film and K_s is the equilibrium solvation constant for the solvation reaction (Eq. 4.4). We note that this analysis does not attempt to distinguish the nature (free or bound) of solvent within the film.

Under the more general - and more likely - case of non-ideal thermodynamic conditions for solvent transfer, the relationship between the solvent population and the charge density will deviate from the linearity represented by Eq. 4.5. A “correction factor” is needed in Eq. 4.5 to describe the more complex relationship between the solvent population and the extent of redox switching. Realistically, there is no prospect of being able to predict such a correction factor *a priori* and there can be no expectation of any functional form having general applicability [32]. Therefore, one possible functional form (a power law) is simply selected as a representative example in order to explore the types of effects one might observe. Extension to any other functional form deemed appropriate to a particular system is readily incorporated into the model, with necessary changes to the detailed algebra. On this basis, a more general form of Eq. 4.5 is:

$$\Gamma_s = \frac{K_s}{K_s + 1} \frac{yQ_T}{F} \left(\frac{Q}{Q_T} \right)^m \quad (4.6)$$

where m is a ‘non-ideality parameter’ that describes the dependence of the solvent population change on film redox composition. Physically, m represents the interactions in the system, which may be attractive or repulsive. Since the activity coefficient of the solvent species varies in a continuous manner [10, 32] with the film charge state, m can in principle take any positive value. In terms of conventional adsorption isotherm models, our approach corresponds to the Freundlich isotherm (generally expressed as $\theta = c_1 p^{1/c_2}$, with $1/m$ formally corresponding to the constant c_2). This model envisages an adsorption enthalpy that varies logarithmically with coverage, i.e. is not constant but does not vary dramatically. It is chosen to explore the range $0.1 < m < 10$, which spans an order of magnitude either side of the value $m = 1$, that corresponds to ideal behaviour and returns Eq. 4.5.

4.3.3 Kinetic Control

When the film redox conversion takes place under kinetic control, the rate of O/R transformation with time can be expressed by [5]:

$$\frac{d\Gamma_{Ox}}{dt} = k_e \left[\Gamma_{Red} \eta^{(1-\alpha)} - \Gamma_{Ox} \eta^{(-\alpha)} \right] \quad (4.7)$$

where $\eta = \exp\left[nF/RT (E - E^0)\right]$, k_e is heterogeneous rate constant describing the coupled electron / counter ion transfer, Γ_{Red} and Γ_{Ox} are the time-dependent populations of reduced and oxidised redox sites (whose sum is always Γ_T , the total film redox site population) and the other symbols have their usual meanings. In the context of a voltammetric experiment, in which E varies linearly with t (with scan rate $v / V s^{-1}$), it is convenient to re-cast Eq. 4.7 in terms of the potential dependence of film composition:

$$\frac{d\Gamma_{Ox}}{dE} = \kappa_e \left[\Gamma_T \eta^{(-\alpha)} - \Gamma_{Ox} \left(\eta^{(-\alpha)} + \eta^{-(1+\alpha)} \right) \right] \frac{nF}{RT} \eta \quad (4.8)$$

where the electron / ion transfer rate constant is represented through the normalized dimensionless parameter $\kappa_e = RTk_e / (nFv)$. As discussed in the literature [5, 29, 31], large values of κ_e (large k_e and/or small v) return the equilibrium result, the Nernst equation, for film redox composition.

Analogously, in the absence of thermodynamic non-idealities (which will be introduced below), the rate of change of solvent population with time can be expressed by [5]:

$$\frac{d\Gamma_s}{dt} = \left[k_f \Gamma_{Ox,T} - \left(k_f + \frac{k_f}{K_s} \right) \frac{\Gamma_s}{y} \right] \quad (4.9)$$

and, in the voltammetric context, with potential by:

$$\frac{d\Gamma_s}{dE} = \kappa_s \left[\Gamma_{Ox,T} - \left(1 + \frac{1}{K_s} \right) \frac{\Gamma_s}{y} \right] \left(\frac{nF}{RT} \right) \quad (4.10)$$

where k_f is the first order rate constant for solvent transfer, incorporated through the normalized dimensionless parameter $\kappa_s = RTk_f / (nFv)$. $\Gamma_{Ox,T}$ is the total population of

oxidised sites, including both solvated and unsolvated forms. K_s and y are as defined above.

4.3.4 Mixed Kinetic and Thermodynamic Control

In practice, the pure (electron/counter ion *or* solvent) kinetic cases discussed above are not generally encountered without the complication of thermodynamic non-ideality. Although the origins of this are beyond the scope of this work, one can readily justify this statement via the general observation that slow ion and solvent transfers are likely when the film is very compact (more gel-like than solution-like). The high concentration environment of a compact film is likely to give rise to thermodynamic non-ideality on the part of the solvent. Thus, as well as being non-trivial, the combining of thermodynamic and kinetic phenomena into a unified model is crucial to the practical application of our approach to real chemical systems.

The impact of non-ideality, represented here through the parameter m , is a change of the equilibrium solvent population (at any given redox state) to which the film aspires. This in turn influences the timescale on which this solvation state is achieved. The novelty of the present work is in large measure associated with exploration of the interplay between these thermodynamic and kinetic factors, which have to date only been considered in isolation - a physically unlikely situation.

In order to describe the simultaneous participation of thermodynamic and kinetic factors, we need to incorporate the non-ideality parameter, m , into Eq. 4.10, somewhat analogous to its incorporation into Eq.4.6 for the case of (non-ideal) thermodynamic control:

$$\frac{d\Gamma_s}{dE} = \kappa_s \left[\Gamma_{Ox,T} \left(\frac{\Gamma_{Ox}}{\Gamma_{Ox,T}} \right)^m - \left(1 + \frac{1}{K_s} \right) \frac{\Gamma_s}{y} \right] \left(\frac{nF}{RT} \right) \quad (4.11)$$

In doing so, we accept that we have selected an arbitrary functional form for describing the non-ideality. There will be no generally applicable function, but the general

approach we describe can accommodate other functional forms, if demonstrated to be more appropriate to a particular system.

The ultimate goal - which will be the subject of the future work - is to extract thermodynamic and kinetic parameters from experimental data. However, it is quite clear that there are a number of parameters whose values could in principle vary quite widely. Thus, the immediate goal - which we address in the present work - is to explore the behaviour of Eq. 4.11 as a function of the various parameters (principally m , κ_e and κ_s). The outcomes of these parameters are visually represented in such a manner that patterns of behaviour can be readily recognized. For example, we would like to be able to distinguish thermodynamic non-ideality from slow solvation, and kinetically slow ion transfer from kinetically slow solvent transfer. The purpose of the visual representations is to be able to make such distinctions *without* having recourse to detailed fitting. This will have the benefits of (i) efficiency, in that effort will be focussed on the physically more important phenomenon and the associated parameter(s) and (ii) non-vulnerability of the *qualitative* outcome to the vagaries of any specific multi-parameter fitting routine or of scatter on experimental data. The detailed mechanics of solution of Eq. 4.11 are described in section 4.4.

4.3.5 Flux ratio concept

The use of a vector trajectory in (E,Q, Γ_s)-space is optimal for visualizing instantaneous film composition at any point in a redox cycle. However, in many dynamic chemical experiments it is also helpful to consider the differentials of the populations, i.e. the fluxes, since the differential is intrinsically more sensitive. Previously it was suggested [29, 31] that a particularly powerful variant of this idea in the context of film redox switching is to consider the *ratio* of the fluxes of solvent and ions (designated as the flux ratio ρ). This essentially provides an immediate identification of the mobile species (here, counter ion or solvent) that dominates the film compositional change at any given point in the transient. In the specific case of the EQCM, for example, this would identify the dominant instantaneous contributor to the mass flux. We suggest that this will have general utility in mechanistic diagnosis and identification of the rate limiting step. In the

permselective case considered here, ρ is the instantaneous value of the number of solvent molecules transferred per counter ion crossing the film/solution interface.

At the electrode surface [29, 31], the flux of solvent, f_s , is $d\Gamma_s/dt$ and the flux of counter ions, f_A , is $d\Gamma_A/dt$. Thus, at any selected point in film redox switching:

$$\rho = \frac{f_s}{f_A} = \left(\frac{d\Gamma_s}{d\xi} \right) / \left(\frac{d\Gamma_A}{d\xi} \right) = \frac{d\Gamma_s}{d\Gamma_A} \quad (4.12)$$

where ξ can be t , E , Q or the instantaneous current (i). Since Γ_s and Γ_A are obtained as described above, evaluation of ρ is straightforward. The only point to note is that at the extremes of the potential range, where the fluxes are necessarily small (indeed, the potential limits are always chosen so as to satisfy this criterion) the flux ratio may be overly sensitive to “noise” (whether calculational or experimental in origin). This is not a significant practical limitation, but requires some judgement in presentational terms.

4.4. Calculations

All the theoretical calculations for the models presented here were carried out using the commercial mathematical software package Maple[®]. Equations (4.8) and (4.11) were solved as a system of differential equations. To find a numerical solution for these equations, we first set initial values for $\Gamma_A(E)$ and $\Gamma_s(E)$ at a selected start value of the potential, the controlled variable. For illustrative purpose, we took the film to be initially in the fully reduced state and assigned $\Gamma_A(-0.3V) = \Gamma_s(-0.3V) = 0$ as initial values for the system. The procedure “*dsolve*” with the option “*type = numeric*” is then called within Maple. The numeric solver in this procedure returns [33] a list comprising an equation describing the value of the potential, E (the independent variable), and two other equations describing the values of the coupled electron/anion (Γ_A), and solvent (Γ_s) populations (dependent variables) at each point of the potential (E , the independent variable). To generate the data illustrated in our models, the solutions provided by the “*dsolve*” procedure for the coupled electron/anion and solvent populations were plotted

as a function of potential over a domain of interest (here, $-0.2 \leq (E-E^\circ) / V \leq 0.2$). A representative example of maple syntax showing how the data were generated is shown in Fig. 4.2. Since the equations we employ here are in differential forms, we used the “odeplot” routine. The ion population data were obtained by inserting the charge data into Faraday’s law, then applying the electroneutrality constraint. To produce the 3D figures of the models presented in this paper, the data generated with the help of Maple® were transferred to Origin® graphical software.

```
>
> approx1:=dsolve({sys1,X(-0.3)=0,S(-0.3)=0},fns,type=numeric,method=rkf45,abserr=
Float(1,-15),startinit=true):
> approx1(0.2);
[E=0.2,X(E)=9.99391072604436690 10-9,S(E)=9.73627453843874900 10-9]
```

Fig. 4.2: A representative example showing the syntax of “dsolve” procedure in Maple worksheet. As highlighted in the figure, the numeric type of the procedure was called. At the bottom, the coupled electron/ion [represented as X(E)] and solvent [represented as S(E)] populations of the system were returned by the procedure at $E = 0.2$ V (as an example, the response from any other potential point is straightforward) using Eqs. 4.8 and 4.11 respectively. Eqs. 4.8 and 4.11 are solved as a system of differential equations - here shown as “sys1” in the syntax. For detailed understanding of Maple syntax encoding, one can consult with Ref # [33]

For the purposes of illustration and of allowing focus on the primary parameters of interest, we selected “typical” values of certain parameters, as follows. We set the value of the charge transfer coefficient, $\alpha = 0.5$, the number of electrons transferred per redox site, $n = 1$, and the temperature, $T = 298$ K. The total population of the redox sites of the film, Γ_T was chosen to be 10^{-8} mol cm⁻²; this is a “mid-range” value for many polymer films. Values of applied potential are referred to the standard electrode potential, E° / V . The effect of the solvation equilibrium constant, K_S , is simply to scale the response on the Γ_S axis [5]. Since this is essentially a thermodynamic effect which was described previously by Jackson et al. [5], we remove this straightforward effect by assigning an arbitrarily large value of 1000 to K_S . This assignment corresponds to O and R states of

very different solvation characteristics. In any given calculation (see below), we fixed the values of the normalised rate constants (κ_e and κ_s) and of m , and then calculated the response of Eqs. 4.8 and 4.11 as the applied potential, E/V , was varied through a complete redox cycle. The potential variation was started from an equilibrated fully reduced film at $E = 0.3$ V. The responses shown below are representative of a large number of calculations for systematically varied values of κ_e , κ_s and m , chosen to highlight different types of behaviour that we anticipate being of experimental relevance. Since the solvation stoichiometry simply “telescopes” the response on the Γ_s axis, we present the population change data as Γ_s/x .

4.5 Results and Discussion

In the following sub-sections, we explore in a systematic manner the effects of varying the thermodynamic and kinetic parameters of the system. In each case (except for the differential, flux, representations at the end of this section) we represent the calculated responses as 3D trajectories in (E, Q, Γ_s) -space. At any point, this represents the ion (charge state) and solvent composition of the film. The individual charge-potential (Q - E), solvent-charge (Γ_s - Q) and solvent-potential (Γ_s - E) projections are also shown on the three 2D planes. The Q - E projection represents the charge isotherm (for an ideal reversible case, this reduces to the Nernst equation). The Γ_s - E and Γ_s - Q projections correspond in the specific context of an EQCM data set to mass-potential and mass-charge plots; this provides an immediate and transparent link to experimental data.

4.5.1 Slow charge and solvent transfers

We first consider the mixed kinetic case of slow transfers of both the charged species (coupled electron/ion transfer) and the neutral species (solvent) in the absence of thermodynamic non-ideality. A range of cases is represented in Figures 4.3 and 4.4. We present the results in terms of normalised kinetic parameters (κ_e and κ_s), so it is the ratio of the kinetic parameter to the potential scan rate that is important, but some notion of a “typical” experiment to which this might pertain is given by noting that a κ value of unity

corresponds, at a scan rate of 100 mV s^{-1} , to a first order rate constant of ca. 4 s^{-1} , i.e. a time constant on the order of 0.25 s .

In Fig.4.3, we show the trajectory of the system through compositional (E, Q, Γ_s) -space for the two possibilities that (a) coupled electron/ion transfer is the slower of the two slow steps and (b) solvent transfer is the slower of the two slow steps. In both panels, we have maintained the (arguably less likely) symmetrical situation that each transfer has the same kinetic parameter for entry into and exit from the film (the issue of “asymmetry” of the kinetic parameters will be addressed later with regard to Figure 4.4). The obvious general comment on all the responses in Figure 4.3 is that they are not single valued with respect to the controlled parameter E . This hysteresis is an immediate diagnostic of kinetic, rather than thermodynamic, control.

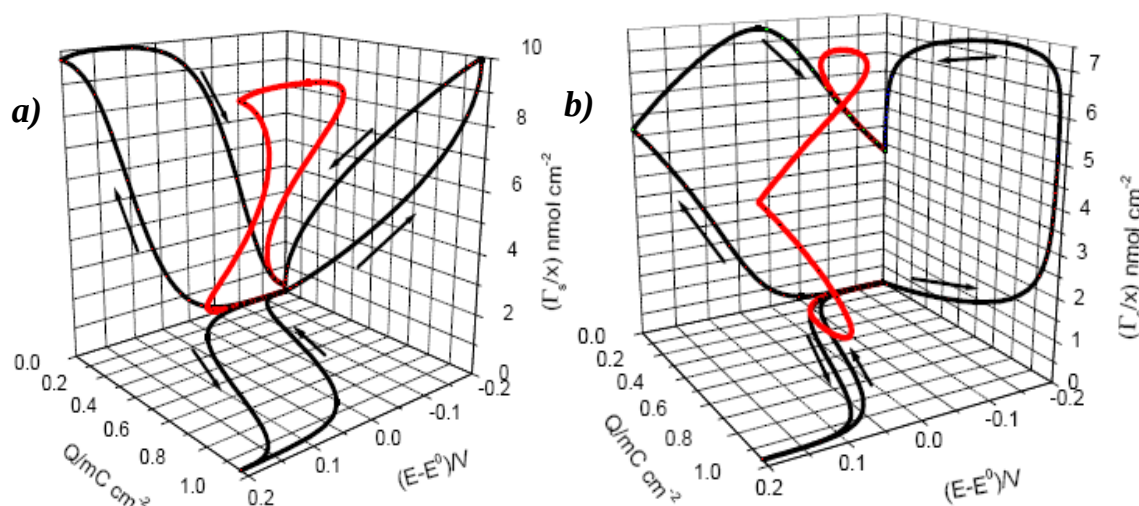


Fig.4.3: Representative calculated excursion through compositional space $\Omega(E, Q, \Gamma_s)$ for films with slow directionally *symmetric* electron/counter ion *and* solvent transfer kinetics, but thermodynamically ideal solvation, subject to a cyclic linear potential sweep. $K_S = 1000$; $m = 1$; $\Gamma_T = 10 \text{ nmol cm}^{-2}$ (other values of coverage and solvation level scale linearly in this first order model): (a) $\kappa_S = 1$; $\kappa_e = 0.1$ (slower charge transfer); (b) $\kappa_S = 0.1$; $\kappa_e = 1$ (slower solvent transfer).

In panel *a* of Fig. 4.3, the fact that (slow) solvent transfer follows (slower) electron/ion transfer is reflected in greater hysteresis in the Γ_s - E projection than in the Q - E projection.

The envelope of the hysteresis in the Γ_S -Q plot lies to either side of a linear (rapid and ideal) response. This should be noted for comparison with the non-ideal cases discussed below. The fairly rapid (though not reversible) solvent transfer kinetics ($\kappa_S = 1$) allow film (de-)solvation to be complete on the experimental timescale (note the full 0 – 10 nmol cm⁻² excursion in Γ_S), and restrict the level of Γ_S -Q hysteresis to modest degrees.

In panel *b* of Fig. 4.3, the interchange of the relative values of the kinetic parameters has dramatic effects. The hysteresis in the Q-E plot, while within the bounds of experimental measurements, is quite small. By contrast, the hysteresis in solvent populations is huge. In fact, during the time that charge transfer takes place, less than 20% of the solvent transfers. Most of the solvent transfer that does take place is on the plateau regions of the charge isotherm and the (de-)solvation processes are incomplete (cf. panel *a* of Fig. 4.3) on the experimental timescale (note the 0 – 7 nmol cm⁻² excursion in Γ_S).

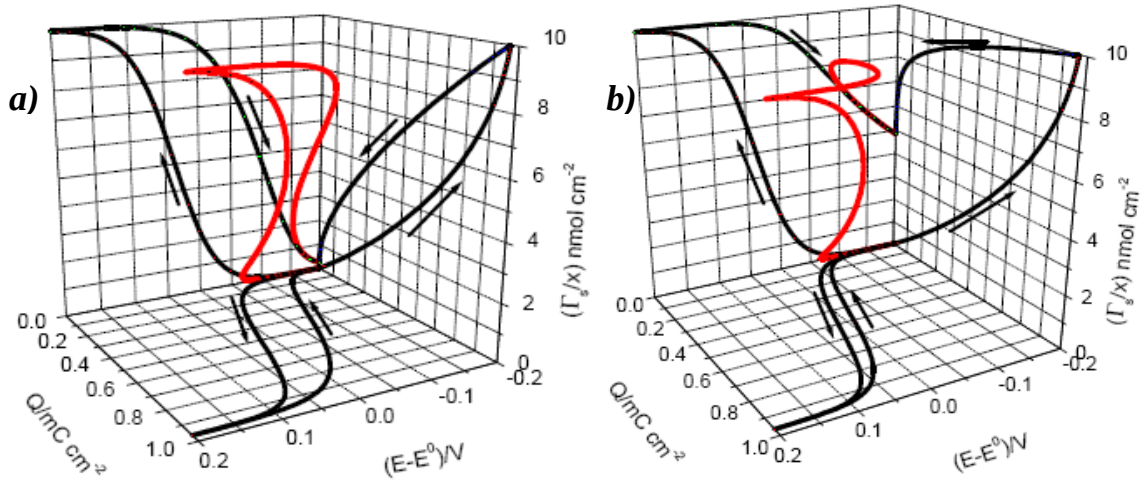


Fig. 4.4: Representative calculated excursion through compositional space $\Omega(E, Q, \Gamma_S)$ for films with slow directionally *asymmetric* electron/counter ion *and* solvent transfer kinetics, but thermodynamically ideal solvation, subject to a cyclic linear potential sweep. $K_S = 1000$; $m = 1$; $\Gamma_T = 10$ nmol cm⁻² (other values of coverage and solvation level scale linearly in this first order model): (a) $\kappa_S = \kappa_e = 1$ in forward half cycle and $\kappa_S = 1$; $\kappa_e = 0.1$ in reverse half cycle (slower charge transfer); (b) $\kappa_S = \kappa_e = 1$; $\kappa_S = 0.1$; $\kappa_e = 1$ (slower solvent transfer).

In Figure 4.4 we explore the effect of introducing “asymmetry” into the kinetic parameters for entry and exit of (a) electrons / counter ions and (b) solvent. For the purposes of illustration we make mobile species exit the slower process, but transposition to slower entry is straightforward. In panel *a* of Fig.4.4, the symmetry of solvent transfer is evident in the Γ_S -Q projection (as in Fig.4.3, panel *a*), but the asymmetry of electron/ion transfer is seen in the Q-E projection, which is a hybrid of the responses in panels *a* and *b* of Fig.4.3. We note that the shape alone of the Q-E plot would make this distinction difficult; it is the asymmetric disposition of the anodic and cathodic half cycle responses about the line $E = E^\circ$ that reveals the effect. The complementary case of slower and “asymmetric” solvent transfer shown in panel *b* of Fig.4.4 reveals a near-reversible Q-E isotherm but huge and obviously asymmetric solvent population responses. In the cases of the Γ_S -E and Γ_S -Q projections, we see that the more rapid solvent entry kinetics result in essentially complete solvation during film oxidation. Conversely, the much slower solvent exit kinetics associated with film reduction result in far from complete de-solvation. This offers an explanation for an occasional phenomenon which may be observed experimentally when using the EQCM to study polymer film redox switching: multiple cycles result in an apparent “drift” in the mass. This “drift” is a real chemical phenomenon, namely the pumping up with solvent or draining of solvent (according to whether film de-solvation or solvation, respectively, is the slower transfer direction). It is a consequence of failure to return to the initial state at the end of a redox cycle. The message is that all measurements should be made from an equilibrated (known) state, rather than an undefined steady state composition arbitrarily accessed during a sequence of redox cycles.

4.5.2 Thermodynamically Non-ideal Solvation coupled with Slow Solvent Transfer

Figure 4.5 illustrates a range of possibilities encompassed within this general scenario. In each of these cases, the large value of κ_e results in a single valued (reversible, Nernstian) charge response; thus all the features of interest lie in the Γ_S response. Panels *a-c* of Fig.4.5 involve values of $m \geq 1$; these “repulsive” interactions impose a “concave” (initially sub-linear with Q) tendency to solvation. Moving through the sequence of panels *a-c* in Fig.4.5, the (symmetrical) solvent transfer rate is decreased by an order of

magnitude. This has the effects of progressively opening up the hysteresis in the Γ_S responses (to E and to Q) and of decreasing the ability of the system to complete solvent transfer on the experimental timescale – solvation complete, nearly complete and far from complete in panels *a*, *b* and *c* of Fig.4.5, respectively.

Superimposed on this is a “dragging” up the potential axis of the solvent population; somewhat similar to the discussion regarding Fig.4.3. This phenomenon makes it imperative to view the Γ_S –E response with a clear view of the datum E° value. The sequence of panels *a*–*c* of Fig.4.5 corresponds to a single experiment in which three measurements are made at progressively increasing scan rate. Despite this fact, when these figures are viewed in isolation they look very different. It is particularly interesting to see how the fully *concave* (in both scan directions) Γ_S –Q responses for $m = 3$ and 10 in panel *a* of Fig.4.5 transform to relatively “*normal*” looking hysteresis loops in panel *c* of Fig.4.5. The intermediate case of panel *b* (Fig.4.5) shows Γ_S –Q responses on the reduction half cycle that are a combination of these two (panels *a* and *c*) and thus show an inflexion point. These observations underscore the importance of varying the experimental timescale - here, potential scan rate - in order to separate thermodynamic and kinetic phenomena.

Analogously, panels *d*–*f* of Fig.4.5 involve values of $m \leq 1$; these “*attractive*” interactions impose a “*convex*” (initially super-linear with Q) tendency to solvation. The same arguments apply as to panels *a*–*c* of Fig.4.5, except that the tendency of the thermodynamic non-idealities is to drag the solvent responses in the opposite direction with respect to E and Q.

In summarising Fig.4.5 and looking forward to application to experimental data interpretation, we make three final observations. First, in the case of very slow solvent transfer (see panels *c* and *f* of Fig.4.5), the ion and solvent transfer contributions (for example, experimentally recorded as the two contributions to a mass response in the EQCM technique) are virtually de-coupled.

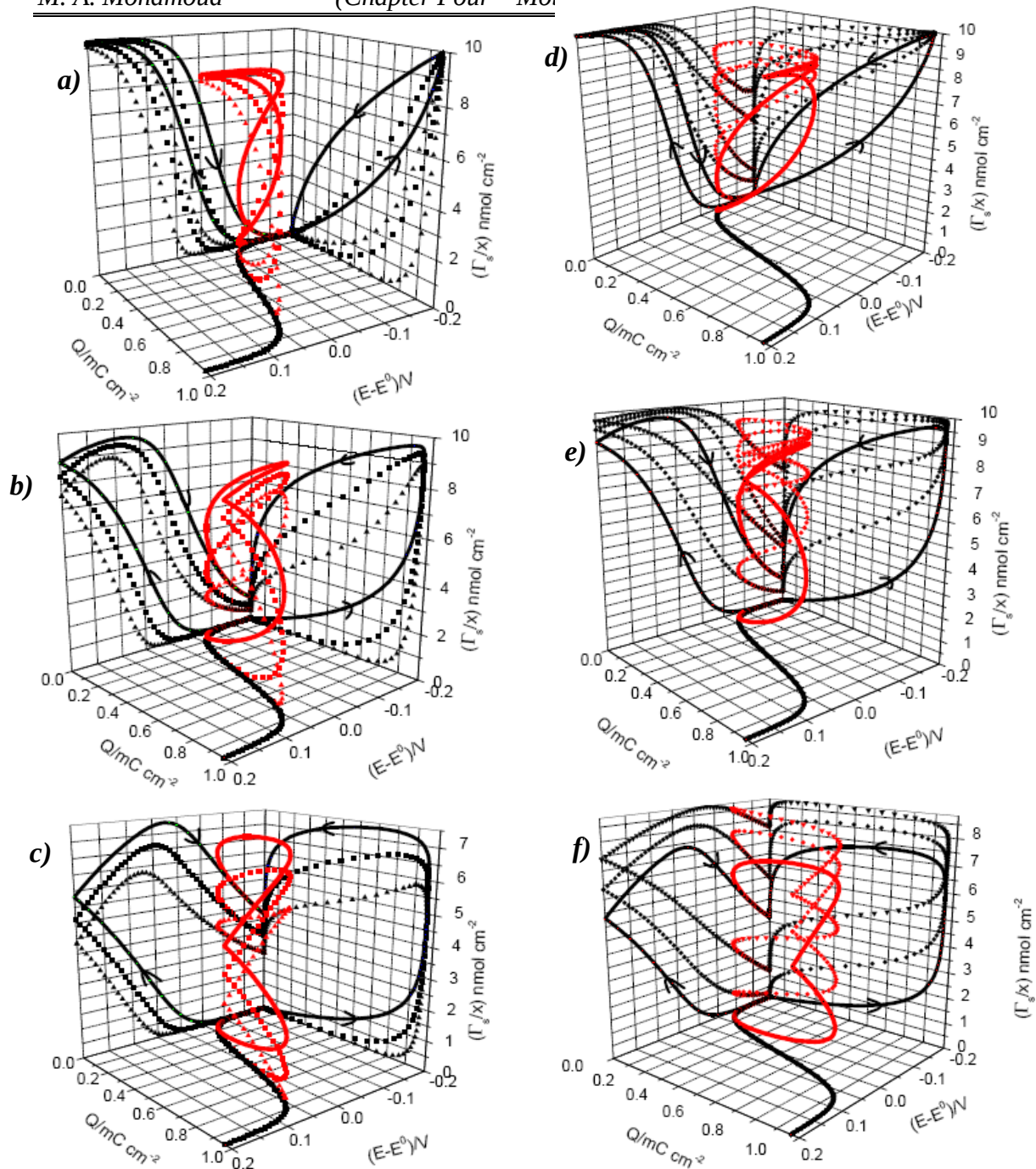


Fig. 4.5: Representative calculated excursion through compositional space $\Omega(E, Q, \Gamma_s)$ for films with rapid charge transfer kinetics, slow symmetrical (de-)solvation kinetics and non-ideal solvation, in response to a cyclic linear potential sweep. $\kappa_e = 10$; $K_S = 1000$; $\Gamma_T = 10 \text{ nmol cm}^{-2}$ (all panels). Panel *a*: $\kappa_S = 1$, $m = 10, 3, 1$; panel *b*: $\kappa_S = 0.3$, $m = 10, 3, 1$; panel *c*: $\kappa_S = 0.1$, $m = 10, 3, 1$; panel *d*: $\kappa_S = 1$, $m = 1, 0.3, 0.1$; panel *e*: $\kappa_S = 0.3$, $m = 1, 0.3, 0.1$; panel *f*: $\kappa_S = 0.1$, $m = 1, 0.3, 0.1$. Values of m : 10 ($\blacktriangle$); 3 ($\blacksquare$); 1 (solid line); 0.3 ($\bullet$); 0.1 ($\blacktriangledown$).

The traversing of the Γ_S -Q plane is accomplished by sequential horizontal (charge-derived, ion) and vertical (neutral-derived, solvent) movements. Second, the ability to parameterize m or to make the qualitative distinction between attractive and repulsive interactions promises no facility to identify the molecular origins of these effects; that is the role of a spectroscopic or other molecularly sensitive probe. Third, although both thermodynamic and kinetic phenomena are operative in all panels in Fig. 4.5, thermodynamic information would be more readily acquired from a response like panel *a* or *d* in Fig. 4.5 (according to whether $m > 1$ or $m < 1$). Similarly, kinetic information would be more readily acquired from a response like panel *c* or *f* of Fig. 4.5 (according to whether $m > 1$ or $m < 1$). This further emphasises the power of varying timescale to emphasise different features of the system.

4.5.3 Thermodynamically Non-ideal Solvation Coupled with Slow Charge Transfer

Figure 4.6 illustrates a range of possibilities encompassed within the general scenario of non-ideal solvation (thermodynamic phenomena) coupled with slow symmetrical charge transfer (kinetic phenomena). The discussion presented here is relatively brief, since most of the features can be deduced by comparison with Figure 4.5.

In the case of Fig. 4.6, the large value of κ_S results in a single valued (reversible) response of solvation to charge state (Γ_S -Q plot). This has the rather attractive feature that, for this particular case, all the kinetic information lies in the Q-E response and all the thermodynamic information in the Γ_S -Q response. This situation can be recognized through the substantial influence of scan rate on the Q-E plot (due to the presence of hysteresis) and zero influence on the Γ_S -Q plot (no hysteresis observed). In all cases, the rapid solvation kinetics ensure full (de-)solvation, irrespective of potential scan rate. This would only be violated if the potential scan rate were sufficiently high (not shown here) that the Q-E plateau were not reached. A rather interesting feature of this case is the nature of the Γ_S -E response. Since there are no observable kinetic limitations to the solvent transfer, the *shape* of the response essentially follows the hysteresis of the charge transfer process. However, the thermodynamic non-idealities influence the *location* of the response on the potential axis (cf. the asymmetric effects on the potential axis in Fig.

4.4). Thus, each of the three projections provides quite distinct information on the overall process represented by the 3D trajectory of the system in compositional space. The discussion about concave vs convex Γ_S -Q projections (for $m > 1$ and $m < 1$, respectively, seen in panels a-c and d-f of Fig. 4.6) is analogous to that presented for Fig. 4.5.

The one unusual feature not seen above is that for the case when $m < 1$ (Fig. 4.6, panels d-f) the thermodynamic “dragging” of the de-solvation process to more negative potentials results in incomplete de-solvation at the end of the reduction half cycle. This could readily be mistaken for a kinetic effect, but is in fact a thermodynamic effect manifested as a consequence of not adequately extending the negative potential limit. This would have significant effects in multiple cycling experiments, somewhat analogous to the “drift” situation described in the previous sub-section 4.5.1 (Fig. 4.4, panel b).

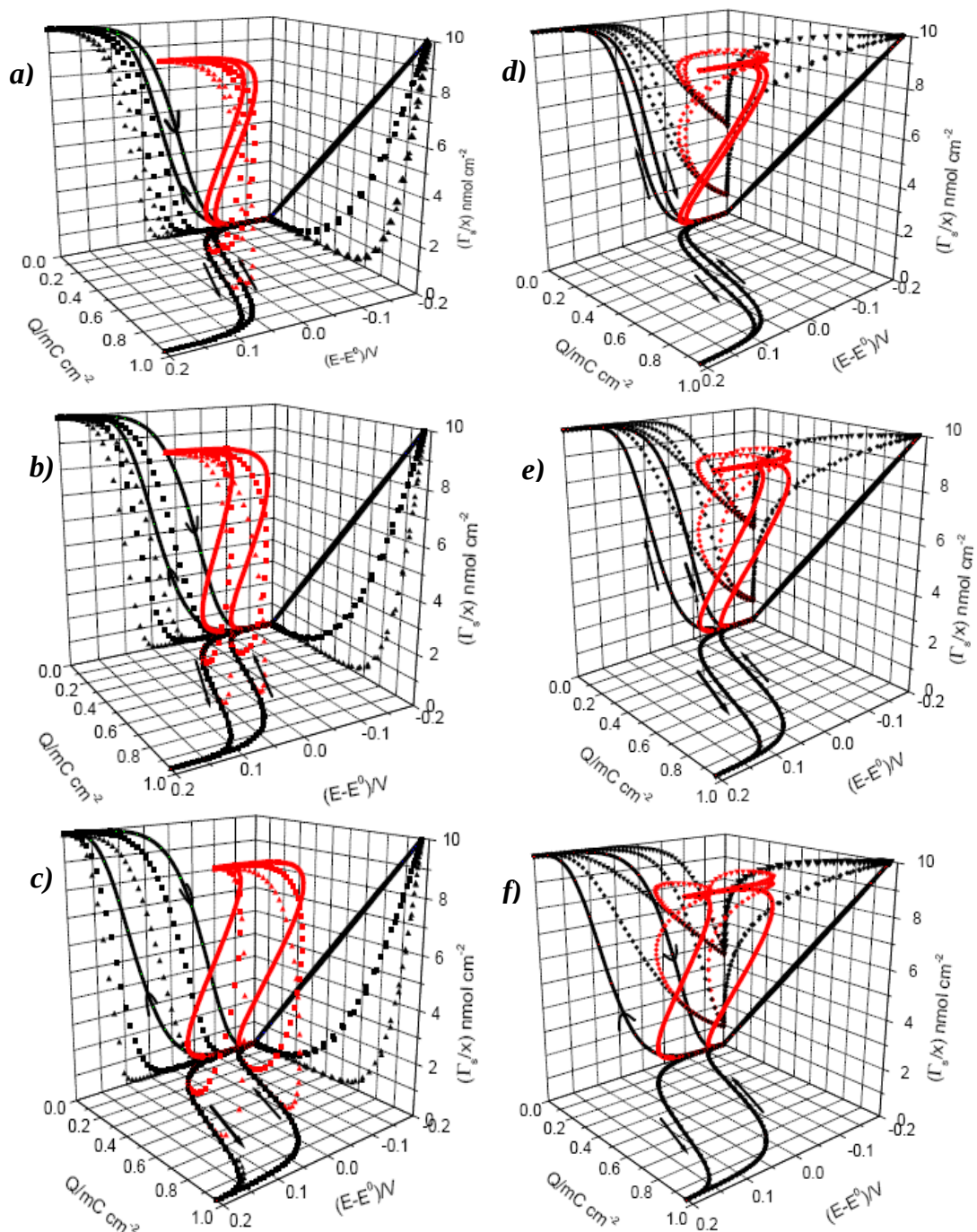


Fig. 4.6: Representative calculated excursion through compositional space $\Omega(E, Q, \Gamma_s)$ for films with rapid solvent transfer kinetics, slow symmetrical charge transfer kinetics and non-ideal solvation, in response to a cyclic linear potential sweep. $\kappa_s = 25$; $K_s = 1000$; $\Gamma_T = 10 \text{ nmol cm}^{-2}$ (all panels). Panel a: $\kappa_e = 1$, $m = 10, 3, 1$; panel b: $\kappa_e = 0.3$, $m = 10, 3, 1$; panel c: $\kappa_e = 0.1$, $m = 10, 3, 1$; panel d: $\kappa_e = 1$, $m = 1, 0.3, 0.1$; panel e: $\kappa_e = 0.3$, $m = 1, 0.3, 0.1$; panel f: $\kappa_e = 0.1$, $m = 1, 0.3, 0.1$. Values of m : 10 ($\blacktriangle$); 3 ($\blacksquare$); 1 (solid line); 0.3 ($\bullet$); 0.1 ($\blacktriangledown$).

4.5.4 Consideration of Solvent and Counter ion Flux Ratios

In the previous sections we have discussed the variation of film compositional changes with potential and charge density under thermodynamic and kinetic control. In this section we explore a more sensitive differential representation of the film compositional variations during the time course of film redox switching. The hypothesis is to explore the flux ratio (solvent:ion ratio) variation with charge density in order to identify changes in behaviour of film at partial conversion of redox transformation. Figures 4.7 and 4.8 show representative flux ratio vs. charge density plots for thermodynamically and kinetically controlled cases, respectively. These are derived from the data of Figures 4.6 and 4.5, respectively. The case of rapid kinetics and ideal thermodynamics returns the rather “simple” result that ρ is constant during the redox conversion in either direction. When normalised with the solvation stoichiometry, as in the presentation of Figures 4.7 and 4.8, ρ/x is unity throughout. In an experimental context, this would result in the same value of ρ/x being “sampled”, regardless of the experimental timescale and whether one looked at partial or complete redox conversion. For any other (thermodynamic or kinetic) situation, the “sampling” conditions, notably of potential scan rate and of the fractional conversion, can result in a misleading conclusion. As an example, we point out the common practice in EQCM experiments of recording the overall (“end-to-end”) mass and charge changes associated with complete redox switching of a film. Perusal of the wide spectrum of behaviours encompassed within Figures 4.7 and 4.8 shows that failure to sample intermediate redox compositions and/or different scan rates leaves one largely ignorant of the true characteristics of the film.

Recognizing that the flux ratio is redox state dependent (ρ -Q curvature) does not alone distinguish thermodynamic and kinetic control. Comparison of Figures 4.7 and 4.8 shows that the test to be applied is a ρ -Q relationship that is single valued, i.e. independent of scan direction and scan rate (more generally, independent of time scale). In the event that this test is satisfied, the direction and extent of curvature can provide the non-ideality parameter; here this is represented by m in a power law dependence, but other functional forms could equally be fitted.

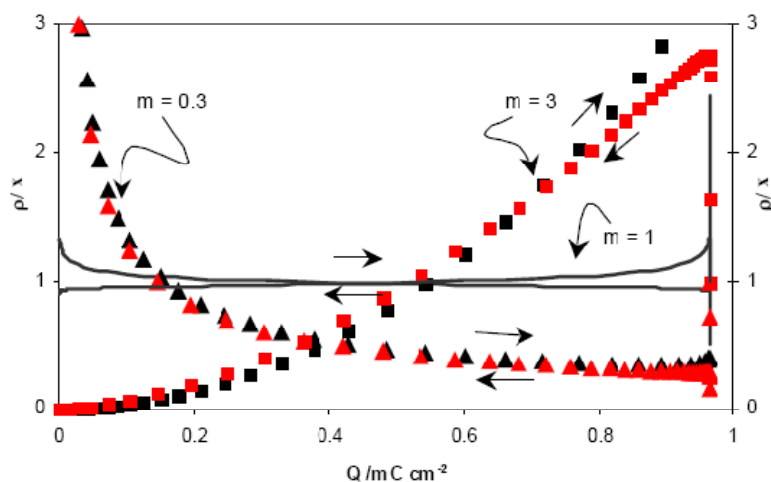


Fig. 4.7: Plots of ρ/x vs Q for selected rapid solvent transfer cases from Figure 4.6 (panels c and f) of $m = 0.3$ ($\blacktriangle$), 1 (solid line) and 3 ($\blacksquare$). Arrows indicate scan direction.

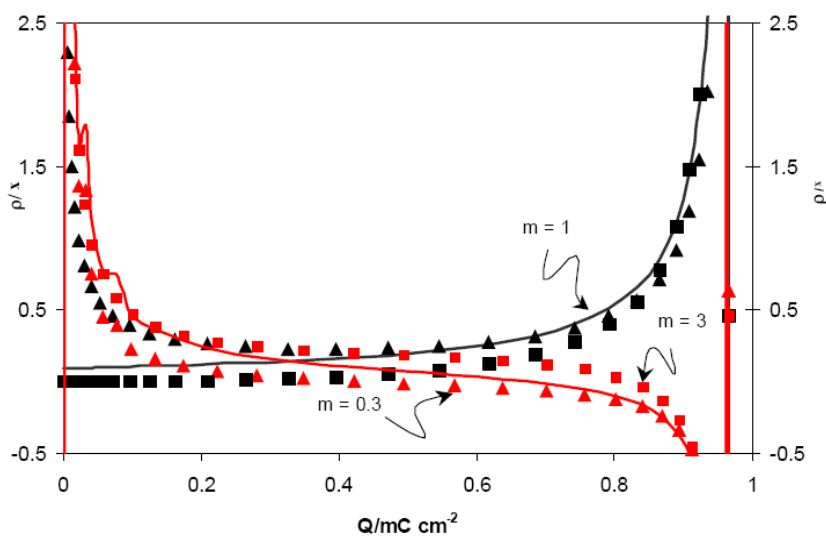


Fig. 4.8: Plots of ρ/x vs Q for the selected slow solvent transfer ($\kappa_S = 0.1$; $\kappa_e = 10$) cases from Figure 4.5 (panels c and f) of $m = 0.3$ ($\blacktriangle$), 1 (solid line) and 3 ($\blacksquare$). Arrows indicate scan direction.

Figure 4.8 provides somewhat more complexity, according to the relative dominance of the kinetic and thermodynamic effects. The obvious features are dependence of the response on experimental timescale (compare with Figure 4.7 responses, even in the ideal

$m = 1$ case) and scan direction: these signal kinetic control. The discussion largely parallels that for panels *c* and *f* of Figure 4.5, although the differential format of Figure 4.8 highlights some features. In particular, we note that the drivers of concave vs convex curvature (deviation to either side of the ideal, rapid kinetic response) compete in a manner that overall is determined by time scale. Specifically, $m > 1$ ($m < 1$) promotes a “concave” (“convex”) response in both switching directions, to an extent that is *independent* of time scale. On the other hand, slow kinetics always promote a “concave” response during oxidation and a “convex” response during film reduction, to an extent that is *dependent* on time scale. These contributions may reinforce or oppose each other, leading to a response whose shape varies with time scale in a complex manner. To exploit this, we suggest that variation of the experimental time scale will allow the thermodynamic features to be explored at low scan rate and the kinetic factors to be explored at higher scan rate. While this strategy may appear obvious, the approach is seldom used and even when scan rate is explored there have not previously been suitable models with which to compare the results.

4.6 Conclusions

The generality and utility of representations of mobile species (ion and solvent) content within electroactive films in 3D (E, Q, Γ_s) compositional space has been discussed. The novelty of approach in this work lies by combining representations of thermodynamic non-ideality with slow electron/counter ion and solvent transfer kinetics. The ability to describe combinations of these effects (which were previously considered in isolation, not in combination) promises the facility to describe practical chemical systems in a more physically realistic manner. In the case of solvent transfer, the physically likely case of different entry and exit kinetic parameters has also been explored. For the purposes of illustration, particular examples were selected. We considered permselective films subject to a voltammetric potential control function and whose solvation non-ideality could be represented by a power law dependence (with index values either side of unity representing attractive and repulsive interactions). It is envisaged that different chemical systems might show a range of interaction behaviours but, at the cost of algebraic

complexity, other functional forms could be incorporated within the formalism developed here.

The representation of film composition in (E, Q, Γ_s) -space is seen on the one hand to be very close to the format of experimental raw data for a range of population probes. On the other hand, this 3D representation is revealed to provide immediate visual recognition of theoretically distinct models. In the former instance, for example, Q and Γ_s represent the charge response and mass response (after subtraction of the ion contribution) in an EQCM experiment. In the latter instance, application of some generally applicable chemical principles, such as (in)dependence on time scale and direction of conversion, allow thermodynamic and kinetic cases to be distinguished. In the thermodynamic case, the direction and extent of curvature (or otherwise) in Γ_s - Q plots provides insight into solvation non-idealities. In the kinetic cases, comparison of hysteresis in the Q - and Γ_s -responses allows one to distinguish slow coupled electron/counter ion transfer and slow solvent transfer.

An important outcome is the sensitivity of the trajectory in (E, Q, Γ_s) -space to the experimental time scale. The interplay of thermodynamic and kinetic factors is rather delicate and, since only the latter responds to time scale (here, represented by potential scan rate), one can manipulate the situation to engineer dominance of thermodynamic or kinetic factors at will. Practically, this provides a means to determine these parameters (in the above models represented by m , κ_e and κ_s) via their temporal “isolation”. In the case of kinetic control, presentation of the composition data in the form of the ratio of fluxes of solvent and counter ions (ρ) - as a function of charge (Q) - provides a sensitive means of exploring composition (and the rate of change thereof) at partial redox conversion. Both the integral and differential presentational formats show the limitations of considering only overall (“end-to-end”) compositional changes; this applies to both thermodynamically and kinetically controlled situations.

4.7 References

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A decorative graphic for the chapter header, consisting of a grey, pill-shaped background with a white, stylized 'C' or 'S' shape on the left side. The text 'Chapter Five' is centered in the white area.

Chapter Five

Gravimetric Studies of Mobile Species Dynamics within Thin Polyaniline Films

5.1 Overview

In this chapter, electrochemical quartz crystal microbalance (EQCM) measurements (see chapters two and three) are used to examine the details of ion and solvent transfers accompanying the redox switching of polyaniline films exposed to aqueous perchloric acid solution. Previous studies of this system have generally focussed on the overall (“end-to-end”) redox process; this effectively “averages” the population changes as a function of injected charge. Through the use of the models described in chapter four, it is possible to show that this is an over-simplification of the situation. The identity of the charge-balancing ion transfer and the amount of solvent transfer that accompanies ion transfer is a function of the state of charge of the film. Furthermore, it is also possible to show that, in the rather unusual environment of a highly charged polymeric matrix, solvent behaves in a thermodynamically non-ideal manner (sections 4.3.2 and 4.5.2 of chapter four).

Polyaniline is one of the most important conducting polymers and has been extensively studied over the last three decades due to its interesting physical and chemical properties and ease of preparation in aqueous media [3]. A combination of high conductivity over a wide range of conditions, processability, reproducibility and physical/chemical stability [2-6] offer potential application to a range of electronic, optical and other devices. Detailed reviews on polyaniline films have been presented elsewhere [7-12].

The electrochemical [13], optical [2] and morphological properties [3, 14] of polyaniline have been investigated by a number of research groups using both electrochemical and *in situ* non-electrochemical techniques [7-12]. From the perspective of electrochemical applications, arguably the most important underlying process is the exchange (between thin films of polyaniline and the solution to which they are exposed) of ions and neutral molecules (primarily solvent) that accompany film redox switching. The rates and extents of these exchange processes as functions of all the relevant parameters (potential, timescale, temperature, etc.) essentially control the characteristics of any device. An ideal and commonly used technique to study this process is the electrochemical quartz crystal microbalance (EQCM) [1-6, 13-28]. This technique has been widely used to study the deposition and redox cycling of diverse electroactive films [29]. From the perspective of the present study, it is a highly sensitive interfacial gravimetric method that responds to all species - charged and neutral - and does so with known sensitivity, given by molar mass. Aspects of polyaniline electrochemistry that have been explored using the EQCM are film growth [3, 14, 15, 25], film degradation [5, 16], and the effects of ion type and size present at time of deposition on film morphology [3, 4, 14, 15, 28] and film redox chemistry (“doping” and “undoping”) [2, 6, 13, 23]. For the first time, the aspects of viscoelastic properties of thin polyaniline films in electrochemical deposition processes have been investigated in this research project and will be discussed in chapters 6 and 7. The discussion in this chapter is restricted to an acoustically thin polyaniline film for which EQCM data can be interpreted gravimetrically.

Despite the large body of information on polyaniline films in the literature, a number of important questions remain to be addressed, notably with regard to the details of mobile species (ion and solvent) transfer accompanying redox switching. Early EQCM studies of polyaniline redox switching were qualitative and used the direction of mass (frequency) change to deduce that the dominant process is anion exchange [20-22]. Quantitative studies comparing the overall (“end-to-end”) mass change and charge transferred for the process arrived at the same conclusion (anion dominance) [3, 13]. The incorporation of a “fixed” polymeric counter anion (e.g. polystyrenesulfonate, PSS) reversed this situation to overall cation (proton) transfer dominance [4]. Depending on

the concentration, pH, temperature and the type of the background electrolyte, mixed cationic and anionic ion transfers have also been previously reported [13, 20, 30-36]. Most of these studies were carried out in different media (sulphuric acid solutions) to that used here (perchloric acid solutions) and are not interpreted at the same level of detail, particularly the earlier ones. However, for many applications, the film will spend much of its time in an intermediate (rather than fully reduced or oxidised) state; charge storage applications illustrate the point. Here, it is critical to understand the details of the process as a function of charge state; this provides an important motivation for the present study.

In this work, the above ideas are extended in two general respects: i) mass-charge comparisons are made as a function of film redox state (i.e. *during*, not simply before and after, redox conversion) and ii) the effect of timescale (represented by potential scan rate) is explored. The effect of varying electrolyte concentration was explored, but our investigation was rather restricted to the behaviour of ion and solvent transfers of polyaniline films in 1 M HClO₄. An important advance is that we are able to separate ion and solvent transfer processes throughout redox switching. Qualitatively we distinguish whether these individual processes are under thermodynamic or kinetic control, and quantitatively we are able to estimate the relevant parameters (e.g. thermodynamic non-ideality parameter as detailed in chapter four).

5.2 Film Growth

The experimental procedures for the polymer deposition were discussed in chapter three. 0.1 M aniline in 1 M HClO₄ solution was used for the potentiodynamic deposition of the film with a potential range of $-0.2 \leq E/V \leq 0.9$ and scan rate of $v = 10 \text{ mV s}^{-1}$. After the film deposition, the electrode was disconnected at the reduced end ($E = -0.2 \text{ V}$) and thoroughly rinsed with distilled water. Subsequently, the freshly prepared thin polyaniline film was tested in a monomer-free 1 M HClO₄ electrolyte; to avoid film degradation, a potential range of $-0.2 \leq E/V \leq 0.5$ was used with three different scan rates as described in section 5.4.1. Fig. 5.1 shows typical results for a polyaniline film deposition experiment. The *i*-*E* curves of panel *a* are similar to those reported by a number of authors [2-5, 15]. In this panel *a* of Fig. 5.1, the current for the film redox

process increases continuously with successive cycling; this provides a continuous coulometric assay of the extent of polymer redox site immobilization ($\Gamma/\text{mol cm}^{-2}$) according to Eq. 5.1:

$$\Gamma = \left(\frac{Q_{\text{red}}}{nF} \right) \quad (5.1)$$

In Eq. 5.1, Q_{red} (C cm^{-2}) is the charge density under the more cathodic of the two reduction peaks; the number of electrons involved in the redox process, $n = 1$; and F is the Faraday. Over the film thickness range encompassed here, peak current is linearly related to potential scan rate (see below), so Q_{red} represents all polymer sites. For the representative example shown in Fig. 5.1 (panel *a*), $\Gamma = 35 \text{ nmol cm}^{-2}$ (where “mol” refers to dimeric aniline redox units, for which $n = 1$).

The simultaneously acquired admittance spectra of panel *b* in Fig. 5.1 show a progressive shift to lower resonant frequency but very little change in peak admittance or width. These are characteristic of an acoustically thin (simplistically, “rigid”) film, for which the frequency shift can be interpreted gravimetrically. Under these conditions, the observed resonant frequency shift, Δf (Hz), can be converted to the underlying areal mass density change, Δm (g cm^{-2}), using the Sauerbrey equation:

$$\Delta f = - \left(\frac{2f_0^2}{\rho_q v_q} \right) \Delta m = -C_1 \Delta m \quad (5.2)$$

where ρ_q is the density of quartz, v_q is the wave velocity within the quartz crystal, and f_0 is the base frequency (here, nominally 10 MHz). For the representative example shown in panel *b* of Fig. 5.1, the final value of Δf was 1.34 kHz. Using Eq. 5.2, the frequency shift, Δf , data of Fig. 5.1 (panel *b*) corresponds to an areal mass density of $7.03 \mu\text{g cm}^{-2}$. Correlation of this frequency shift (Eq. 5.2) with the coulometrically determined surface population (Eq. 5.1) yields an effective redox site molar mass (in the fully reduced state)

of 200 g mol^{-1} . Since the molar mass of a redox unit (dimeric aniline redox unit as defined above) in the polymeric component is 182 g mol^{-1} , the implication is that the film contains 9 % electrolyte. To a first approximation this is solvent; it represents a baseline of ca. 1 water molecule per redox site (as defined above), upon which the redox-driven changes we now consider take place. Solvent within the film facilitates movement of polymer chains past each other. The presence of solvent within the film is consistent with the fact that thicker films are viscoelastic and imposes the restriction to the relatively thin films used here in order that the present gravimetric interpretation be used.

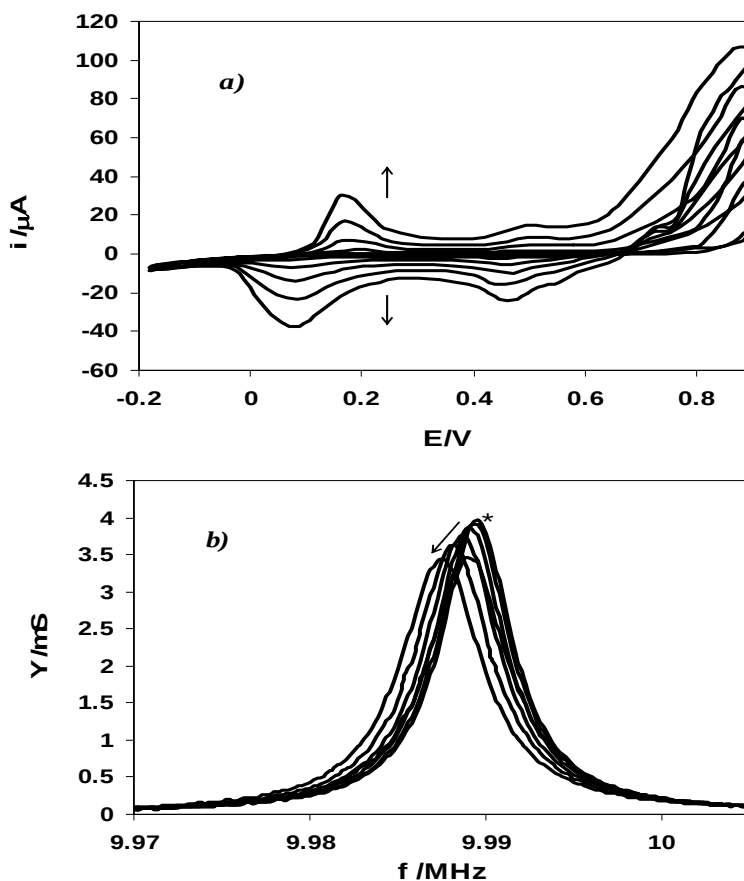


Fig. 1: EQCM data acquired during potentiodynamic deposition of a polyaniline film. Solution: 0.1 M of aniline / 1 M HClO_4 . Potential scan rate, $\nu = 10 \text{ mV s}^{-1}$. (a) i-E curves; (b) Crystal admittance spectra, Y/mS vs f/Hz , recorded at the end of each potentiodynamic cycle. The asterisk (*) shows the admittance plot for the bare electrode before the film deposition and the arrow indicates the direction of the successive cycles for the film growth.

5.3 Approach to data interpretation

In this section we establish the procedure by which the experimental data will be processed. The particular targets are the changes in ion and solvent population as functions of potential under the dynamic conditions of potential cycling.

Ion transfer(s) at the polymer/solution interface are required to satisfy the electroneutrality condition as electrons are transferred across the metal/polymer interface. Quite generally, the contributions of anion and cation transfers may assume any individual values, so long as their algebraic sum equates to the instantaneous change in electron population. This overall constraint will in practice be met on any accessible timescale, although the relative participation of opposing anion and cation transfers may well be timescale dependent. Solvent transfer, on the other hand, is required to satisfy an activity constraint between the polymer and solution phases [37]. Transfer of solvent, as a neutral species, can assume any non-integer value per electron transferred, even under thermodynamically controlled conditions (refer to Eq. 4.4 in chapter four). Under kinetically controlled conditions, there is no *a priori* relationship between solvent transfer and injected charge. This relationship has been modelled in Eqs. 4.5 and 4.6 in chapter four as well.

Based on the crystal admittance data on panel *b* in Fig. 5.1, the QCM frequency response is interpretable in gravimetric terms. In the context of the voltammetric redox switching experiments considered here, the gravimetric data of Fig. 5.1 corresponds to a total mass response, Δm , that reflects the sum of redox-driven population changes, $\Delta\Gamma_j$, of cation (C), anion (A) and solvent (S), appropriately weighted by their respective molar masses, m_j (where $j = C, A$ or S):

$$\Delta m = m_A \Delta\Gamma_A + m_C \Delta\Gamma_C + m_S \Delta\Gamma_S \quad (5.3)$$

In the simplest case - a commonly used assumption that will be tested in more detail below - only counter ion (A) and solvent (S) transfers occur across the film/solution interface. This case, for which $\Delta\Gamma_C$ is zero, corresponds to a permselective film. Now,

the change in anion population, $\Delta\Gamma_A$, can be calculated from the charge using Faraday's law:

$$\Delta\Gamma_A = Q/z_A F \quad (5.4)$$

The combination of Eq. 5.4 with Eqs. 5.2 and 5.3 then yields:

$$\Delta\Gamma_S = m_S^{-1} \left[\left(\frac{-\Delta f}{C_1} \right) + m_A \left(\frac{Q}{z_A F} \right) \right] \quad (5.5)$$

where C_1 represents the collected (known) constants in the Sauerbrey equation (see above). Eq. 5.5 allows direct calculation of changes in the film's solvent population from the experimentally observed values of Q and Δf as functions of potential (E).

5.4 Film population changes accompanying polyaniline redox switching

5.4.1 Overview.

The results of a typical voltammetric experiment for a polyaniline film exposed to monomer-free 1 M HClO_4 background electrolyte are shown in Fig. 5.2. The responses of the data are shown for three potential scan rates (5, 10 and 20 mV s^{-1}). In this experiment, the attention is restricted to the first redox switching process of polyaniline films. This is to avoid issues associated with partial attribution of the current to irreversible film overoxidation processes (and/or film degradation). Current responses normalise with scan rate, as indicated by the linear variation of peak current (i_p) with scan rate (see panel *b* of Fig. 5.2). Therefore, on the timescales investigated (controlled via potential scan rate and film thickness), there is complete redox conversion of the film.

The associated QCM resonant frequency changes, Δf , are presented in panel *c* of Fig. 5.2. As justified above, we interpret these gravimetrically. Previous studies of “end-to-end” mass changes [3, 20-22] have suggested dominance of anion transfer for the *overall*

redox process. Our first objective is to explore whether this is true *throughout* the redox process.

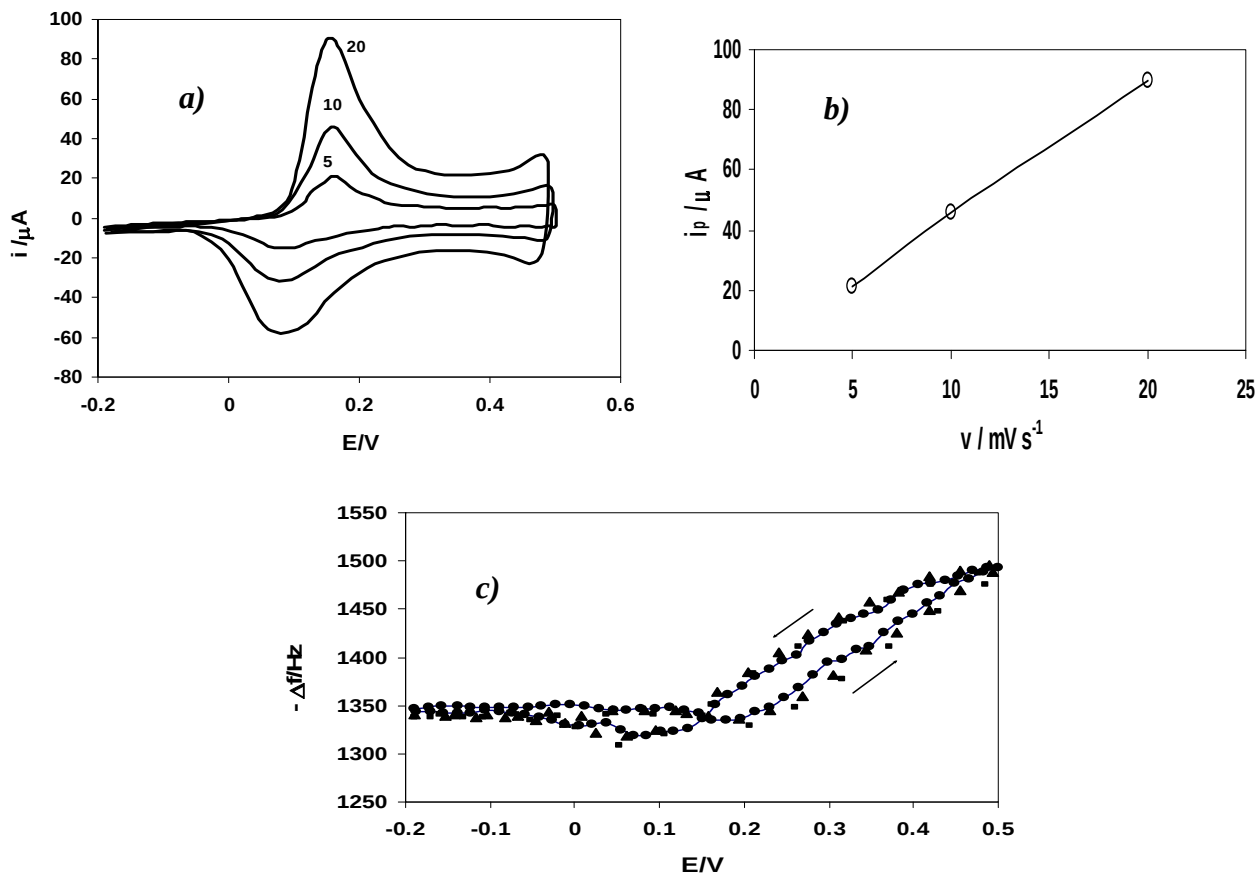


Fig. 5.2: Voltammetric EQCM characterization in 1 M HClO_4 of polyaniline film (as deposited in the experiment of Fig. 5.1). Numbers indicate scan rate, $v / \text{mV s}^{-1}$. (a) i - E responses. (b) the peak current against scan rate. (c) Δf - E responses; $v / \text{mV s}^{-1} = 5$ ($\bullet$), 10 ($\blacktriangle$), 20 ($\blacklozenge$).

5.4.2 Establishing the predominant ion transfer

The anion-based hypothesis (the permselective limit of Eq. 5.5, corresponding to $\Delta\Gamma_C = 0$ in Eq. 5.3) was used to calculate film solvent population changes as a function of potential during the redox transformation for each data set (scan rate) shown in Fig. 5.2. Commencing with a fully reduced film, the outcome of this analysis is a solvent population that initially *decreases* quite substantially (between 0.11 V and 0.19 V). After this initial fall, the solvent population then *increases* (between 0.2 V and 0.5 V) to a final

level for the oxidised film that is somewhat higher than for the reduced film. While it is not impossible for the solvent flow to reverse in this manner, it is physically rather unlikely; for polyaniline the film is solvated more readily in the oxidised form. Furthermore, the types of situation that one might imagine leading to an “ebb and flow” situation generally involve slow transfer kinetics, which would give timescale-dependent responses. However, the pattern of solvent exit and entry is essentially independent of scan rate (see Fig. 5.2, panel c). We therefore suggest that, while anion transfer may dominate the overall redox switching process, it does not represent the full picture of mobile species transfers across film/solution interface.

In pursuit of an alternative hypothesis, the raw mass (frequency) response is compared with the charge response in Fig. 5.2. Without the application of any model, simple inspection shows that a large fraction of the charge is passed before the film mass changes significantly. This situation could prevail if electroneutrality were maintained by transfer of an ion of very low mass - proton (the cation in this electrolyte) is the obvious candidate. We therefore explore the more complex mechanism that has proton (cation) as the charge-balancing ion transfer in the early stages of film oxidation, supplanted by anion transfer (in the opposite direction) in the later stages of film oxidation. While the underlying chemistry is clearly more complex, this is still consistent with the deductions of previous investigations of the overall redox process. Since the anion molar mass is two orders of magnitude larger than the cation molar mass, it is trivial to assume that the anion exchange dominates the overall gravimetric response [3, 6, 13, 38].

5.4.3 Solvent population changes.

The process of solvent transfer has been modelled under both thermodynamically- and kinetically-controlled conditions in chapter four. In both cases, the effects of non-idealities (attractive or repulsive interactions between solvent and redox sites) were considered through the models presented in Eqs. 4.6 and 4.11. In this section, we apply the theoretical outcomes of the 3D compositional models discussed in chapter four to the experimental data of Fig. 5.2. The advantage of the data representation in this manner is that different mechanistic scenarios can be recognized by the redox-driven trajectory in

compositional space [39]. The variation (or otherwise) of the trajectory with timescale can be used to identify kinetic (or thermodynamic) control, without the application of any model or assumptions. Although simpler models using this visual compositional representation have been applied previously [40-42], the present work represents the first application of the more general model (encompassing the possibilities of thermodynamic or kinetic control *and* the presence or absence of solvation non-idealities) to any electrochemical system.

Fig. 4.1 (chapter four) illustrates in schematic form the way in which we utilise the concept to interpret the data in Fig. 5.2. The (unlikely) situation that both ion and solvent transfers are rapid and solvation is ideal is represented by the central line on each of the three 2D-planes. The projections on the (E,Q)-, (E, Γ_s)- and (Q, Γ_s)-planes, respectively, represent the Nernst equation, the ideal solvent isotherm, and a linear redox site solvation relationship. The latter is essentially the assumption that is made when one acquires only the overall (“end-to-end”) EQCM measurement. As equilibrium relationships, all these are single valued, i.e. independent of timescale and scan direction.

As explained in chapter four (sections 4.3.1 and 4.5.2), the introduction of non-ideal solvation results in curvature to the (Q, Γ_s)-plane projection, with the direction of curvature determined by whether the interactions are repulsive or attractive (indicated by the arrows in Fig. 4.1 and corresponding to interaction parameters $m > 1$ and $m < 1$, respectively) [39]. Kinetic effects also result in curvature, but with the critical distinction that they introduce hysteresis into the responses. In section 4.5, it was discussed how slow redox kinetics and slow solvent transfer give characteristically different patterns of hysteresis.

The key hypothesis which we now apply to our polyaniline data is that (Q, Γ_s)-plane curvature alone is not a diagnostic of the system kinetics. However, the curvature in (Q, Γ_s)-plane together with the pattern of (or absence of) hysteresis in the charge and solvation responses can provide mechanistic diagnosis.

The experimental values of the polyaniline film compositional changes in response to the potentiodynamic control function (at different scan rates) are shown in Fig. 5.3 panels *a-c*. This 3D $\Omega(E, Q, \Gamma_s)$ -space representation shows the film's instantaneous composition as it traverses the redox cycle.

Two qualitative observations can be quickly made out of the data in Fig. 5.3. First, there is relatively little hysteresis in any of the responses (in the individual 2D projections). The (Q, Γ_s) -projection shows least hysteresis, implying that solvent transfer is relatively rapid (cf. the 3D compositional models presented in chapter four, section 4.5). The (E, Q) -projection shows some hysteresis, suggesting that coupled electron/ion transfer kinetics are not equilibrated in this timescale regime. Second, there is obvious curvature to the (Q, Γ_s) -plot. Since this is not associated with hysteresis or significant timescale dependence, the origin must be thermodynamic, not kinetic; this observation can be better explained in the light of the models presented in section 4.3.2 of chapter four.

The second observation (curvature in (Q, Γ_s) -plot without hysteresis) can be pursued to a quantitative conclusion. The concave (“upward”) nature of the curvature suggests that the solvent interactions are repulsive; in the formalism of the Freundlich-like isotherm of Eq. 5.5, $m > 1$. More detailed analysis, using the calculational method described in the theoretical 3D models resulting from Eqs. 4.6 and 4.11 [39] yields a value of the non-ideality thermodynamic parameter, $m = 2 (\pm 0.5)$. This is a case intermediate of models presented in panel *a* of Fig. 4.5 (chapter four)

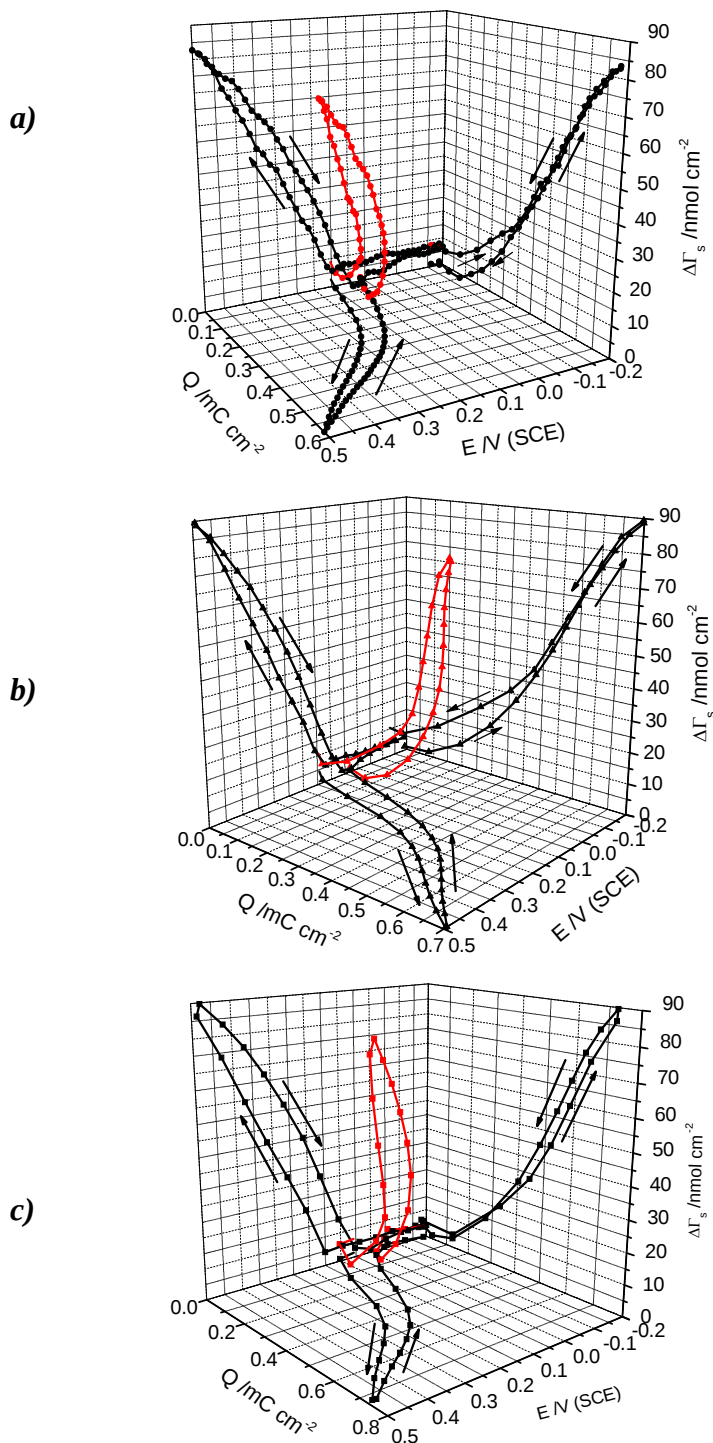


Fig. 5.3: Representation of film ion (Q) and solvent (Γ_s) populations in $\Omega(E, Q, \Gamma_s)$ compositional space during potentiodynamic redox state switching. Data from Fig. 2, processed according to Eq. 5.5. $v / \text{mV s}^{-1} = (a) 5; (b) 10; (c) 20$.

The power of the model we have used is illustrated by the fact that it allows separation of the charged and uncharged species populations. The separation of mobile species populations can be visualised through the (E,Q)-plane and (Q, Γ_s)-plane projections for the coupled electron/counter-ion and solvent content, respectively, of the film compositional vector Ω . By means of this separation, it is then possible to ascertain whether each mobile species transfer takes place under thermodynamically- or kinetically-controlled conditions on the experimental timescale. Commonly, there is ambiguity as to whether a non-linear solvation response is the result of slow kinetics or non-ideal thermodynamics: here we can unequivocally identify the latter as the cause of the curvature.

5.4.4 Ion and solvent fluxes

In the theoretical treatment of chapter four, it was proposed that the variation - if any - from linearity of film compositional change with charge state could be explored more sensitively in dynamic experiments. This can be done by the determination (as a function of injected charge) of the ratio, ρ , of the fluxes of solvent (f_s) and ions (f_j , where $j = C$ or A , as appropriate):

$$\rho = \frac{f_s}{f_j} = \frac{(d\Gamma_s/d\xi)}{(d\Gamma_j/d\xi)} \quad (5.6)$$

where $d\Gamma_s/d\xi$ and $d\Gamma_j/d\xi$ are the differential forms of the solvent and counter ion transfers as a function of potential ($\xi = E$), charge density ($\xi = Q$) or time ($\xi = t$). For the case of the potentiodynamic experiments of Fig. 5.2, it makes no difference whether we select $\xi = E$ or t . The result of applying this procedure to the data of Fig. 5.3 is shown in Fig. 5.4.

From Fig. 5.3, the overall result of the redox transformation yields an *average* solvent:ion ratio of about 13. This may be compared with values of 18 [13] and 27 [38] reported previously in the literature for polyaniline oxidation in perchloric acid. However, it is quite clear that this does not represent what happens *during* the course of the redox transformation; were this so, the plots in Fig. 5.4 would be horizontal lines. In Fig. 5.4,

the solvent:ion ratio is ca. 5 for the first part of the oxidation and is ca. 25 in the later stages - a significant variation. Furthermore, the absence of hysteresis previously identified, albeit less sensitively, in the integrated population data of Fig. 5.3 confirms that one cannot simply assign the non-linear solvation changes to kinetic effects.

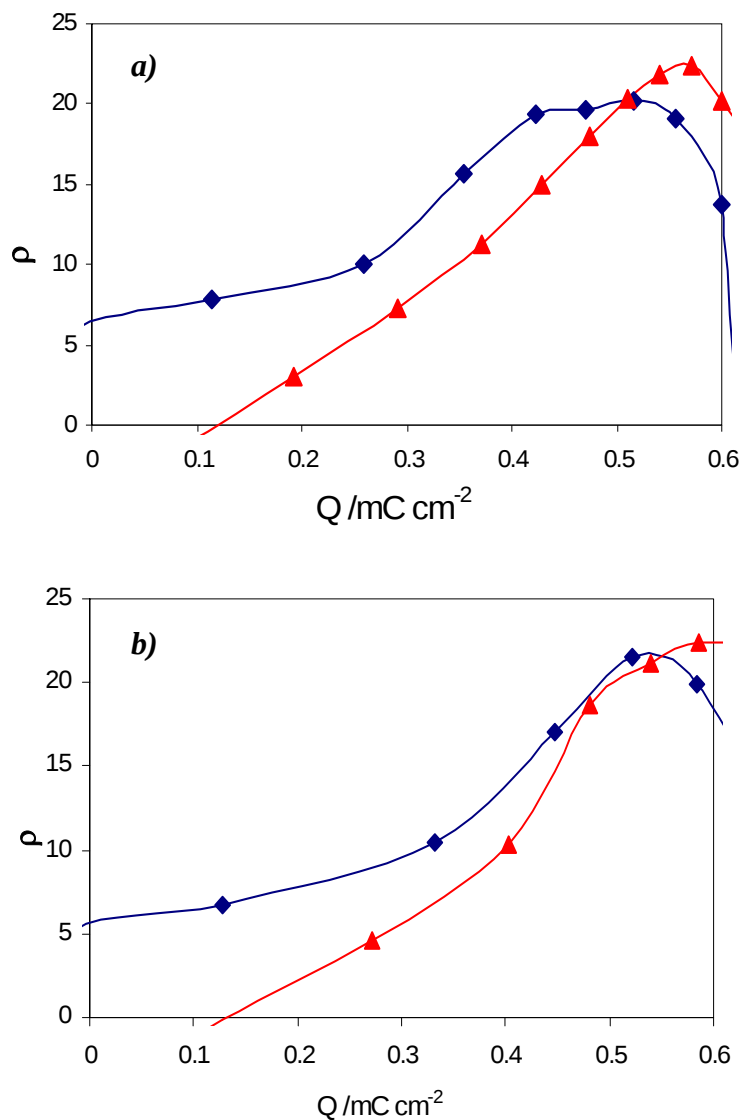


Fig. 5.4: The flux ratio, ρ , of solvent (water) to counter ion (ClO_4^-) transfers potentiodynamic redox state switching. $\nu / \text{mV s}^{-1} =$ (a) 10, (b) 20. Scan direction: oxidation ($\blacklozenge$); reduction ($\blacktriangle$). (Lines are simply a guide to the eye.)

5.5 Summary

The application of the models described earlier (chapter four) for the visualization of mobile species transfers accompanying redox switching of electroactive films reveals that considerably more information is contained within EQCM responses than is commonly extracted. In particular, one can readily distinguish thermodynamic from kinetic control for the *individual* transfers of ion and solvent. In the case of solvent transfer, for which there is no realistic prospect of predicting the variation of population with redox state, it is possible to use experimental data to identify and quantify non-ideal behaviour.

For the case of the first redox process of polyaniline films exposed to aqueous perchloric acid, film mass and charge data show that the assumption of electroneutrality maintenance by anion transfer alone would require a non-monotonic transfer of solvent. While in principle possible, this is relatively unlikely, particularly in the absence of kinetic effects. The film mass- and charge- responses are best described by a mechanism in which the early stages of film oxidation are associated with proton transfer (exit) and the latter stages with perchlorate transfer (entry) in order to satisfy electroneutrality. This situation is consistent with the more physically realistic scenario of monotonic solvent transfer in a given switching direction, namely entry throughout film oxidation and exit throughout film reduction. Application of the model's diagnostic criteria indicates that the film solvent population is in equilibrium on the timescale of slow scan voltammetry ($v = 10 \text{ mV s}^{-1}$), but shows thermodynamic non-idealities. Hysteresis in the film ion population signals failure of the redox state to maintain equilibrium with the applied potential.

5.6 References

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A graphic element for the chapter title, consisting of a grey, elongated oval shape with a white, curved, arrow-like cutout on the left side. The text "Chapter Six" is centered within the oval in a bold, black, serif font.
Chapter Six

Viscoelastic Investigations of Polyaniline Films during Film Electrodeposition

6.1 Overview

As discussed in section 5.1, polyaniline is a conducting polymer that has attracted considerable research interest, notably with regard to its chemical, electrochemical and optical properties [1-10]. Fundamental understandings of these properties - based on the underlying elementary processes - are required for device optimisation. Detailed studies of various features of the polyaniline redox switching dynamics and its polymer structure have been reported in the literature [3, 8, 11-18]. In contrast, and rather surprisingly, polymer dynamics have received less attention. In this chapter the focus is devoted to this aspect (polymer dynamics) of polyaniline behaviour, via an exploration of film viscoelastic properties. This is the first time that viscoelastic data have been reported for polyaniline film electrodeposition.

Quite generally, as one might envisage, the composition, structure and dynamics of electroactive films are interrelated. Consequently, the absence of information on any one of these aspects prevents fundamental understanding of film behaviour. The motivation is that - as indicated above - the current paucity of information on polymer dynamics is the weak link in this chain of understanding. The primary focus of most of the studies [11-14] reported so far has been the transfer of mobile species (electrons, ions and solvent); these are most directly linked to the measured responses, for example current-voltage curves. However, partition into and transport through the film of the mobile species is clearly highly dependent on the characteristics of the medium through which they move. One obvious example is that the rate of ion diffusion through a fluid-like film

will be dependent upon the film viscosity. As will be discussed later, the movements of mobile species within polymer films can be related to film viscoelastic properties, which are ultimately a manifestation of polymer chain dynamics. Through arguments of this nature, it becomes clear that polymer dynamics (film viscoelastic properties) can generally be expected to be key determinants of device performance in practical applications.

The structure and properties of polyaniline films were reported to show significant dependence on the background electrolyte composition, notably concentration and the identity of the “dopant” anion [17, 19]. Based on SEM images [3, 17] and electrochemical quartz crystal microbalance (EQCM) data [3, 11, 17] of polyaniline films, it has been proposed that anions fall into two categories, according to their effect on film morphology. Up to date, the effects of anions in terms of film growth and surface morphology have been studied. Empirically, so-called “class 1” anions (BF_4^- , ClO_4^- and CF_3CO_2^-) lead to compact films, while so-called “class 2” anions (SO_4^{2-} , NO_3^- and Cl^-) lead to more open films (based on SEM images) [17]. However, the underlying rationale for this distinction is not clear, i.e. whether this distinction is based on the electrostatic interaction (charge state) or the geometric size of the anion. Correlation of EQCM and SEM morphological data could in principle be helpful in this respect, but the fact that the former technique is applied *in situ* and the latter *ex situ* means that comparisons are not necessarily straightforward.

Simplistically, one might reasonably speculate that the void spaces will be filled with solvent *in situ*. Since the amount of void space is observed to be quite different (due to anion-induced morphological features) for polyaniline films prepared using anions from different “classes”, the effect of these anions on film mechanical properties is more practically feasible; this effect will be explored in more detail in chapter seven. The hypothesis to be explored is that different film solvent populations will result in varying degrees of plasticisation and thereby different film viscoelastic properties; the discussion in this chapter is restricted to the exploration of film viscoelastic properties during polyaniline films deposition in the presence of perchlorate ion (see section 6.2 below).

The experimental approach (as explained in chapter three) is to use a high frequency acoustic wave device (a thickness shear mode, TSM, resonator [20]) to determine the surface mechanical impedance, from which one can extract the film mechanical behaviour [21-23]. This is generally parameterized in terms of the shear modulus (G), expressed as the complex quantity $G' + jG''$, where G' is the storage modulus, G'' is the loss modulus and j indicates the phase relationship. Ultimately, the value of G and its response to external stimuli are manifestations of the underlying molecular dynamics.

6.2 Objectives

In this chapter, consideration is given to a range of aspects regarding the viscoelastic properties of polyaniline films. The aspects of interest can be associated with either viscoelastic properties of polyaniline films during film electrodeposition and/or the responses of film structural dynamics (viscoelastic properties) to the testing medium during film redox switching in monomer-free solutions. The effects of anion identity on the film viscoelastic properties and responses are addressed in chapter seven.

During film electrodeposition, attention is focused on the following apparently most important practical aspects of film viscoelastic properties: i) the evolution of film dynamic behaviour from liquid-like to bulk-polymer properties - as the film thickness progressively grows, and ii) the variation of viscoelastic properties as a function of potential (control parameter) within a single deposition cycle. This emphasises the variation of the shear modulus of the film during deposition at fixed film thickness (freezing the growth), but changing film redox state between extreme ends (reduced to oxidised or *vice versa*).

6.3 Qualitative overview of film deposition

The experimental procedures for polyaniline film electrodeposition and the strategies of data fitting were discussed in chapter three. The potential range and the scan rate used for the film growth were $-0.2 \leq E/V \leq 0.9$ and $v = 10 \text{ mV s}^{-1}$, respectively. In this chapter, the viscoelastic data for the film electrodeposition in perchloric acid solutions

are described. The effects of different anions on film dynamic properties will be the subject of discussion in chapter seven.

Fig. 6.1 shows the raw data for polyaniline film electrodeposition from 0.1 M aniline in 1 M HClO₄ solution. Voltammetric current data were taken for all cycles during film electropolymerisation and the corresponding admittance spectra were acquired at 20 mV intervals throughout the experiment (as detailed in chapter three). For clarity we only show selected responses of the film electrodeposition data. Panel *a* of Fig. 6.1 shows the *i*-E responses for cycles 5, 10, 15 and 20, representing different stages of the film growth. Using fresh solution for each experiment, the voltammetric curves shown in Fig. 6.1 (panel *a*) were reproducible and similar to those reported in the literature [3, 4, 24]. Selected admittance spectra for the film growth are shown for the extreme negative ($E = -0.2$ V; panel *b*) and positive ($E = 0.9$ V; panel *c*) ends of the scans.

Qualitatively, the trends in resonant peak admittance values in panel *b* (reduced film state) and panel *c* (oxidised film state) are of progressive damping as the film grows. For small numbers of deposition cycles, typically 1-3, the total damping in the system is very similar to that for the immersed bare electrode prior to initiation of electropolymerization. This corresponds to the presence of an acoustically thin film, for which the EQCM response is gravimetrically interpretable, according to the Sauerbrey equation (see below). Beyond 5 deposition cycles, the additional damping associated with electropolymerization is substantial: this corresponds to an acoustically thick film, for which the EQCM response is viscoelastically interpretable, according to Eq. 6.3 (also discussed in Eqs. 2.42 and 2.43 of chapter two).

It is visually discernable from a detailed comparison of panels *b* and *c* in Fig. 6.1 that the magnitude of the peak admittance with the film in the oxidised form is slightly higher than that for the same film in the reduced state. This comparison may physically mean that the polyaniline film is more rigid and/or less viscous in the oxidised form than the reduced one even as the film thickness progressively grows after each deposition cycle.

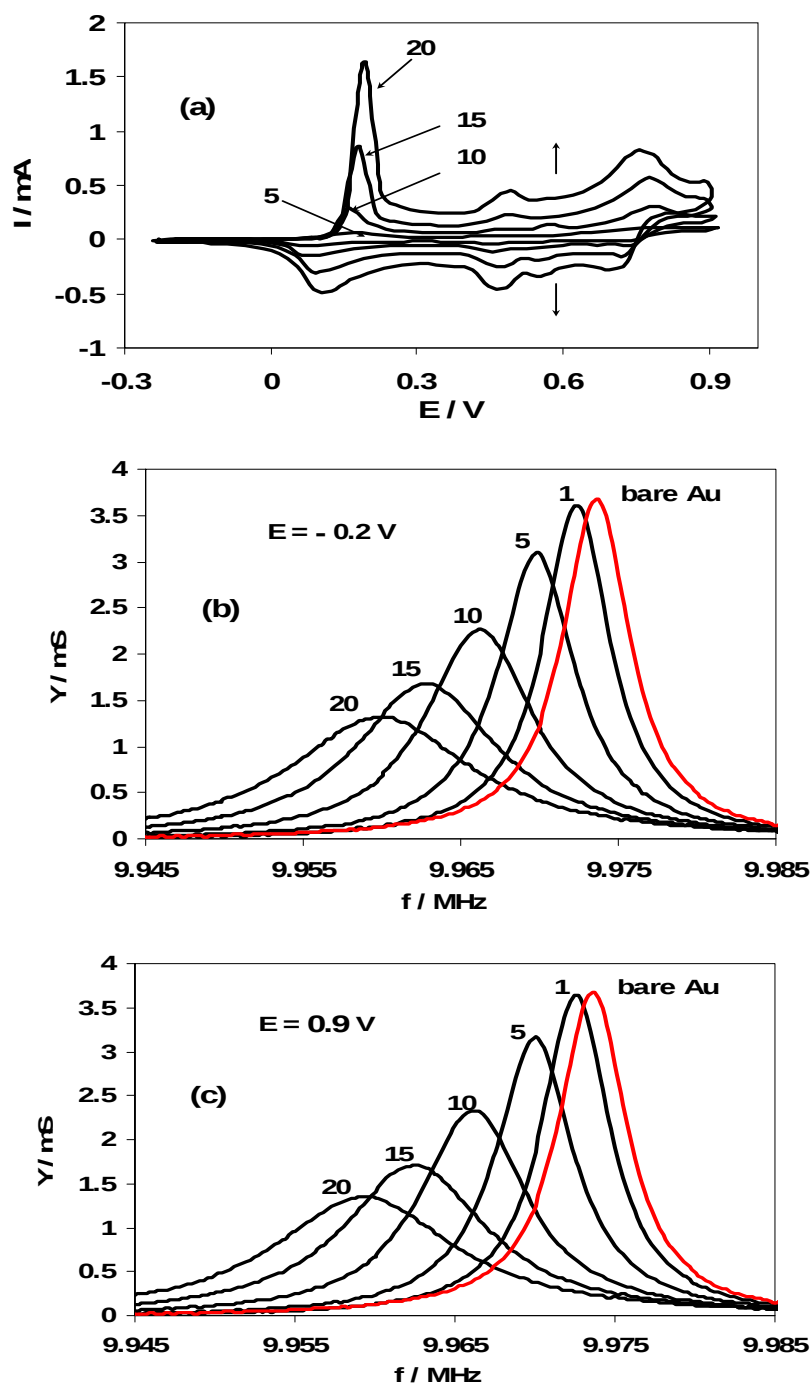


Fig. 6.1: Representative voltammetric experiment for deposition of a polyaniline film deposition from 0.1 M aniline / 1 M $HClO_4$. Panel a: i-E curves for deposition cycles 5, 10, 15 and 20 (as annotated). Potential range: $-0.2 \leq E/V \leq 0.9$. Scan rate, $v = 10 \text{ mV s}^{-1}$. Panel b: Admittance spectra recorded at $E = -0.2 V$ after each indicated potential cycle. Spectrum at right hand side (highest peak admittance) represents bare Au electrode, in solution, prior to film deposition. Panel c: As panel b, but at the positive end of the indicated deposition cycle ($E = 0.9V$).

The quantitative interpretation of film deposition data (Fig. 6.1) with the trends discussed above (i) from the acoustically thin to thick regime and (ii) between different applied potentials will subsequently be used to extract polyaniline shear moduli as functions of film thickness and redox state.

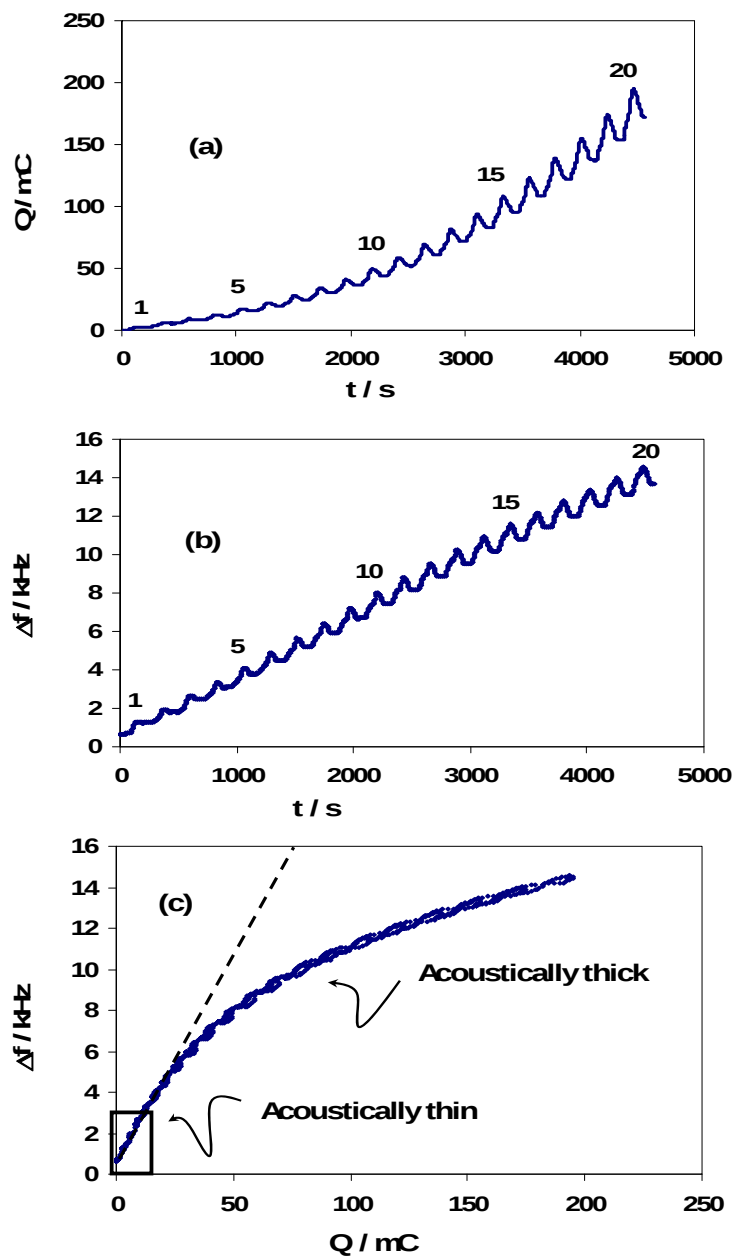


Fig. 6.2: EQCM charge (Q) and frequency shift (Δf) responses to polyaniline film deposition. Panel *a*: Q vs t response; numbers indicate deposition cycles. Panel *b*: Δf vs t response; numbers indicate deposition cycles. Panel *c*: correlation of Δf vs Q ; rectangle indicates regime for which viscoelastic parameters cannot be extracted. Data from the experiment of Fig. 6.1.

The data in Fig. 6.2 are taken from the raw experimental results of film deposition of voltammetric and EQCM data shown in Fig. 6.1. Fig. 6.2 shows the coulometric (panel *a*: charge, Q / mC) and acoustic (panel *b*: frequency change, $-\Delta f$ / kHz) responses as functions of time (t / s) during film deposition. The charge response (panel *a*) comprises two components. One is an oscillatory component which represents the changes *within* a deposition cycle and associated with the reversible redox switching of the film deposited in previous cycles. This component naturally increases in magnitude during the experiment; this may be due to the increase of redox sites population as the film deposition proceeds. The second is a monotonically rising component with time, which is attributable to the irreversible polymerization and deposition of the film. Interestingly, the monotonic charge component (panel *a* of Fig. 6.2) is initially linear but, after approximately 10 cycles, increases as a sharper function of time. This is consistent with the self-catalytic behaviour of polyaniline growth reported in the literature [17, 25-27] and may reflect an increase in surface area associated with a rough film [28] – the degree of film surface roughness will be discussed later. The corresponding frequency change (panel *b* of Fig. 6.2) as a function of time similarly shows two components, one associated with film deposition *per se* and the other with redox switching of the previously deposited material. The difference here is that the monotonic frequency response component associated with film growth is linear with time; this may also be related to the rate of film growth. The effects of the nature of background electrolyte on the growth rate of film deposition will be highlighted in chapter seven.

The hypothesis we now explore is that this distinction between the functional forms of the coulometric and acoustic responses is associated with viscoelastic effects. This is explored in panel *c* of Fig. 6.2, via direct correlation between the change in resonant frequency and the deposition charge. It is immediately apparent that the initial stages of film deposition (first few cycles) are characterized by a linear Δf vs Q relationship. This is the acoustically thin regime, in which the frequency response is a gravimetric probe of the mass of film deposited (Δm / g). Combining the Sauerbrey equation:

$$\Delta f = -\left(\frac{2}{\rho_q v_q}\right) f_0^2 \frac{\Delta m}{A_p} = C_1 \Delta m \quad (6.1)$$

(where $C_1 = -2.26 \times 10^8 \text{ Hz cm}^2 \text{ g}^{-1}$ represents the combination of quartz and crystal constants) with Faraday's law, the mass vs charge relationship yields the equivalent molar mass of deposited polymer, $M / \text{g mol}^{-1}$:

$$M = \frac{nFA_e}{Q} \frac{\Delta f}{C_1} \quad (6.2)$$

Using the data in Fig. 6.2 at $E = -0.2 \text{ V}$ (reduced film) at short times (within the box labelled “acoustically thin” in panel c), one can find $M = 93.8 \text{ g mol}^{-1}$. This is close to the molar mass of an aniline unit.

At longer times (higher deposition charge), the frequency response (panel c of Fig. 6.2) departs from the limiting linear relationship found at low charge. This signals a shift to a viscoelastically controlled frequency response, quantified via the fuller interpretation of Eq. 6.3 (for details of the equation, see Eqs. 2.42 and 2.43 in chapter two). As a final observation with regard to the data in Fig. 6.2, the gravimetric nature of the short time (low charge) response is confirmed by the inability to make any physically meaningful fit to the viscoelastic model described by Eq. 2.43 (chapter two).

6.4 Evolution of shear modulus during polyaniline film growth

In Fig. 6.2, the regime where the EQCM response is viscoelastically controlled has been defined. In this section, we now focus on the determination of the shear modulus of the film during film deposition; viscoelastic responses of polyaniline films to background electrolytes will later be examined in chapter seven as indicated above.

The prime aspects explored in this section of polyaniline shear modulus properties are focused on two facets of G' and G'' variations: i) the evolution of G values with the number of deposition cycles (effectively, film thickness) at a given potential. We choose

two potentials corresponding to the film being reduced ($E = -0.2$ V) and the film being oxidised ($E = 0.9$ V), and ii) the variation of shear modulus data with potential during a single deposition cycle (at fixed film thickness).

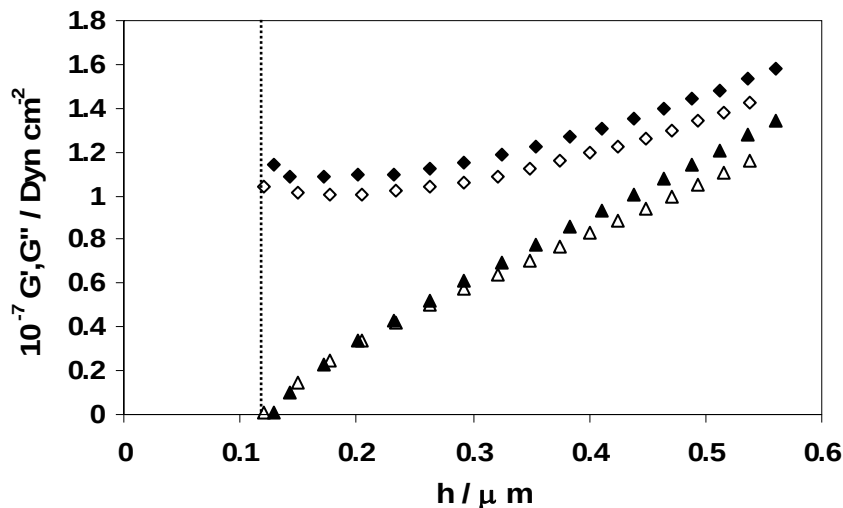


Fig. 6.3: Shear modulus component values as a function of film thickness. Open symbols: $E = -0.2$ V; filled symbols: $E = 0.9$ V. Diamond symbols: G' . Triangle symbols: G'' . Vertical line separate acoustically thin and thick regimes; region to left of line corresponds to box in Fig. 6.2, panel c. Data from experiment of Fig. 6.1.

Fig. 6.3 shows values of G' and G'' at the extremes of the potential scan ($E = -0.2$ V and 0.9 V) as functions of the growing film thickness, determined by the optimization procedure described in the experimental chapter (chapter three). AFM images of films were consistent with the shear modulus protocol optimized film thickness values (see appendix B); these images also revealed film surface roughness, so the values found should be regarded as effective averages of the shear modulus quantities. The effect of surface roughness on the morphology of electrodeposited films was advanced for poly(3,4-ethylenedioxythiophene) (PEDOT) films by Calvo et al. [28]. The vertical dotted line in Fig. 6.3 represents the lower limit of film thickness ($h_f \approx 0.12$ μm) at which physically meaningful shear modulus components were obtainable. The area to the left of the dotted line represents the acoustically thin regime, discussed above (section 6.3).

In Fig. 6.3, both shear modulus components of the polyaniline film apparently increase with film thickness, but the extent of this variation is somewhat different between the storage and loss shear components. The storage shear modulus, G' , increases rather modestly (e.g. from 1.14×10^7 to 1.58×10^7 dyn cm⁻² at $E = 0.9$ V). On the other hand, the loss shear modulus, G'' , increases rather dramatically (e.g. from 8×10^4 to 1.34×10^7 dyn cm⁻² at $E = 0.9$ V). At the lower end of this range, there is no great precision attributed to the values of shear modulus components computed using Eq. 6.3 (also see Eq. 2.43 in chapter two):

$$Z = j \omega \rho_s + Z_f \left[\frac{Z_L \cosh(\gamma h_f) + Z_f \sinh(\gamma h_f)}{Z_f \cosh(\gamma h_f) + Z_L \sin(\gamma h_f)} \right] \quad (6.3)$$

where all of the parameters were defined earlier in Eq. 2.43 in chapter two.

It is our experience that when the loss tangent (G''/G') is far from unity (i.e. outside the range $0.1 < G''/G' < 10$) the viscoelastic response of the film is not particularly sensitive to the smaller of the two shear modulus components. In other words, the smaller component of G' and G'' is not determined with precision. Nevertheless, the order of magnitude of G'' at short times is consistent with a liquid-like layer. The effect of further polymer deposition is to increase both components, but G'' far more dramatically. It is speculated that there is some displacement of solvent by the polymer, with the result that the loss tangent increases to values more typical of a bulk polymer material, to 0.81 at $E = -0.2$ V (reduced form) and 0.85 at $E = 0.9$ V (oxidised form) by the end of the experiment shown in Fig. 6.3.

The systematically differing G' and G'' values at the extrema of the scans, i.e. $E = -0.2$ V or $E = 0.9$ V (see Fig. 6.3), suggest that there is merit in exploring the variations of these parameters with potential. The results of this more detailed study are shown in Fig. 6.4 at three selected stages of the deposition; the thickness and composition of the film are quite different at these stages. The data shown are for the stages just into the acoustically thick

regime (5 cycles), in the middle of the range explored (9 cycles) and at the end of the experiment (20 cycles). For G'' particularly, the variations are generally much more subtle within a cycle (E-dependence) than between cycles (h_f -dependence). There is appreciable hysteresis in the plots, but this is at least in part due to the fact that there is more polymer present at any given potential during the cathodic half cycle than at the same potential during the preceding anodic half cycle; the end result is a gradual “ascent” up the y-axis.

Although the variations in G' and G'' values during a potential cycle are rather small (a few percent), they are nonetheless significant. As an example, consider the qualitative changes in G' during an anodic half cycle (Fig. 6.4, panel *a*, cycle 20). The shear modulus is constant for $E < 0.15$ V, starts to increase at $E \approx 0.15$ V, peaks at $E \approx 0.6$ V, then decreases slightly up to $E = 0.9$ V. Comparing this with the current response in panel *a* of Fig. 6.1, one can see that the increase is associated with the least anodic redox process and the decrease with the most anodic process. The straightforward explanation of this may be that there is a clear correlation of film dynamics with film composition. Similar effects have been reported during redox switching of layer-by-layer self-assembled films of a polymeric osmium complex [29]. The compositional aspects of this correlation, particularly in terms of spatial distributions of film components, are recommended to be the subject of investigation in the future work (see chapter 10) using neutron reflectivity technique.

The variations in shear modulus shown in Fig. 6.4 are made rather clearer by the differential presentational format of Fig. 6.5; to our knowledge, this approach has not been used previously.

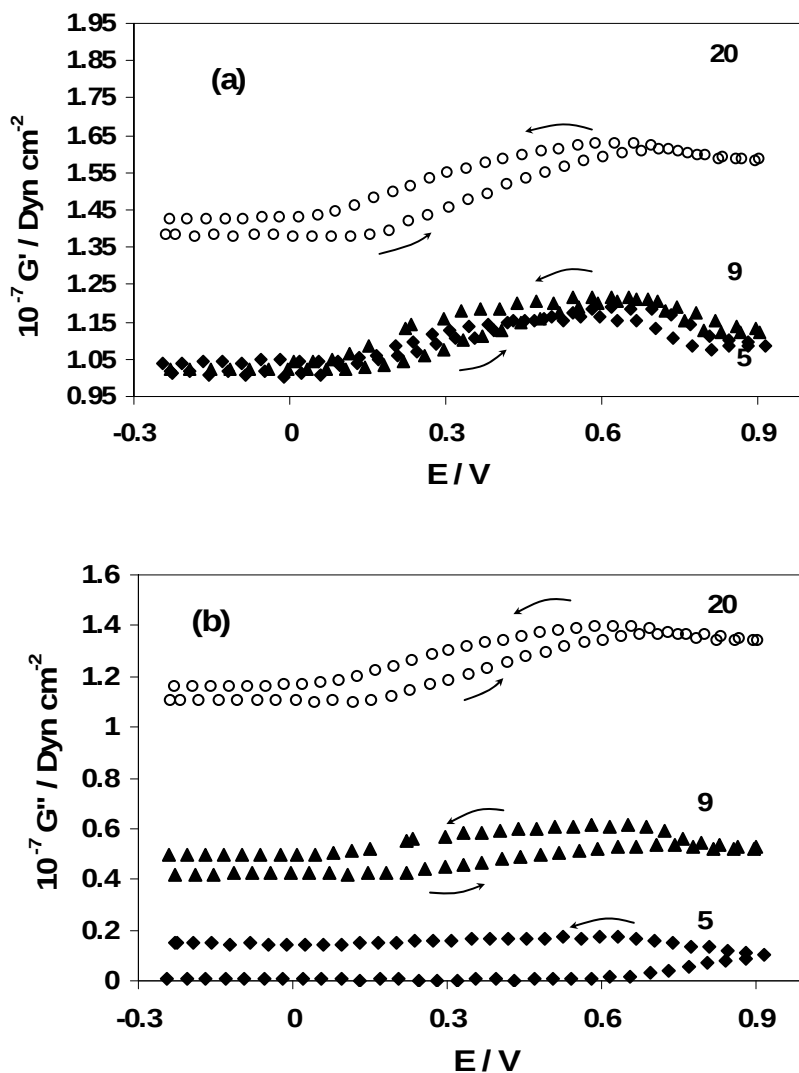


Fig. 6.4: Shear modulus components as functions of potential for deposition cycles 5, 9 and 20 (as indicated). Panel *a*: G' . Panel *b*: G'' . Arrows indicate potential scan direction. Data from experiment of Fig. 6.1.

For presentational purposes, it is useful to normalise the functional dependence of the shear modulus variation on potential by the initial values of each cycle ($E = -0.2 \text{ V}$):

$$\xi' = \frac{1}{G'_{(-0.2V)}} \frac{dG'}{dE} \quad (6.4)$$

and

$$\xi'' = \frac{1}{G''_{(-0.2V)}} \frac{dG''}{dE} \quad (6.5)$$

Although there is clearly some scatter in the data of Fig. 6.5, the qualitative result is a pair of peaks (in opposite directions) in each half cycle at $E \approx 0.2$ V and $E \approx 0.75$ V. The positions of these peaks coincide with the potentials of the first film redox peak and the onset of monomer oxidation, respectively (see Fig. 6.1, panel *a*). The response during the cathodic half cycle is a mirror image of the anodic response. The correlation of film mechanical properties with composition is unquestionable and suggests that this new presentational format may have considerable general utility.

There is one interesting quantitative distinction between the storage and loss shear moduli variations demonstrated in Fig. 6.5. The relative changes in G' for the peak centred at $E = 0.2$ V are relatively independent of film thickness (i.e. the curves for different numbers of deposition cycles superimpose) over a factor of ca. 5 variation in h_f . The corresponding changes in G'' increase substantially with film thickness. For both shear modulus components, film thickness exerts an influence in the region of the second peak: the relative effect diminishes with increasing thickness. The compositional origins of the redox switching-driven changes will be explored in a future study of polyaniline films using neutron reflectivity. The strategy is to carry out the exploration in a monomer-free solution for which any possible complications of monomer oxidation and oligomer inclusion can be ruled out. It is clear from the data plots in Fig. 6.5 that electrostatic stiffening due to charge injection and solvent plasticization will be competing processes.

Further insight into the mechanics of the system can be obtained by consideration of the decay length (δ , defined by Eq. 3.5 in chapter three) and the acoustic phase shift across the film (ϕ , defined by Eq. 3.2 in chapter three). The former is a material property and the latter is a property of both the material and of the sample, via film thickness. Using the shear modulus data of Fig. 6.3, one can obtain the decay length and phase shift values shown in Fig. 6.6.

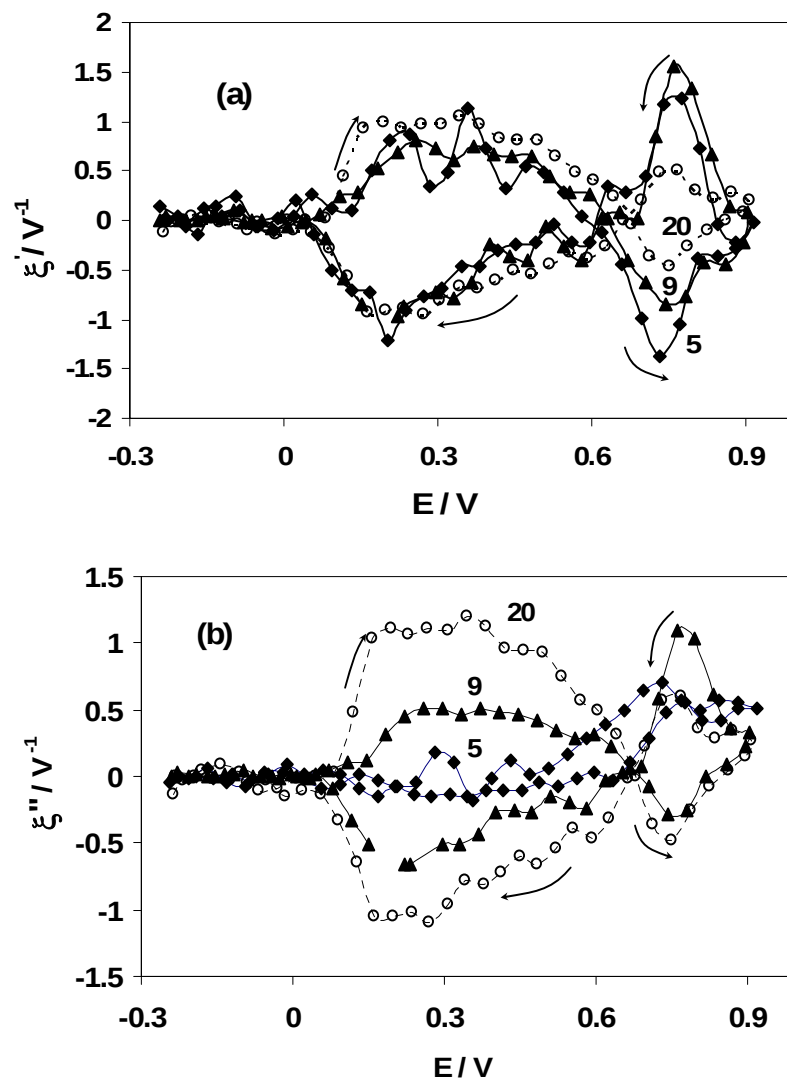


Fig. 6.5: Differential shear modulus components as functions of potential for deposition cycles 5, 9 and 20 (as indicated). Arrows indicate potential scan direction. Data from Fig. 6.4.

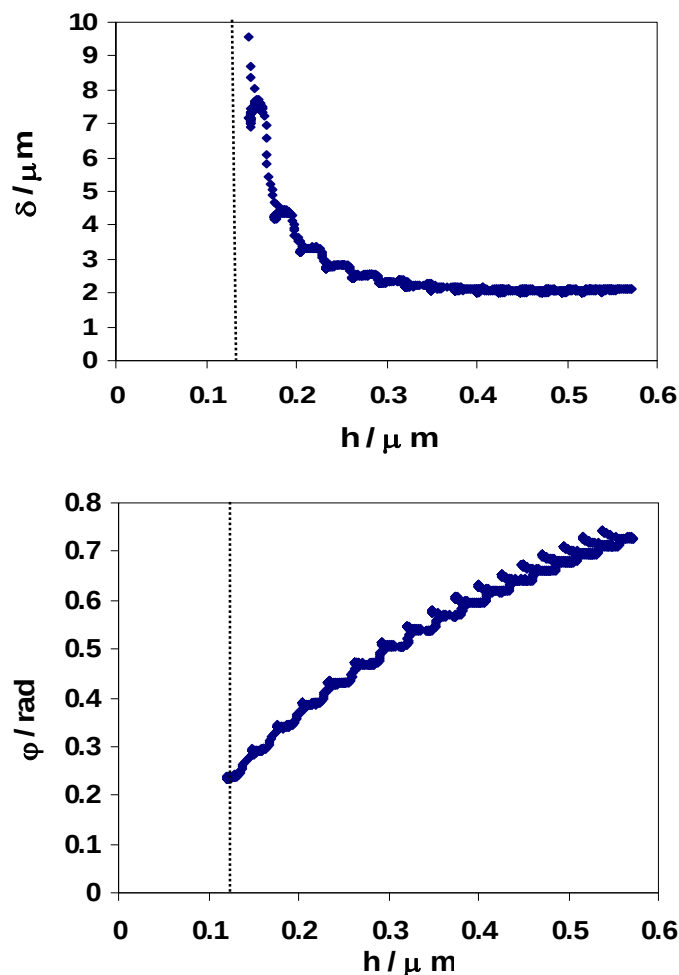


Fig. 6.6: Panel *a*: decay length as a function of film thickness. Panel *b*: Acoustic wave phase shift as a function of film thickness. Data from experiment of Fig. 6.1, calculated using shear moduli of Fig. 6.3. Vertical dotted line as in Fig. 6.3.

During the initial period of deposition the values of the acoustic wave decay length (panel *a* of Fig. 6.6) were very large. The vertical scale in Fig. 6.6 was chosen to allow better appraisal of the longer time data, but at the shortest times for which shear moduli were calculable $\delta > 30$ μm . This is a consequence of the low loss liquid-like nature of the film noted earlier. By the time the film thickness has growth to 0.2 μm , the decay length has fallen dramatically to 3.3 μm ; thereafter it approaches a steady state (“bulk”) value of ca. 2 μm . Since the decay length is always significantly larger than the film thickness

throughout the experiment ($h_f = 0.57 \mu\text{m}$ at the end of the representative experiment shown), we never enter the semi-infinite regime; the model and analysis used are therefore appropriate.

The acoustic phase shift (Fig. 6.6, panel *b*), on the other hand, steadily increases with the film thickness. The key observation is that, over the interval shown, it remains in the optimal range for shear modulus determination. In particular, it does not approach the value of $\pi/2$ associated with film resonance. Again, the modelling protocol is validated.

6.5 Summary

For the first time viscoelastic investigations of electrochemically deposited polyaniline films have been performed using the high frequency thickness shear mode (TSM) acoustic resonator. Use of the full frequency response (admittance spectrum) of the TSM resonator allows one to follow the extent of electrodeposition and the viscoelastic properties of polyaniline films as the film progressively grows. In this chapter, using a potentiodynamic control function and perchloric acid electrolyte (as the medium of film preparation), the admittance spectra of polyaniline electropolymerization have been utilised to observe the transition from acoustically thin films at low deposition charge to acoustically thick films at high deposition charge (Fig. 6.2). In terms of film thickness, the boundary between the two regimes was at a film thickness of ca. $0.12 \mu\text{m}$ for a 10 MHz resonator (Figs. 6.2-6.6). The single shot nature of a deposition experiment does not allow exploration of the frequency regime (higher harmonics) within a single experiment. Values of acoustic decay length (a material property) and acoustic phase shift (a function of film properties and film thickness), subsequently calculated using the shear moduli resulting from the full analysis, validate the identification of this distinction.

Frequency shift data within the acoustically thin film regime, associated with negligible energy dissipation, can be interpreted gravimetrically via the Sauerbrey equation. On the other hand, frequency responses within the acoustically thick film, associated with significant energy dissipation (decreased peak admittance) are interpreted viscoelastically. In this latter case, acoustic admittance spectra acquired as a function of

potential (20 mV intervals) for multiple (typically 25) deposition cycles are recorded simultaneously with the voltammetric data (Fig. 6.1). The outcome is a set of film shear storage and loss moduli as functions of potential (within a given deposition cycle) and number of deposition cycles (thickness dependent).

At a fixed potential, represented by the negative ($E = -0.2$ V) or positive ($E = 0.9$ V) extreme of the deposition cycle, the storage modulus increases modestly (over the range ca. $1.1\text{--}1.6 \times 10^7$ dyn cm⁻²) with film thickness. Simultaneously, the loss modulus increases more dramatically (over the range ca. $0.008\text{--}1.3 \times 10^7$ dyn cm⁻²). Qualitatively, this is consistent with a matrix that shifts from being liquid-like to viscoelastic.

Within a given deposition (and redox) cycle there are more subtle, but highly reproducible, variations in shear modulus components. By presenting these in a novel differential (with respect to potential) format, we find two peaks in the response to potential, one of which correlates with the first redox process and the other of which correlates with further film oxidation and polymerization (Fig. 6.5).

6.6 References

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Chapter Seven

The Effect of Anion Identity on the Viscoelastic Properties of Polyaniline Films

7.1 Overview

In chapter six, viscoelastic properties of polyaniline films during film electrodeposition were discussed. The consideration was restricted to the presence of a single anion during film preparation. In this chapter, however, we focus on two key issues of viscoelastic properties of polyaniline: i) the effect of different anions on polymer film dynamics at the time of electropolymerization, and ii) the viscoelastic responses of polyaniline films to background electrolytes. In addition, the influence of potential during the film redox cycling on the dynamics of the film matrix will be discussed. Another important aspect studied is the effect of anion-switching between film preparation (during deposition) and testing (redox cycling). This is to question whether the film retains the “*memory*” of deposition condition via templating or other structural feature of the anion/polymer combination. In this case, the film is deposited in the presence of anion and redox-cycled in a different anion. In the following sections, we attempt to address above the questions in the context of the preparation and exploitation of polyaniline films in practical applications.

Studies of the morphology of polyaniline at different stages during film growth suggest that two of the more important parameters are the background electrolyte concentration and the identity of the anion present during film deposition [1, 2]. In general, on the basis of SEM images and electrochemical quartz crystal microbalance (EQCM) data of polyaniline films the anions studied so far fall empirically into two main categories [1, 3-5]. As described in chapter six, the so-called “class 1” anions (BF_4^- , ClO_4^- and CF_3CO_2^-)

lead to compact films, while so-called “class 2” anions (SO_4^{2-} , NO_3^- and Cl^-) promote more open films [1, 5]. In the current study, the emphasis is given to the effect of anions from these two categories on film mechanical properties. The hypothesis is that the film composition, notably the solvent population, associated with different anions has a direct influence on the resultant film structural dynamics. The hypothesis is that different solvent populations will result in varying degrees of film plasticization and thereby leading to different viscoelastic properties.

Experimentally, the film mechanical behaviour can be determined from the surface mechanical impedance obtained using the high frequency acoustic device, the thickness shear mode (TSM) resonator [2, 6-11]; both theoretical and practical aspects of this technique have been detailed in chapter two. As previously explained in chapter six, the mechanical properties of the film can be parameterised in terms of the shear modulus ($\mathbf{G}$) expressed as the complex quantity $G' + jG''$, where G' is the storage modulus, G'' is the loss modulus and j indicates the phase relationship.

7.2 Film Deposition in the Presence of Different Anions

Polyaniline films were grown potentiodynamically ($-0.2 \leq E/V \leq 0.9$; $v = 10 \text{ mV s}^{-1}$) from aqueous 0.1 M aniline / 1 M aqueous acid (HClO_4 , H_2SO_4 or HCl). For each deposition experiment of the film (from different background electrolytes), a fresh sample of solution was used. All deposition and characterization measurements were carried out at room temperature ($20 \pm 2 \text{ }^\circ\text{C}$).

During deposition of polyaniline films, acoustic admittance spectra were recorded at 2 s (20 mV) intervals for all of the experiments carried out. Preliminary experiments showed that the rate of film deposition is different for the different deposition media (background electrolytes). As a result, different polyaniline films grown in different deposition media may have material properties that might differ in different thickness regimes [1, 3, 5, 12-14]. As a consequence of this, the deposition experiments were terminated after different numbers of potential cycles such that the resultant films were of comparable thickness (i.e. similar polymer coverage). The requirement here is not that films are of identical

thickness, but simply in a similar thickness regime. From the experimental data, we were able to establish empirical relationships between film thickness (determined through the optimisation process described in chapter three) and the number of deposition cycles for each of the deposition media. Using this approach, films of thickness in the range 0.5-0.7 μm were obtained. As will be discussed below, polyaniline films deposited from different background electrolytes (HClO_4 , H_2SO_4 and HCl) were all prepared in a suitable range (in terms of acoustic phase shift; see below) for shear modulus determination. This strategy required 20 cycles in HClO_4 , 10 cycles in HCl and 9 cycles in H_2SO_4 . At the end of each of these procedures, the cell was disconnected at the negative end ($E = -0.2 \text{ V}$) of a potential cycle (fully reduced films).

Procedures for the extraction of shear moduli (storage and loss components) have been discussed in detail elsewhere [2, 6, 9, 15, 16] and reviewed in chapter three. Values of G' and G'' were calculated using the Maple package by fitting experimental mechanical impedance (Z) data, which is linearly related to the electrical impedance data through the piezoelectric coupling constant [2, 6, 10, 11, 17], using Eq. 7.1:

$$Z = j\omega\rho_s + Z_f \left[\frac{Z_L \cosh(\gamma h_f) + Z_f \sinh(\gamma h_f)}{Z_f \cosh(\gamma h_f) + Z_L \sin(\gamma h_f)} \right] \quad (7.1)$$

Polymer trapped within surface features (roughness) of the electrode was treated as a rigidly coupled ideal mass and is represented by the first term on the right hand side of Eq. 7.1 (also refer to chapter two, Eq. 2.43). To determine viscoelastic properties, one should minimize the effect of this term with respect to the second (viscoelastic) term in Eq. 7.1. This was accomplished by the use of polished crystals, for which the scale of roughness (ca. 5 nm by AFM imaging) is ca. 1-5% of the film thickness across the range where shear moduli are determined. Specifically, for the polished crystal used, surface features entrap polymer that contributes ca. $70 \text{ g cm}^{-2} \text{ s}^{-1}$, compared to ca. $9 \times 10^5 \text{ g cm}^{-2} \text{ s}^{-1}$ for the bare crystal, ca. $8 \times 10^2 \text{ g cm}^{-2} \text{ s}^{-1}$ for the bulk solution, and $4 \times 10^3 \text{ g cm}^{-2} \text{ s}^{-1}$ for the remainder of the polymer film (all values to one significant figure). For films of the thickness described here, such entrapped polymer typically contributes ca. 2% of the total

film mechanical impedance; this does not significantly impact on the precision of the shear modulus values.

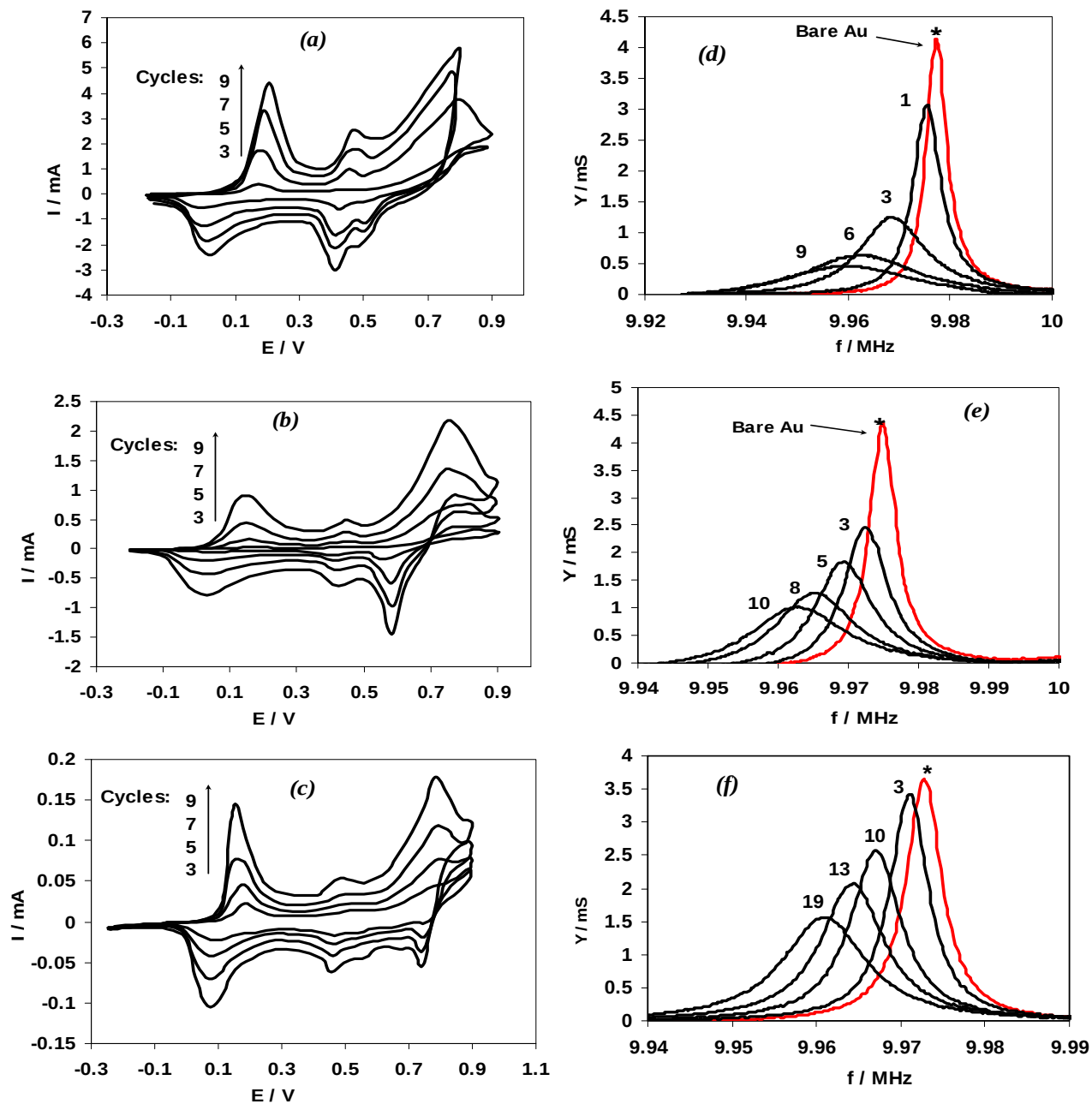


Fig. 7.1: Data for the potentiodynamic deposition of polyaniline films. Panels *a-c*: i - E responses. Panels *d-f*: acoustic admittance spectra at the end of selected potential cycles (as indicated by numbers on individual spectra; asterisk indicates response for bare electrode prior to initiation of polymerization), at $E = -0.2$ V; selected spectra only shown, for presentational clarity. Electrolyte anion: panels *a, d*: sulphate; panels *b, e*: chloride; panels *c, f*: perchlorate. Other details are as in the main text.

7.3 Qualitative Analysis of Raw Data

Fig. 7.1 shows the raw voltammetric and acoustic data for polyaniline deposition in the presence of each of the different anions (SO_4^{2-} , Cl^- and ClO_4^-). Data were collected during all deposition cycles, continuously in the case of the current and at 20 mV intervals in the case of the admittance spectrum. However, for presentational clarity, the same strategy as in chapter six was followed by only showing selected responses. Panels *a-c* (Fig. 7.1) show the *i-E* curves in the presence of SO_4^{2-} , Cl^- and ClO_4^- anion, respectively; these were reproducible and similar to those reported in the literature [3, 13, 14, 18, 19].

Corresponding admittance spectra for film deposition acquired at the end of the indicated deposition scans (at $E = -0.2$ V) are shown in panels *d-f* (Fig. 7.1). Since the patterns of admittance and current variation with anion are different, data are shown after different numbers of deposition cycles in panels *a-c* (*i-E* curves) and *d-f* (admittance spectra). Without imposition of any model, these variations immediately signal the formation of materials with viscoelastic characteristic which we now quantify.

The obvious qualitative trend in peak admittance values seen in panels *d-f* (Fig. 7.1) is progressive damping with film growth. To have a clear insight of the underlying film behaviour of this progressively decreasing trend of peak admittance, it is more helpful to first consider the early stages of polymerization. In panel *d* (SO_4^{2-} anion), the peak admittance after a single deposition cycle is decreased to ca. 80% of that for the bare electrode in the deposition solution. Similar increases in damping in Cl^- and ClO_4^- media (panels *e* and *f*) require 2-3 and 7 deposition cycles, respectively. Turning to the end of the deposition experiments shown (9, 10 and 19 cycles) for SO_4^{2-} , Cl^- and ClO_4^- media, respectively, the resonant admittance had diminished to 13, 22 and 40% of that for the bare electrode. In other words, the experiment with the *least* number of deposition cycles (SO_4^{2-}) showed the *largest* damping effects and the experiment with the *most* number of deposition cycles (ClO_4^-) showed the *least* damping. The physical meaning of this unexpected pattern is explained below.

It is clear from the data shown above (Fig. 7.1) that the type of anion present during polyaniline deposition exerts a decisive influence on film rheological properties. The goal now is to distinguish the contributions to this from the *rate* of film growth and the intrinsic *materials properties*, both of which vary across the portfolio of experiments represented in Fig. 7.1.

The data of Fig. 7.1 show that damping (energy loss) increase with respect to the number of deposition cycles is fastest for SO_4^{2-} and slowest for ClO_4^- . At a superficial level, one might interpret this to mean that polyaniline films are progressively softer in the order $\text{ClO}_4^- > \text{Cl}^- > \text{SO}_4^{2-}$. However, different growth rates in these three media mean that the loss (damping) relates to different amounts of polymer and is thus not itself a material property, i.e. it represents a combination of film properties and thickness. This variation of growth rate with anion has been reported by a number of other authors [3, 4, 13, 14, 20-23] and the consensus view is that the relative growth rates in aqueous acid media are in the order $\text{H}_2\text{SO}_4 > \text{HCl} > \text{HClO}_4$. Consistent with this, in the experiments of Fig. 7.1 (panels *a–c*) the polymerization currents in Cl^- and ClO_4^- , respectively, are ca. 25% and 2.5% of that in SO_4^{2-} . Various authors have rationalised this in terms of: (i) different polymer growth mechanisms [23-25] involving progressive or instantaneous nucleation, 2D or 3D growth and the presence of diffusional control, according to the electrolyte; (ii) stability differences due to differing anion lyophilicity [3, 23] in ion pair formation between the anion and the anilinium species produced during monomer oxidation (ClO_4^{-1} ions are more lyophilic than SO_4^{2-} ions and expected to form the most stable ion pairs with anilinium ions [23]); or (iii) the Gibbs energy change associated with ion formation in aqueous solution [14], which follows the order $\text{SO}_4^{2-} < \text{Cl}^- < \text{NO}_3^- < \text{ClO}_4^-$ for polyaniline salt formation. We do not duplicate these efforts by pursuing the *origins* of these effects, but rather extend the investigation by exploring their *consequences* in terms of materials properties. In this respect, we note two examples of the qualitative recognition of a relationship between growth rate and properties. First, faster polyaniline growth (by a factor of 3) in SO_4^{2-} than in ClO_4^- was attributed [26, 27] to a more open morphology in SO_4^{2-} and a more compact morphology in ClO_4^- . Second, direct

observation of surface features by SEM images supported the same order of polyaniline film growth (fastest in SO_4^{2-} , moderate in Cl^- and slowest in ClO_4^-) [3].

7.4 Coulometric and Acoustic Responses of Film Deposition

Fig. 7.2 shows the coulometric (Q ; panel *a*), and the acoustic (Δf ; panel *b*) responses as functions of time (t / s) and their direct correlation (Δf - Q plot; panel *c*). Each panel shows three data sets representing deposition in the presence of each of the anions (SO_4^{2-} , Cl^- , and ClO_4^- , as indicated). The responses in panels *a* and *b* all contain two components, an oscillatory one and a monotonic one. The oscillatory components represent changes *within* a deposition cycle and are attributable to the reversible redox switching of film deposited in previous cycles.

The oscillatory component is shown in more detail for a representative cycle in the insets in panels *a* and *b*. As pointed out in chapter six for polyaniline films grown in the presence of perchlorate ion, the magnitudes of these components of the charge and frequency responses (from different electrolytes) progressively increase during the experiment, as polyaniline is deposited. The monotonically increasing components are attributable to the irreversible polymerisation and deposition of the film.

Interestingly, the monotonic charge component (panel *a*, Fig. 7.2) is initially linear, but after a few cycles (typically three in SO_4^{2-} and Cl^- media and seven in ClO_4^-) increases more sharply with time. This charge behaviour has been attributed previously to self-catalytic behaviour [4, 28-30].

A similar explanation applies to the frequency response data (panel *b*, Fig. 7.2), with regard to the presence of oscillatory and monotonically increasing components. Here, differences in film growth rates in the different electrolytes result in resonant frequency responses (representative of surface coverage, initially gravimetrically and subsequently in a more complex manner) with an obviously different time dependence.

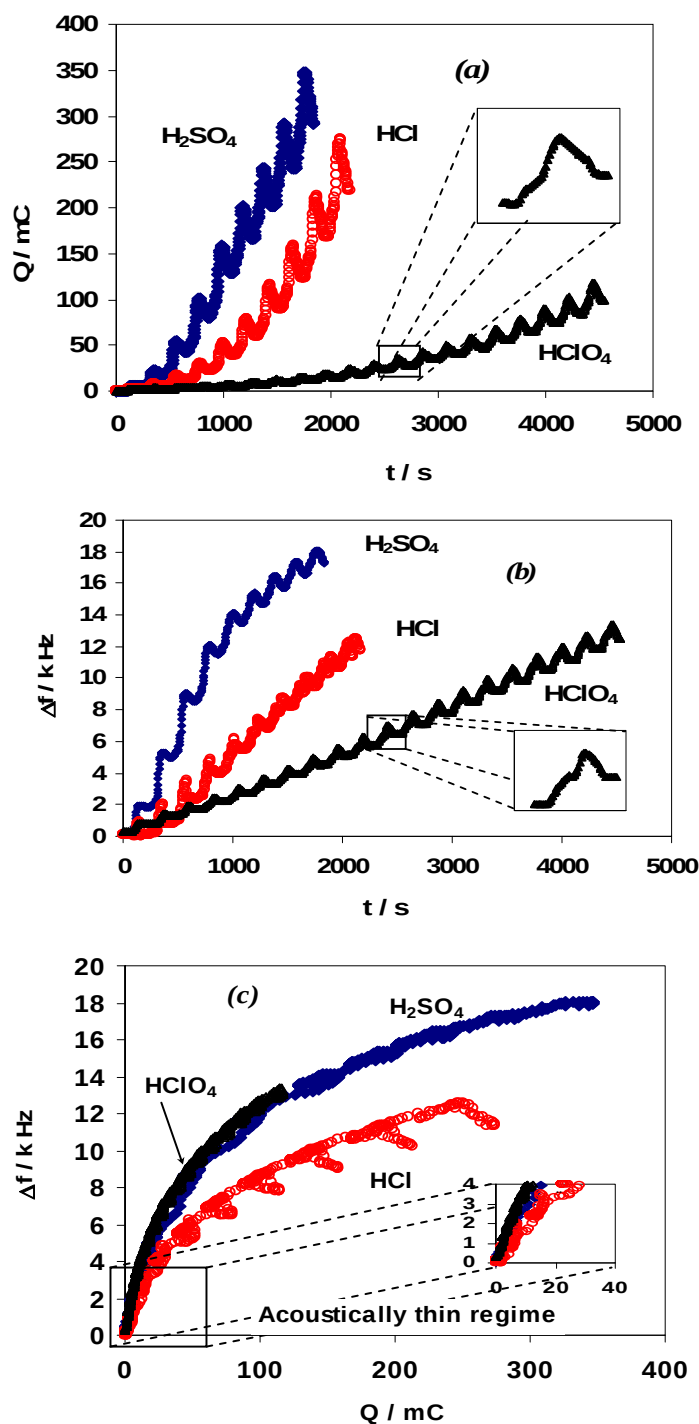


Fig. 7.2: Coulometric and resonant frequency responses from the experiments of Fig. 7.1. Panel *a*: coulometric response as a function of time. Panel *b*: resonant frequency shift as a function of time. Panel *c*: frequency shift (from panel *b*) as a function of charge (from panel *a*). Annotation indicates electrolyte species. Insets in panels *a* and *b* show reversible components of responses within a single potential cycle.

The time dependence of resonant frequency responses of polyaniline deposition rate (due to the effects of different electrolytes) is linear in ClO_4^- , almost linear in Cl^- (though with a gradient ca. three times greater than in ClO_4^-) and nonlinear (power law significantly greater than unity) in SO_4^{2-} . The situation here is more complicated than for the charge response since it has been shown that the frequency response can be influenced by film surface roughness variations [31].

As general comparisons with earlier work in this area, we note the qualitative similarity of the presence of the two components (monotonic and oscillatory) to the behaviour observed when using SDS surfactant as the electrolyte for polyaniline deposition [32-35] and the substantial variation in deposition rate constant with anion identity [33-35]. In the former case, although viscoelastic measurements were not performed, it was noted that the SDS increased the participation of solvent.

Direct correlation between the change in resonant frequency and charge is shown in panel c of Fig. 7.2. The initial stages of the film deposition - regardless of the nature of background electrolyte - are characterised by a linear Δf vs Q relationship. This corresponds to the acoustically thin regime in which the frequency response is interpretable gravimetrically. Surprisingly, in this regime (labelled “acoustically thin regime” in Fig. 7.2, panel c) the deposition data for all three electrolytes are qualitatively rather similar, i.e. do not show the divergence of behaviour seen in the viscoelastic regime. At this point it is worth noting that the charge response represents the consumption of monomer and the frequency response represents the formation *and deposition on the electrode surface* of polymer. Within the acoustically thin regime, the relationship between the two can, in principle, be influenced by Faradaic efficiency, as well as solvent content; as one moves into the acoustically thick regime, viscoelastic effects also come into play. Staying with the acoustically thin regime for the present, combination of the Sauerbrey equation (for the frequency response) with Faraday’s law (for the coulometric response) yields the equivalent molar mass of deposited polymer, $M / \text{g mol}^{-1}$; this was discussed in chapter six.

At higher deposition charges (longer times), the frequency response (see Fig. 7.2, panel c) departs from the limiting linear relationship found at lower charge. This is a clear indication of regime change from rigid to viscoelastic. The manner in which this occurs varies with anion identity. The Δf -Q relationship for films grown in ClO_4^- and SO_4^{2-} follow the same trajectory, although at different rates: the rate of change of resonant frequency is much higher in SO_4^{2-} (18 kHz in 9 deposition cycles) than in ClO_4^- (13 kHz in 20 deposition cycles). As a crude comparison, the average rate of traversing the plot is ca. 2 kHz per deposition cycle from SO_4^{2-} medium, 1.3 kHz per cycle from Cl^- and <1 kHz per cycle from ClO_4^- .

7.5 Effect of anion on film viscoelastic properties during deposition

In this section, we explore the temporal evolution of film mechanical properties during deposition as a function of the anion present, via the shear modulus component values as functions of anion and film thickness. This explicitly focuses on the direct effect of the *medium of preparation* on the resultant film properties. In section 7.6 (below), we will focus on if/how exposure to a different medium re-directs the film dynamics, which will test the film's "memory" of preparation conditions.

Fig. 7.3 shows values of G' and G'' as a function of the growing thickness of polyaniline films during deposition from different electrolytes. The final values of film thickness for the films grown from HClO_4 , HCl and H_2SO_4 were ca. 0.6, 0.5 and 0.7 μm , respectively. This careful use of control parameters to generate films of similar thickness (irrespective of the deposition rate, see section 7.4) allows fair comparisons to be made of film mechanical properties within the same thickness regime. AFM images of the films revealed some surface roughness (typically, film thicknesses are mean values with a vertical feature size of ca. 50 nm, i.e. $\sim 0.1 h_f$), so the shear modulus values presented here should be regarded as effective averages.

For all electrolytes, both shear modulus components increase with film thickness, but to an extent that varies with respect to the anion. Storage shear modulus, G' , values at any given thickness decrease with anion identity in the order $\text{ClO}_4^- > \text{SO}_4^{2-} > \text{Cl}^-$.

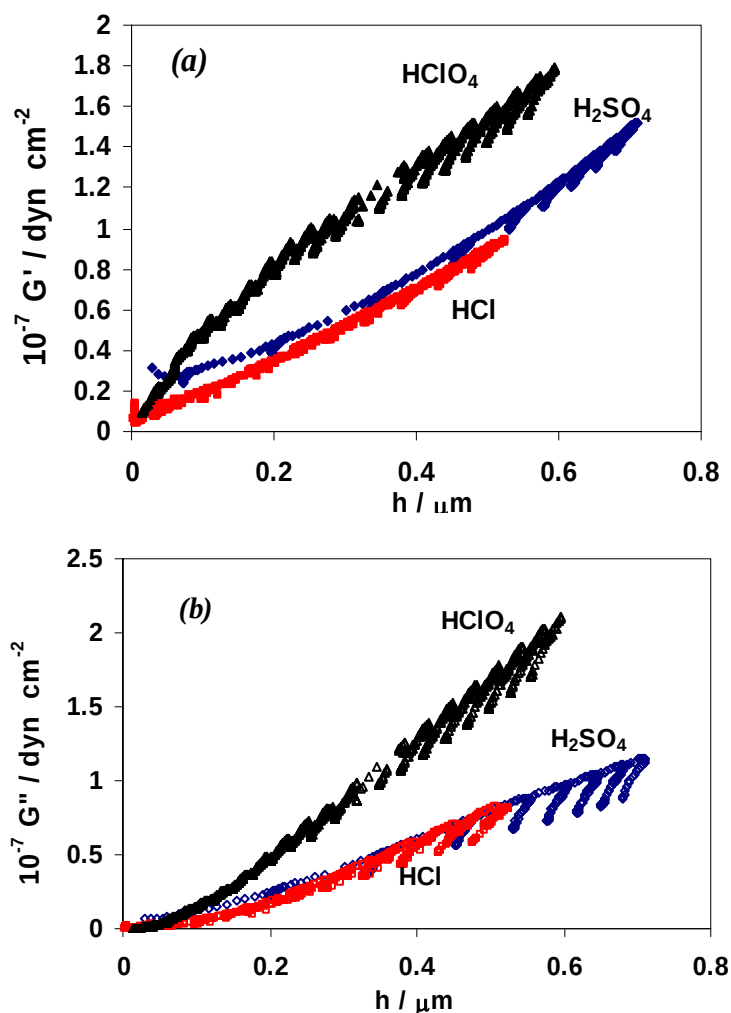


Fig. 7.3: Shear moduli as a function of film thickness for the experiments of Fig. 7.1. Panel *a*: storage modulus data. Panel *b*: loss modulus data. Annotation indicates electrolyte species.

At the end of the deposition process, for the films represented by the experiments of Fig. 7.1, G' values for the reduced films ($E = -0.2 \text{ V}$) were 1.8×10^7 (ClO_4^-), 1.5×10^7 (SO_4^{2-}) and 9.2×10^6 (Cl^-) dyn cm^{-2} . One can express the extent of variation of storage modulus with respect to the growing film thickness by comparing the value after the final deposition cycle, G'_f , with that after the first cycle at which it can be evaluated, G'_i ; in practice, G'_i corresponds to the value at $h_f \sim 0.1 \mu\text{m}$ (marked in Fig. 7.3 as the vertical dotted line). To facilitate comparison of films in different media, with different absolute values of shear modulus, it is useful to define a normalized quantity, $\psi' = (G'_f - G'_i) / G'_f$. For the data in panel *a* of Fig. 7.3, one can find that the increase in G' values of

polyaniline films grown in HClO_4 corresponds to $\psi' = 0.8$, experimentally indistinguishable from that value for films grown in HCl , and slightly larger than that for films grown in H_2SO_4 , for which $\psi' = 0.7$.

The loss shear modulus, G'' (Fig. 7.3, panel *b*), data show similar trends as do the G' data with regard to anion, and the final G'' values in the different media are broadly similar: 2×10^7 (ClO_4^-), 1.13×10^7 (SO_4^{2-}) and 7.9×10^6 (Cl^-) dyn cm^{-2} . The main difference was the somewhat greater variation (as compared to G') *during* deposition; detailed explanation for this observation must await further compositional studies (recommended for future work as will be pointed out in chapter 10), but the broad explanation is presumed to be associated with the film still being rather liquid-like in the early stages of deposition (see below). Similar to the variations in G' , we define $\psi'' = (G_f'' - G_i'')/G_f''$ for the loss shear modulus, G'' variation. Using the data in Fig. 7.3, one can find that $\psi'' = 0.97$, 0.94 and 0.92 for films grown in ClO_4^- , SO_4^{2-} and Cl^- , respectively. Given the likely experimental uncertainties, we view these *relative* values as not significantly different, although of course the *absolute* values of G'' are significantly different. Based on the magnitude of G'' at short times (ca. 6.7×10^5 dyn cm^{-2} for all films), we suggest that the film is rather liquid-like, i.e. a layer of diffuse solvent-separated polymer strands. By the end of deposition, in-filling between the polymer strands (replacement of solvent by polymer) results in composition and properties more typical of a bulk viscoelastic material, in particular, loss tangents of 1.0 (ClO_4^-), 0.8 (SO_4^{2-}) and 0.86 (Cl^-), respectively. Interestingly, the shear modulus components in SO_4^{2-} and Cl^- follow the same trajectory with film thickness. This similarity of film characteristics is consistent with the grouping of these dopants within the same family (so-called “class 2” anions). Furthermore, the lower shear moduli (*cf.* ClO_4^-) provides a link between their electrochemical dynamics and morphology [3, 4]: more open structures are associated with greater solvation, which facilitates chain motion and thereby generates a medium of lower viscosity through which dopant ions can diffuse more rapidly.

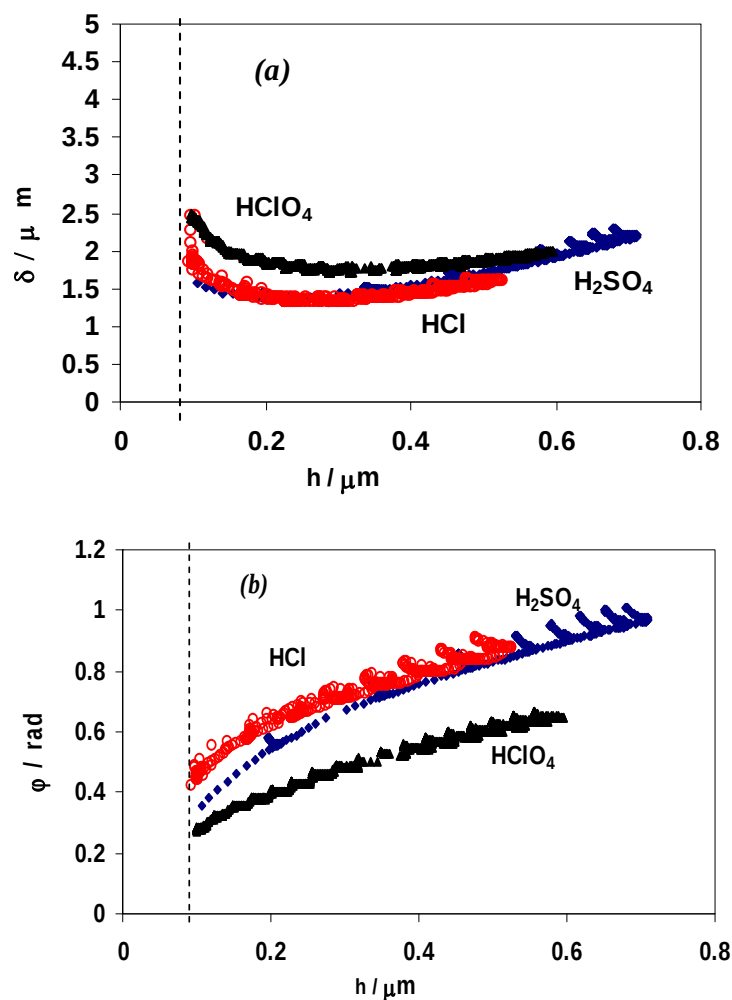


Fig. 7.4: Acoustic wave propagation parameters within growing polyaniline films as a function of film thickness, h_f . Panel *a*: decay length (defined by Eq. 3.5, chapter three); panel *b*: phase shift (defined by Eq. 3.2, chapter three).

From the shear moduli shown in Fig. 7.3, we can determine the decay length (defined by Eq. 3.5 in chapter three) and the acoustic phase shift (ϕ , defined by Eq. 3.2, also in chapter three); the outcomes are shown in Fig. 7.4. We note that δ is a material property, but ϕ is a property of both the material *and* the sample (via film thickness). The decay lengths all follow a similar pattern and a combination of the relatively similar shear moduli and their modest (square root) influence over decay length results in similar long time limiting values of decay length in all media, ca. $2 \mu\text{m}$. It is worth noting that the decay length is always significantly larger than the film thickness ($h_f \leq 0.7 \mu\text{m}$). This

validates the “acoustically thick, but finite, film” analysis used here; the system never enters the semi-infinite regime, in which the response becomes insensitive to film thickness because the acoustic wave does not traverse the film.

In contrast to the decay length, the acoustic phase shift (Fig. 7.4, panel *b*) steadily increases with the film thickness. Over the interval shown, the phase shift for each film remains in the optimal range for shear modulus determination. In particular, it does not approach the value of $\pi/2$ associated with film resonance. Again, the modelling protocol is validated. The phase shift trajectories of films grown in H_2SO_4 and HCl are similar to each other, while the phase shift trajectory of films grown in HClO_4 is distinct and traverses the phase shift dimension more slowly. This is another manifestation of the fact that films grown in HClO_4 are stiffer (less deformable) than those grown in either H_2SO_4 or HCl .

7.6 Polyaniline Film Characterisation in Monomer-free Electrolytes

In the previous sections (see above), the viscoelastic signatures of polyaniline films were discussed as a function of thickness during film deposition from different media (HClO_4 , HCl and H_2SO_4). In this section, the discussion is shifted to the determination of shear moduli of polyaniline films in monomer-free electrolyte solutions; this is to test the effects of different anions on film viscoelastic behaviour during film redox cycling. The obvious variation we explore here is that with film oxidation state (doping level), as controlled via applied potential; the exploration is restricted to the first redox peak of polyaniline films, and therefore the potential domain was limited to $-0.2 \leq E/\text{V} \leq 0.5$. This problem is addressed for two parallel sets of experiments: (i) for films exposed to the same electrolyte (anion) as used in film deposition and (ii) for films exposed to a different anion to that used in film deposition. In the latter case, we illustrate the principles by showing data for one representative permutation of deposition / cycling anions, rather than presenting an encyclopaedic tour of all possible permutations.

Fig. 7.5 shows cyclic voltammograms of polyaniline films recorded in the same monomer-free background electrolytes as those used for film deposition. According to

the voltammetric data shown in Fig. 7.5, peak shapes, currents and potentials for polyaniline film oxidation vary with the type of anion. Films grown and cycled in HClO_4 show sharper oxidation peaks and higher $I_{\text{pa}}/I_{\text{pc}}$ values than for the other two electrolytes used: $I_{\text{pa}}/I_{\text{p}} = 3, 2$ and 1.6 for HClO_4 , H_2SO_4 and HCl , respectively. In contrast, the peak potentials of films grown and cycled in all three electrolytes are very similar. As indicated in section 7.1, the emphasis of the present study is on *polymer* dynamics; the *electron* dynamics - which underlie the *i*-*E* response here - have been explored by other workers [13, 20]. In particular, ESR [13] and *in-situ* conductivity [20] experiments revealed that the use of ClO_4^- as a dopant yields more metal-like polyaniline films than does use of SO_4^{2-} . This was attributed to greater interaction of SO_4^{2-} ions with the positive charges (polarons) on the polymer chains and thereby greater charge localisation. We suggest that in general polymer-anion interactions can be expected to constrain polymer chain dynamics and thus be a determinant of film mechanical properties.

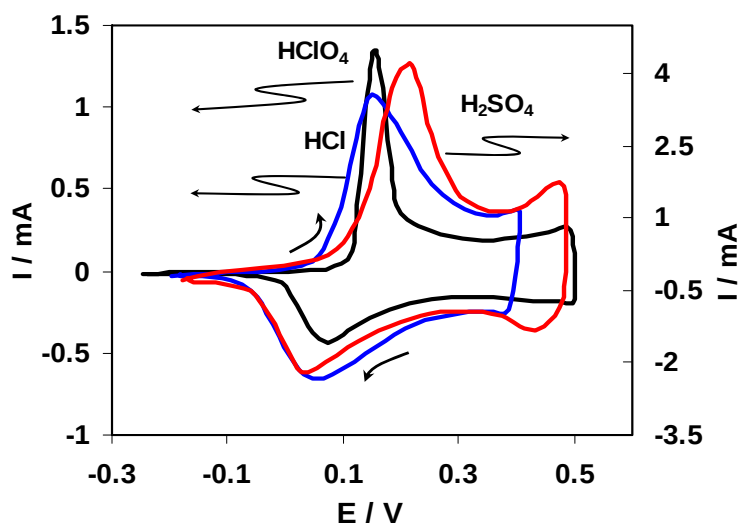


Fig. 7.5: Voltammetric responses ($v = 10 \text{ mV s}^{-1}$) for the polyaniline films prepared by the experiments of Fig. 7.1 following transfer to background electrolyte. In each case, the background electrolyte (see annotations) was identical to that used in the deposition experiment. Note different current scales, reflecting different *i*-*E* waveshapes.

In Fig. 7.6, G' and G'' values are shown for polyaniline films exposed to various background electrolyte solutions and subjected to a cyclic linear potential sweep. The qualitative potential dependences of shear moduli values (both storage and loss components) are similar in all background electrolytes used.

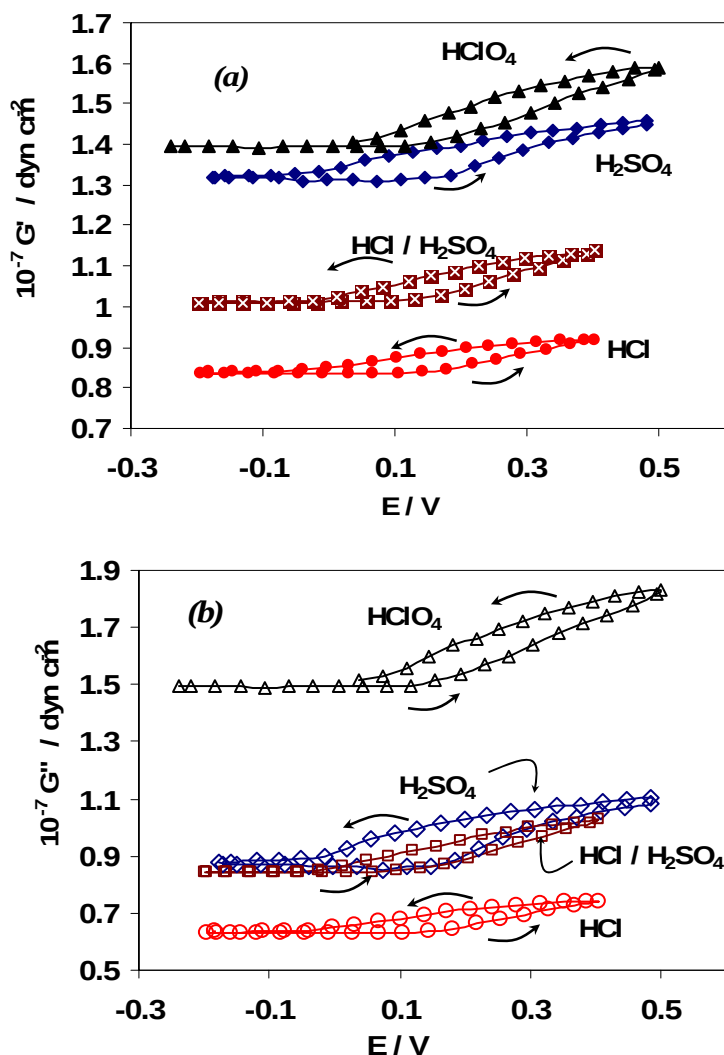


Figure 7.6: Shear moduli as functions of potential for polyaniline films exposed to background electrolyte (as annotated) and subject to voltammetric potential cycles ($\nu = 10 \text{ mV s}^{-1}$). Points indicate data; lines are a guide to the eye; arrows indicate scan direction. Panel *a*: storage modulus; panel *b*: loss modulus. In cases marked HClO₄, H₂SO₄ and HCl, the background electrolyte was the same for film deposition and redox cycling. In case marked HCl/H₂SO₄, the film was deposited from HCl electrolyte and cycled in H₂SO₄ electrolyte.

Starting from a fully reduced film ($E = -0.2$ V) and scanning to positive potentials ($E = 0.5$ V), both shear modulus components are constant for $E < 0.15$ V then increase monotonically throughout the first redox process ($0.15 < E / \text{V} < 0.5$). In the reduction half cycle, the trends are reversed. There is clear hysteresis with respect to scan direction in all data sets, but this is more pronounced for films grown and characterized in SO_4^{2-} than for those grown and characterized either in ClO_4^- or Cl^- ; the same is true for films deposited in Cl^- then subsequently cycled in SO_4^{2-} .

Quantitatively, the shear modulus values for different anion exposure regimes are distinctly – though not dramatically – different. For films deposited and cycled in the same electrolyte, the shear moduli (both components) decrease in the order $\text{ClO}_4^- > \text{SO}_4^{2-} > \text{Cl}^-$. The interesting follow-up question is whether the film retains a “memory” of the deposition conditions, for example via a templating or other structural feature of the anion/polymer combination, or simply adopts a structure and dynamics that correspond to the immediate ion of exposure. The evidence we found, as illustrated in Fig. 7.6 by the example of a film grown in Cl^- then cycled in SO_4^{2-} , is that there is a clear response to changing anion identity. For this particular example, the observed shifts of the G' and G'' values of polyaniline film towards those of the “new” electrolyte (partially for G' and indistinguishably so for G'') were complete within one potential cycle. The explanation for these differences in “memory” of the deposition electrolyte must await more direct compositional information. As a result we recommend acquiring the effects of film composition on its viscoelastic properties in the form of solvent permeation profiles using neutron reflectivity; this will be discussed in the recommendations suggested for the future work (chapter 10).

Analogous effects have been reported [12] in photocurrent transient experiments, in which photocurrents produced by polyaniline films were sensitive to the particular electrolyte solution (probing medium) rather than to the deposition solution (preparation medium). The same has also been observed for electrochemical impedance responses [36], which are governed by a combination of electron and ion dynamics. Turning to the polymer component of the system, SEM images of newly prepared films show film

morphologies that are characteristically different for different deposition medium anions [3, 4]; the effect of cycling in changed electrolytes was not explored using this technique. In our experiments, we attribute this rather significant property of responding to the electrolyte to the fact that the films are relatively soft, so the polymer chains are mobile (on the timescale of the experiment) and can reconfigure their molecular geometry to that optimum for the electrolyte that permeates them at any given time.

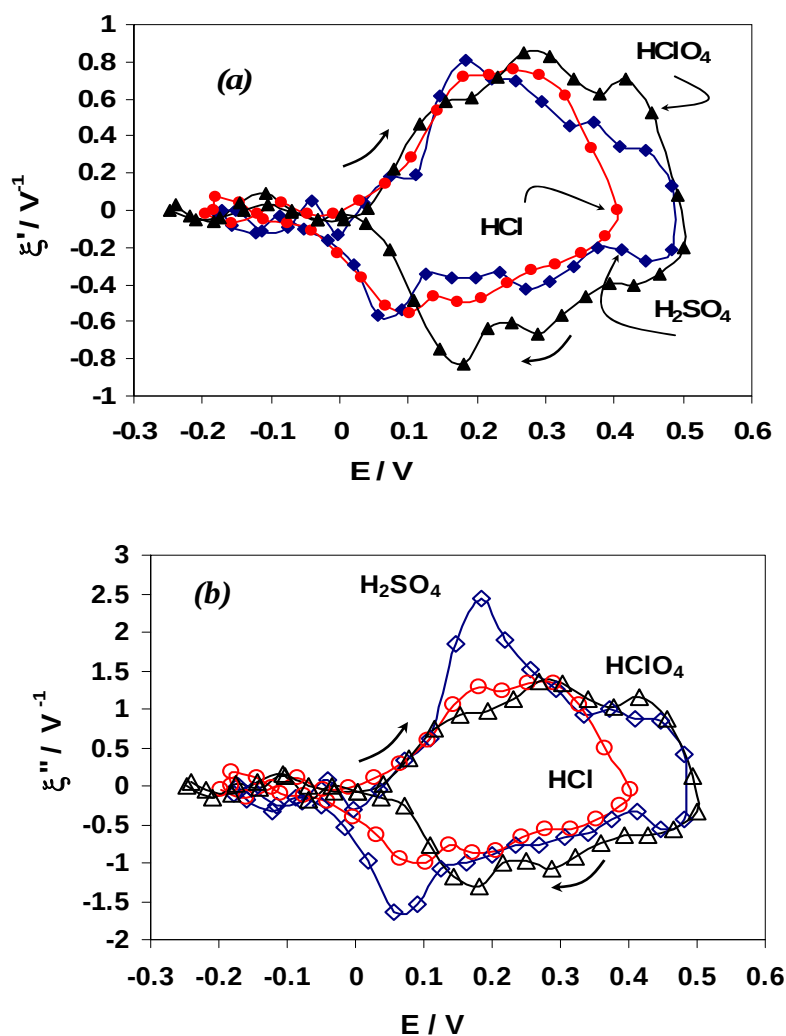


Fig. 7.7: Variations with applied potential of normalised differential shear moduli of polyaniline films exposed to different electrolytes (as annotated). Panel *a*: differential storage moduli, ξ' (defined by Eq. 7.1); panel *b*: differential loss moduli, ξ'' (defined by Eq. 7.2). Data from Fig. 7.6. Points indicate data; lines are a guide to the eye; arrows indicate scan direction.

The relatively modest, though indisputable, variations of G' and G'' with potential are highlighted by means of a differential presentation format in Fig. 7.7. We have previously shown (for the restricted case of a single electrolyte in chapter six) that it is useful to define normalized differential (with respect to potential) functions of the shear modulus components as follows:

$$\xi' = \frac{1}{G'_{(-0.2V)}} \frac{dG'}{dE} \quad (7.1)$$

and

$$\xi'' = \frac{1}{G''_{(-0.2V)}} \frac{dG''}{dE} \quad (7.2)$$

Through the magnitudes of ξ' and ξ'' we see that, in general, relative variations of G'' with potential are larger than those of G' . With respect to anion, the variations of $\xi'(E)$ are perhaps slightly larger in ClO_4^- , particularly during reduction, but the effect is not large. On the other hand, the variations of $\xi''(E)$ are significantly larger in SO_4^{2-} than in ClO_4^- or Cl^- . One feature that is noticeable is that the marked asymmetry with respect to potential scan direction that is visible in the i - E responses (and widely reported in the polyaniline literature) is *not* seen in the ξ' - E and ξ'' - E responses. The implication is that the factors that determine these responses are distinct in some way: since charged species (electron/ion) populations and motions control the current response, it is a reasonable speculation that uncharged (e.g. solvent) species populations are more directly correlated with viscoelastic properties.

Correlating our observations more widely with those in the literature (see above), the picture is one in which probes of electron, ion and polymer dynamics all show film response to the immediate electrolyte of exposure; there is no permanent “memory” of the deposition medium. We suggest that there are three significant features of the polymer-based dynamics explored here through viscoelastic properties. First, one of the factors in controlling electron mobility will be chain planarity, which in turn will be

partly controlled by polymer/anion interactions. The ability of the polymer chains to move and re-orient to the structure – of which ring-ring co-planarity is one aspect – associated with a given anion thus influences the facility for electron transport rates to respond to electrolyte composition. Second, one can relate the loss modulus to the viscosity (η) through the relationship $G'' = \omega\eta$, where $\omega = 2\pi f$ is the angular frequency of the modulation. Thus, changes in G'' control the film viscosity, which in turn (simplistically through the classical Stokes-Einstein relation, $D \propto 1/\eta$) governs the rate of ion diffusion; if one wishes to focus on ion migration, the classical Einstein equation relates mobility linearly to D . Finally, we note that the larger scale motions in both length and mass terms of polymer segmental motion, as compared to the motions of mobile species (electrons, ions and solvent), will generally result in polymer being the slowest to respond. The fact that we do observe changes in polymer dynamics means that the cascade of other processes (associated with electron, ion and solvent transport) will necessarily occur.

The one feature that has not been explored here is the relationship of polymer dynamics to film solvation. In order to do this, we require the *absolute* population of solvent within the film; gravimetric measurements using the EQCM on acoustically thin films only provide *relative* populations, i.e. population changes derived from mass (frequency) changes. It is recommended to pursue this matter in subsequent studies (future work) using neutron reflectivity, a powerful *in situ* technique capable of determining both the overall *absolute* populations of film components and their spatial distributions.

7.7 Summary

In this study, we were able to determine storage and loss shear moduli *in situ* for polyaniline films in the thickness range 0.1-0.7 μm during the electrochemical deposition of films and subsequently during redox cycling in different background electrolytes. The technique used – as described in chapters two and three – was the thickness shear mode (TSM) resonator operating at the fundamental resonant frequency of 10 MHz. The shear modulus measurements of polyaniline films have been accomplished for a range of dopant anions (perchlorate, sulphate, chloride). The two general results are that the film

viscoelastic properties evolve during the deposition process and that they respond significantly to the identity of the dopant anion (see sections 7.4 and 7.5 above).

It has been reported in the literature (as cited above) that the deposition rate of polyaniline films varies in the presence of different dopant anions (all other parameters being identical). Based on this, simplistic considerations of shear moduli as a function of deposition time (here, controlled by the number of voltammetric cycles) are not helpful. Consequently, in order to make meaningful comparisons, it is necessary to consider films of the same thickness. This has been accomplished across the thickness range $h_f \sim 0.1$ - $0.7 \mu\text{m}$. Within this range, the films under all conditions have shear moduli characteristic of typical viscoelastic materials. For $h_f < 0.1 \mu\text{m}$ the acoustic deformation is too small for reliable viscoelastic measurements to be made and for $h_f > 0.7 \mu\text{m}$ one approaches film resonance, where the interpretation is more complicated (the data for film resonance will be discussed later in appendix A).

Within the range explored, we find that the shear modulus components are largest (i.e. the films are stiffest and have the greatest loss) in perchlorate medium; the values in sulphate and chloride media are similar to each other and somewhat smaller than in perchlorate medium. It is noteworthy that a previous empirical classification of anions as polyaniline dopants placed perchlorate in one category (“class 1”) that is characteristic of compact films with low transport rates, and sulphate and chloride in another category (“class 2”) that is characteristic of more diffuse films with faster transport rates. This pattern is consistent with the notion that the loss modulus is a measure of film viscosity, η , via $G'' = \eta\omega$: higher loss moduli represent higher viscosity and thereby slower mobile species transport (by diffusion or migration).

In monomer-free background electrolyte solution (section 7.6), the film shear moduli responded to the applied potential. For all anions and both components, shear moduli increased modestly with film oxidation. This effect was chemically reversible, although there was some hysteresis with applied potential on the timescale of slow scan voltammetric experiments. Through one test case, involving chloride-prepared films

subsequently exposed to sulphate, it was found that redox cycling in an electrolyte involving a different anion to that used for film deposition resulted in a rapid shift in viscoelastic properties towards those of the ambient medium. For the relatively soft films involved, this behaviour of film viscoelastic response to the ion of exposure can be associated with rapid and complete exchange of dopant within a redox cycle.

7.8 References

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A graphic element for the chapter header, consisting of a grey, pill-shaped background with a white, curved, arrow-like shape on the left side. The text "Chapter Eight" is written in a bold, italicized, black serif font in the center.

Chapter Eight

Timescale and Temperature Dependence of Polyaniline Viscoelastic Properties

8.1 Overview

Viscoelastic properties of polyaniline films during deposition and film redox switching have been discussed in chapters six and seven. In those chapters, the evolution of polyaniline viscoelastic properties as the film progressively grows during deposition and the effects of different anions on film mechanical properties were discussed in detail. In this chapter we explore the effects of potential, temperature and timescale on the viscoelastic responses of the film. In the previous chapters (chapters six and seven) we focused on the quantification of film rheological properties via shear modulus measurements. In this chapter we exploit this quantification to extract technologically useful parameters of film viscoelastic responses; glass transition temperature, film fractional free volume and solvation energetics of the system are determined using sophisticated analysis and molecular level models capable of predicting film viscoelastic responses.

In electroactive thin polymer films, the potential controls film composition (ions, solvent or neutral species), the temperature variation influences the characteristic relaxation time, τ , of film viscoelastic processes and the timescale ($t = 2\pi/\omega$) of particular experiments determines the observational window of film stress relaxation processes. Since viscoelastic responses of polymer films are a function of film history (influenced by time and temperature effects), the experimental timescale controlled via ω provides a restricted observational window of the particular regime (state) of film viscoelastic

processes. The overall stress relaxation process is unpredictable and may take a very long time (years). During potential polarization, solvent composition of the film has - in general – a plasticization effect on film structural dynamics (lubricating effect). The exchange of charged species (ions) between the film and the medium, on the other hand, contributes to film stiffening due to the electrostatic interaction between ions and film redox sites. Here we examine the variation of film viscoelastic responses quantified via shear modulus measurement, $G(\omega\tau)$, with both experimental timescale, t , and film stress relaxation time, τ . This is done through changes in the harmonics of thickness shear mode (TSM) resonator and temperature, respectively. The use of harmonics is under-explored in viscoelastic studies and temperature variation is rarely used in electrochemical systems; here both control variables are combined.

For the first time, we explore viscoelastic properties of polyaniline films deposited on electrode surfaces using electrochemical and high frequency acoustic wave devices. The study of temperature dependent rheological properties of the film is of great importance for commercial applications and the thermal stability of bulk polyaniline films has been discussed in the literature [1-12]. For example, the ability of processing polyaniline into free standing, tough, and stable films has useful applications. Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) were among the techniques used for the probe of polyaniline thermal stability and bulk viscoelastic properties [1, 4, 12-14]. One of the major limitations of previous studies was that experiments were based on dissolved polyaniline films; in this regard polyaniline films can only be processed in N-methylpyrrolidone (NMP) or *m*-cresol solvents and their mixtures with water [4, 13, 15, 16]. In the experiments carried out in this research project, polyaniline films were electropolymerised and characterized in aqueous solutions.

8.2 Strategies and Motivation

The novel feature of the work performed here is the determination and characterization of polyaniline viscoelastic phenomena using harmonic frequencies (timescale), temperature and potential variation. In electrochemical investigations, the temperature variation is

underexploited [17-19]. In common viscoelastic investigations, the variation of resonator harmonics are rarely employed [20, 21]. The unprecedented combination of temperature control, acoustic wave device and electrochemical studies provides a unique perspective on the fundamental understanding of these combined and complex phenomena [17-19].

The question of what determines viscoelastic properties of polyaniline films under the influence of electrochemical control needs to be addressed. The power of the methodology we use here relies upon the manipulation of the normalized timescale, $\omega\tau$, of the viscoelastic responses of the system. This manipulation can be exploited directly through resonator harmonic frequency ($f = \omega/2\pi$) and indirectly through temperature (via changes in film relaxation time, $\tau = \tau_0 \exp(\Delta H/RT)$, where ΔH is the activation energy associated with film relaxation processes) and potential (controlling film solvent composition and thus limiting film relaxation time, τ_0).

The normalization of timescale, $\omega\tau$, is achieved by the use of the principle of “*time-temperature superposition*” [22-26]. In section 2.4.1 (chapter two), the basic concepts of the principle have been reviewed. The principle is a well-established approach initially developed for the rationalization of viscoelastic phenomena in bulk polymeric materials [23, 26]. It describes the possibility of placing different polymer dynamics data acquired at different temperatures (driving different stress relaxation rates) on a single “*master relaxation curve*”. In section 8.8.1 (below) we describe the details of master curve construction and its application to experimental data.

8.3 Qualitative Overview of Experimental Outcome

Experimentally our approach for the deposition and characterisation of polyaniline films was to use the EQCM in dispersive mode. Crystal admittance (impedance, $Z = 1/Y$) responses were acquired as a function of frequency ($f = \omega/2\pi$) in the vicinity of peak resonance. This gives the complete resonance feature instead of just the resonant peak frequency (cf. gravimetric approach). Procedures for the extraction of film viscoelastic data quantified via shear moduli measurements were based on fitting the components of a lumped element equivalent circuit (also known as Butterworth van Dyke (BvD) model) to

experimental data. Quantitative values of G' and G'' were calculated with the help of the Maple program as complex roots of Eq. 8.1. Eq. 8.1 relates the experimentally measured electrical impedance, Z , of the system to the mechanical impedance of the composite resonator [27-32]:

$$Z = j\omega\rho_s + Z_f \left[\frac{Z_L \cosh(\gamma h_f) + Z_f \sinh(\gamma h_f)}{Z_f \cosh(\gamma h_f) + Z_L \sinh(\gamma h_f)} \right] \quad (8.1)$$

where Z_f is the characteristic mechanical impedance of the film, γ is the shear wave propagation constant in the film [30-34], and Z_L is the characteristic mechanical impedance of the background electrolyte solution (a semi-infinite Newtonian fluid) [30-34].

The viscoelastic data of polyaniline films as functions of potential and the identity of anion present during film electropolymerization have been discussed in chapters six and seven. In the current study, we focus on the characterisation of polyaniline films in background electrolytes as a function of three control variables. The three variables used are the resonator harmonics (effectively, experimental frequency or timescale), the applied potential (driving changes in film composition of small molecules, solvent and ion) and temperature (varying film chain relaxation time). The electrochemical cell was immersed in thermostatic bath and the temperature range explored was $5 \leq T/^\circ\text{C} \leq 60$. For the single-shot experiment of film deposition, the temperature was held at 20°C and fundamental frequency, $f = 10$ MHz was used. For each temperature change, the harmonics of the thickness shear mode (TSM) resonator were varied over the range $10 \leq f / \text{MHz} \leq 110$ during film redox cycling. The details of experimental setup and procedures were discussed in chapter three.

The raw data for a typical polyaniline film in 1 M HClO_4 background electrolyte are shown in Fig. 8.1. The voltammetric data (i-E curve) of the film in the electrolyte solution are shown in panel *a*. Here the first redox peak of polyaniline film was studied

with a potential range of $-0.2 \leq E/V \leq 0.4$ and scan rate of $\nu = 10 \text{ mV s}^{-1}$. Extension of the potential beyond this range in monomer-free acidic electrolyte solutions (fixed film thickness) may overoxidize the film and lead to film degradation [35-37].

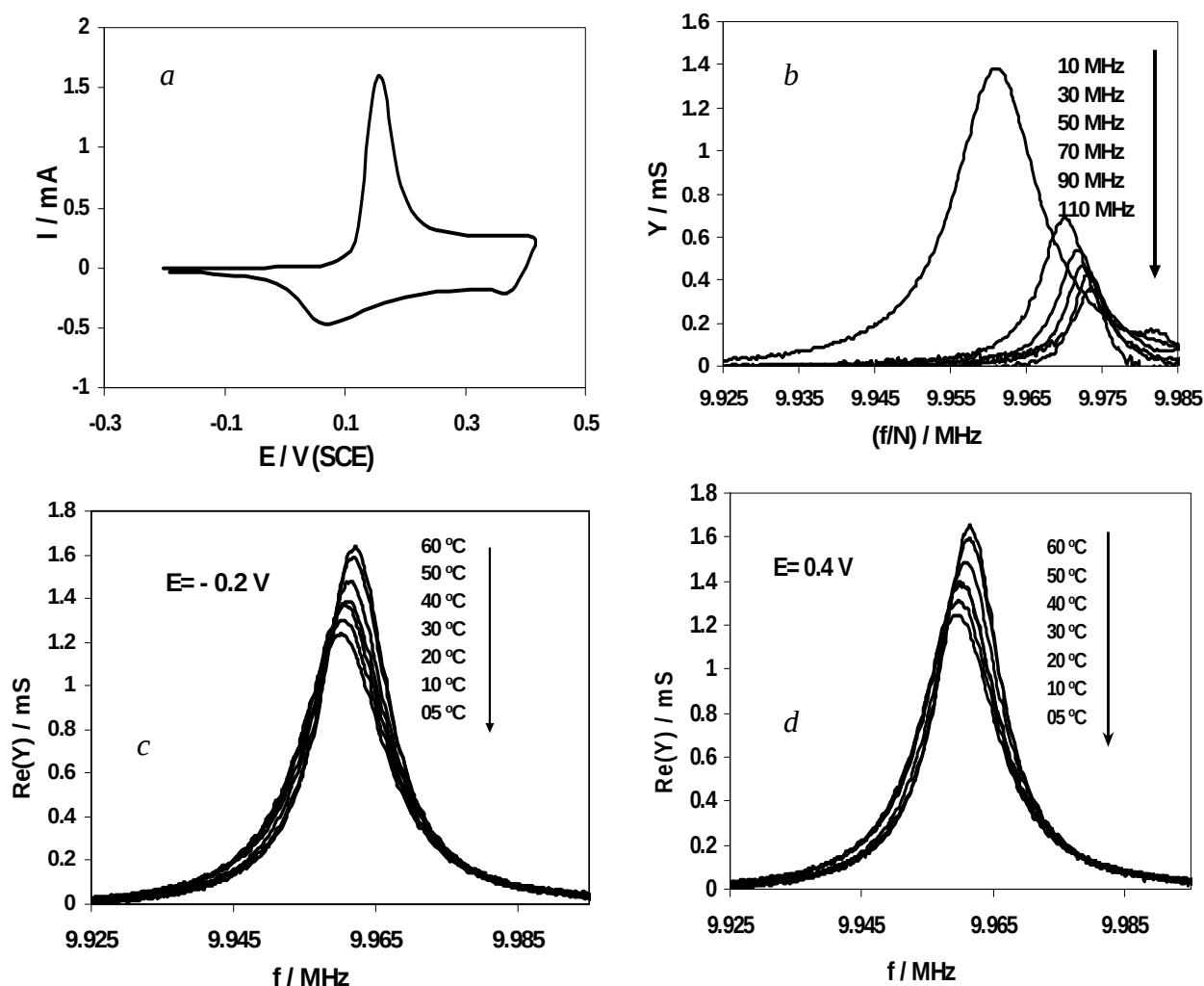


Fig. 8.1: Voltammetric and crystal admittance spectra for polyaniline film deposited and characterised in 1 M HClO_4 background electrolyte. The data for film deposition were presented in chapter six, Fig. 6.1. Panel *a*: cyclic voltammogram at scan rate, $\nu = 10 \text{ mV s}^{-1}$ over the potential range of $-0.2 \leq E/V \leq 0.4$. Panel *b*: admittance spectra of the film for different harmonics (as marked inside the figure) as a function of frequency at $E = -0.2 \text{ V}$ and $T = 20 \text{ }^\circ\text{C}$; all the harmonics are placed on the same axis as the fundamental frequency by normalising them via their corresponding harmonic number; the characteristics of the device assumes odd integer number values. Panels *c* and *d*: admittance spectra of the film for the fundamental mode at $E = -0.2 \text{ V}$ (film reduced) and $E = 0.4 \text{ V}$ (film oxidised) at $T = 20 \text{ }^\circ\text{C}$.

Panels *b-d* show admittance spectra associated with the film (within the above potential range) as a function of temperature ($T = 5\text{-}60^\circ\text{C}$) and the resonator harmonics ($\omega = 2\pi f$, $f = 10\text{-}110\text{ MHz}$). In panel *b*, the harmonic data (odd integers of the fundamental frequency; here for the first five overtones) of the film (at $T = 20^\circ\text{C}$ and $E = -0.2\text{ V}$) are placed on the same scale as the fundamental frequency. This is done via simply dividing each admittance spectra data by its corresponding harmonic number (N). Qualitatively, the raw data in panel *b* show that effect of the timescale variable on film mechanical responses is dramatic; the quantitative interpretation of this effect through the variation of shear moduli with timescale will be discussed below (section 8.8). In panels *c* and *d*, the admittance spectra at the two extrema of film redox state ($E = -0.2\text{ V}$ and $E = 0.4\text{ V}$, respectively) are demonstrated as a function of temperature over the range $5 \leq T/^\circ\text{C} \leq 60$.

8.4 Potential Dependence of Shear Modulus

According to Fig. 8.1 (panels *c* and *d*), the effect of potential at given temperature looks relatively negligible at the fundamental device frequency. The peak admittance reduces ca. 6% for the spectra measured at $E = -0.2\text{ V}$ than $E = 0.4\text{ V}$. With respect to temperature variation ($T = 5\text{-}60^\circ\text{C}$) at either the reduced ($E = -0.2\text{ V}$) or oxidised end of film redox state ($E = 0.4\text{ V}$), the peak admittance spectra dropped by ca. 25% from $T = 5^\circ\text{C}$ to 60°C . The temperature effect is relatively small though measurable and some of this effect is associated with solution viscosity changes. Compared to potential or temperature effects, 75% drop of peak admittance was observed for the normalised timescale effects (panel *b*) on polymer structural dynamics. In general terms, the observed qualitative effects of potential, temperature and timescale, respectively, on film structural dynamics are minimal, modest and significant. Quantitative aspects of these effects through shear moduli measurements of the film viscoelastic responses are discussed below.

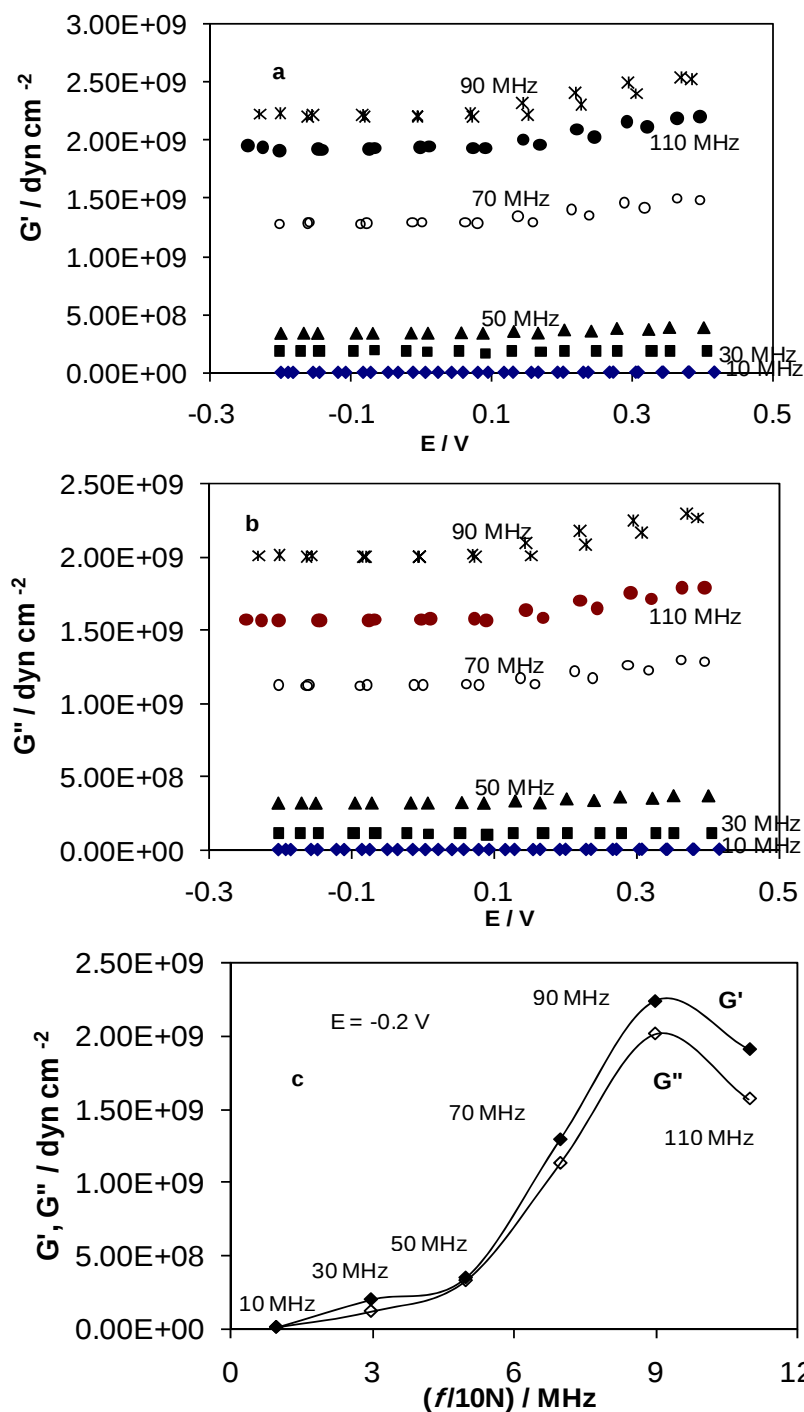


Fig.8.2: Shear moduli data as a function of experimental timescale ($1/f = 2\pi/\omega$) in potentiodynamic experiments at $T = 20^\circ\text{C}$; panel a: G' values as a function of potential and measured for the resonator harmonic frequencies of $10 \leq f/\text{MHz} \leq 110$; panel b: G'' values as in a; panel c: G' and G'' data in panels a and b plotted against normalised frequency scale ($E = -0.2 \text{ V}$, $T = 20^\circ\text{C}$).

8.5 Frequency Dependence of Shear Modulus

Fig. 8.2 shows the values of shear modulus data as a function of acoustic wave device harmonic frequencies ($\omega = 2\pi f$; $f = 10$ -110 MHz) of a polyaniline film exposed to background electrolyte (1 M HClO₄) in potentiodynamic experiments (at a given temperature, $T = 20$ °C).

The protocols of shear modulus extraction have been discussed in chapter three and elsewhere [28, 32, 33, 38]. Shear modulus data in Fig. 8.2 show significant variation with frequency; the data shown are for $T = 20$ °C, but other temperatures have also been studied. In panels *a* and *b*, the values of shear modulus values for G' and G'' , respectively, increased two orders of magnitude, i.e. the effect of experimental timescale on film relaxation process is predominant. This effect can better be demonstrated in panel *c* where shear moduli values increase dramatically after the fifth harmonic, peak at the ninth harmonic and drop slightly at the eleventh harmonic; the data in panel *c* is taken from panels *a* and *b* of Fig. 8.2 at given potential of $E = -0.2$ V (reduced film) and temperature of $T = 20$ °C.

8.6 Temperature Dependence of Shear Modulus

In Fig. 8.3, the temperature-dependent data of G' and G'' values (at $f = 10$ MHz) are shown for potentiodynamic experiments. In panel *a*, though not dramatic, the G' values decrease as the temperature is raised. This implies that the effect of temperature is reflected in the mechanical softening of the film; according to the data in panel *a*, G' values have decreased to ca. 50% of initial values before temperature change (from 1.81×10^7 at 5 °C to 0.9×10^7 at 60 °C, at $E = -0.2$ V). The effect of temperature on G'' values seems (panel *b*) to be slightly different from that on G' values in terms of pattern and magnitude. The overall change in G'' (though not in the same order and direction as G') was found to be 35% increase (cf. decrease in G') of the loss shear modulus values at 5 °C ($E = -0.2$ V). This temperature-dependent effect of G'' shows moderate reduction in film viscosity ($G'' = \omega\eta$) over the temperature range $T = 5$ -60 °C. For each temperature explored here, both G' and G'' values remain constant below $E < 0.15$ V, but rise

concomitantly at $E = 0.15$ V until $E = 0.4$ V (end point of these particular experiments). In addition, there is a clear hysteresis in all individual data plots (for each temperature) between the potential range $0.15 < E/V < 0.4$. Both the hysteresis and increase in shear moduli values beyond $E = 0.15$ V (the position of the first redox peak of polyaniline films) can be attributed to film compositional changes following the potential redox cycling of the film. In future work, it is recommended to establish direct correlation between film composition and viscoelastic responses in quantitative mode.

Quite generally, one can observe that the overall variation of shear modulus components with temperature control over the range 5-60 °C does not exceed a factor of ~ 2 . This may suggest that film structural dynamics are not under the direct influence of strongly activated processes within the temperature range explored.

Furthermore, the loss tangent (G''/G') of shear moduli data varies – due to the temperature effect - from 0.5 at 5 °C, through 0.8 at 20 °C and to 1.16 at 60 °C. A film with these values of loss tangent can be thought to have relaxation times similar to the observational timescale; this is characteristic to a typical viscoelastic material according to the Maxwell model (chapter two) [17, 18].

8.7 Time-Temperature dependence of Shear Modulus

Having discussed the viscoelastic responses to the effects of the timescale (frequency), temperature and potential in separate manners, we now focus on the combined effects of time (frequency)-temperature interaction. Combination of frequency and temperature effects enables us the observation of film viscoelastic processes within a controllable experimental timescale.

The results of $\log(G')$ vs $\log(f)$ and $\log(G'')$ vs $\log(f)$ collected at various temperatures are shown in Fig. 8.4, panels *a* and *b*, respectively. Shear modulus data extracted for the potentiodynamic experiments of polyaniline films in 1 M HClO₄ electrolyte have been huge, but selected points of $E = -0.2$ V are shown in Fig. 8.4.

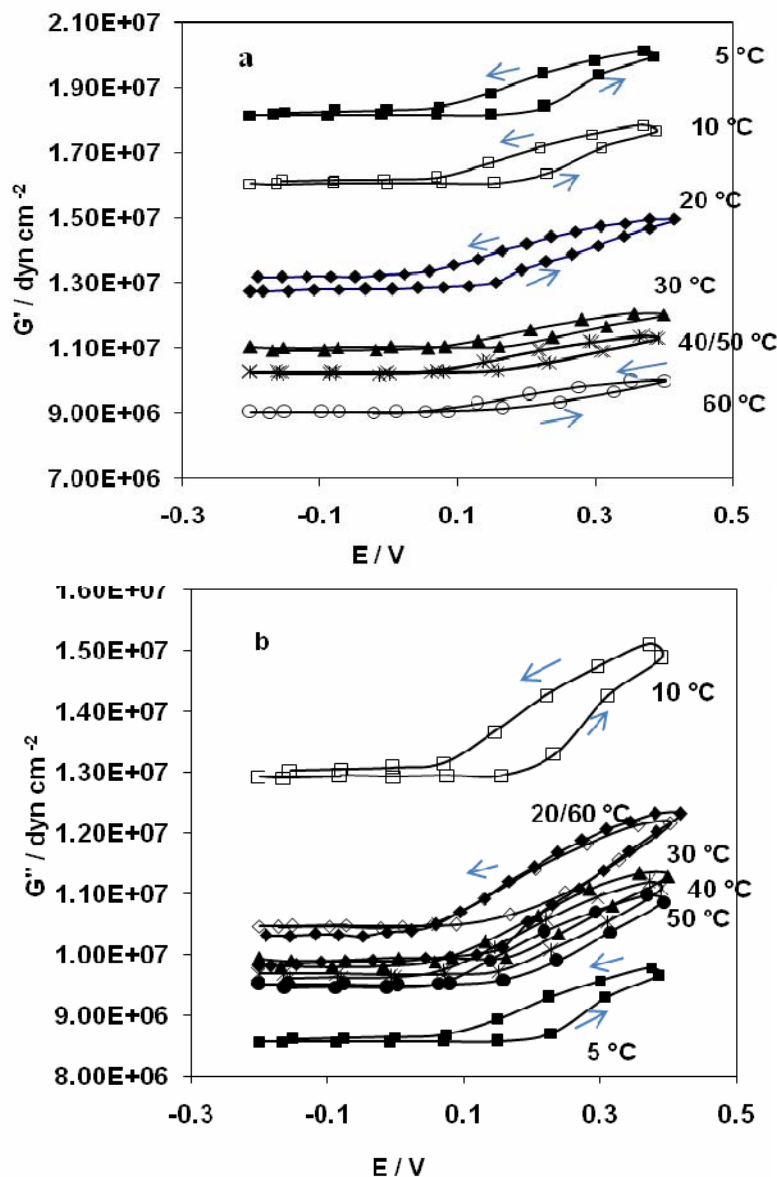


Fig. 8.3: Shear modulus data as a function of potential measured at the fundamental frequency, $f = 10$ MHz and over the temperature range of $5 \leq T / ^\circ\text{C} \leq 60$; a) storage shear modulus, G' ; b) loss shear modulus, G'' .

It is obvious that the effect of timescale on the viscoelastic signatures of the film is substantial for all data recorded at any temperature in the range 5-60 °C; the variation of G' and G'' span by ca. 3 orders of magnitude. Surprisingly, the temperature effect on the shear modulus data is minor (around one order of magnitude) in the observational timescale window of Fig. 8.4. Due to the smaller size of the admittance signal at higher

frequency (Fig. 8.1, panel *b*), both G' and G'' measurements show minor (if any) variation above experimental scatter.

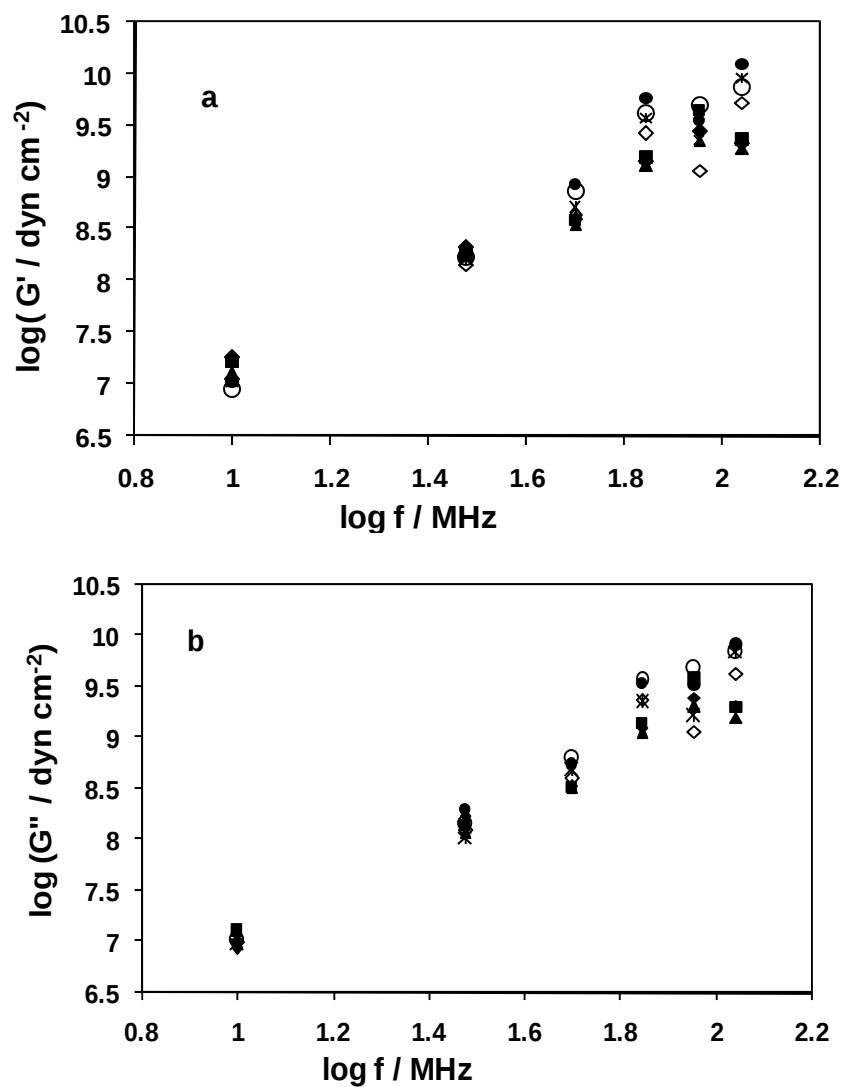


Fig. 8.4: Double logarithmic plot of a) G' b) G'' as function of device higher harmonic frequencies (timescale) and temperature at $E = -0.2$ V; the symbols $\blacklozenge$, $\blacksquare$, $\blacktriangle$, $\diamond$, $*$, $\bullet$, and $\circ$ indicate the temperatures: 5, 10, 30, 40, 50 and 60 °C respectively. The data shown here were taken from Figs. 8.2 and 8.3.

8.8 Viscoelastic Models

Underlying molecular processes for the macroscopic viscoelastic responses (quantified via shear moduli measurements) can be accessed through the application of the experimental data to some theoretical and/or empirical models. Our primary goal is to rationalise the variations of the acquired shear modulus data (according to Figs. 8.2-8.4) with E , T , and ω on the basis of the models discussed below. Among well-established models applied for the interpretation of viscoelastic responses to timescale and temperature control variables are: the Williams-Landel-Ferry (WLF) model, Rouse-Zimm model and the activation model. These models were initially developed for bulk polymer materials and applied to low-frequency (sub-kHz) dynamic experiments. The application of these models to thin films has received relatively very little attention; this research group has applied these models – for the first time – to surface immobilised thin electroactive films under electrochemical control conditions.

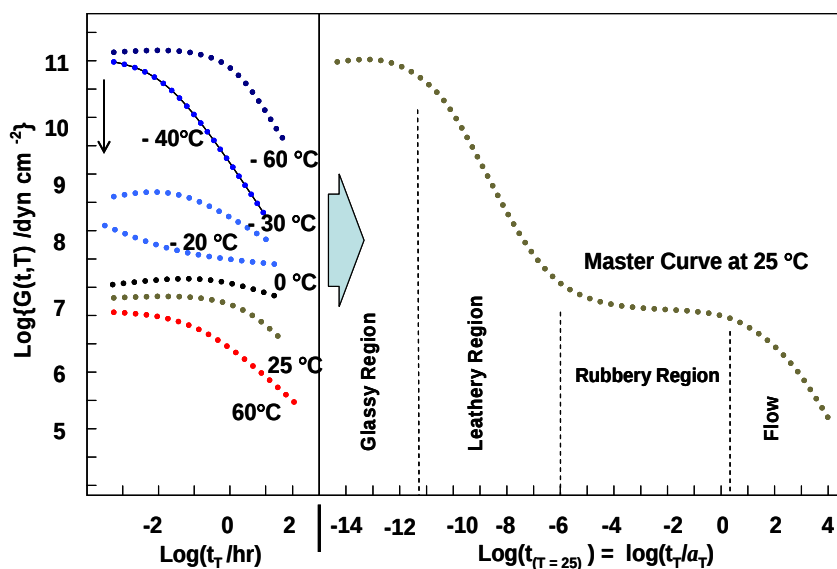


Fig. 8.5: Schematic representation of double logarithmic shear modulus data as a function of experimental timescale and temperature. On the left side, shear moduli data at different temperatures over controllable experimental timescale are represented. On the right side, the outcome of isothermal data superimposition at an arbitrary reference temperature of $T = 25\text{ }^{\circ}\text{C}$ is drawn. The temperature values and the numbers on the axes are assumed for presentational purpose, but not based on experimental or theoretical calculations. This is called a “master curve” and can be achieved by shifting data on the logarithmic time (frequency) axis at points of same gradient. For details, see text.

8.8.1 WLF model

The WLF model was developed to describe the long-range spinal motions of polymer chains. The application of this model is based on the principle of time-temperature superposition. This principle has been discussed elsewhere [22-26], but for presentational purposes and for the benefit of the reader we summarize the main concepts of the principle (also reviewed in chapter two). The strategy is to construct on a single curve (known as a “*master curve*”) the viscoelastic material behaviour over a much broader range of time (frequency) that can be measured at a single temperature or feasible experimental timescale.

Basically, shear modulus data, $G(t,T)$, measured at different temperatures are plotted on a common logarithmic time-(frequency)-scale as depicted in Fig. 8.5 in a cartoon form. The isothermal curves are shifted horizontally with respect to an arbitrary reference temperature, T_o , so that the curves superimpose at points of the same gradient (i.e. have similar habit) producing a single “*master curve*” covering the whole relaxation timescale. For a perfect superimposition, a slight vertical shift is also required due to the material softening effect of temperature [22, 23]; this is to compensate for the changes in film density due to temperature variation. One of the characteristic parameters of this principle is the so-called “*shift factor*, a_T ” which is the logarithmic horizontal displacement necessary to superimpose individual isothermals at T on the dynamic viscoelastic data measured at the arbitrary reference temperature, T_o [22, 23, 26]. This “*shift factor*” parameter is used as a gauge for the temperature dependence of material’s viscoelastic manifestations.

Practically, one should note that if $T > T_o$, then $a_T < 1$ and if $T < T_o$, $a_T > 1$; the consequence is that if the temperature of the system is varied, a corresponding time (frequency) of the polymer mechanical relaxation can be found at which the dynamic viscoelastic responses will be the same. In other words, the temperature variation is effectively accelerating or retarding dominant viscoelastic processes. Observably, isothermals measured at high temperatures reflect the responses of viscoelastic data associated with long experimental timescales (low frequencies). In addition, mechanical

excitations associated with relatively short times (higher frequencies) are detected at temperatures close to the glass transition temperature, T_g , a temperature below which the mobility of polymer chains is practically frozen.

In the WLF model, the relaxation function, due to the time-temperature superimposition principle, will be of the form [22, 23, 26]:

$$G(t, T) = G\left(\frac{t}{a_T(T)}, T_o\right) \text{ or } G(\omega, T) = G(a_T \omega, T_o) \quad (8.2)$$

where T_o is the reference temperature and $a_T(T)$ is the temperature shift factor obtained from the master curve.

The shift factors, a_T , should be same for all viscoelastic functions (within the precision of the experiment), i.e. for both $G'(t, T)$ and $G''(t, T)$. However, if the material undergoes a phase transformation in the temperature range of interest or if the dominant relaxation mechanism is not thermally activated, the principle will not hold.

The term $t/a_T(T)$ in Eq. 8.2 is sometimes called the “*reduced time*” and gives the full-scale observational time-dependent window of the relaxation process if one would perform the experiment at the arbitrary reference temperature, T_o .

In the common case, the mechanical properties of viscoelastic films depend on the ratio (τ/t or $\omega\tau$) of the films characteristic relaxation time, τ (temperature dependent variable), and the observational timescale, t . With the knowledge of the temperature dependence of τ , the values of the shift factors, a_T , can be predicted. Conversely, with the determination of shift factors (via the construction of the master curve), one can get an insight into the underlying physicochemical processes and the energetics of the system.

The master relaxation curve of polyaniline viscoelastic responses described in terms of log-log shear modulus values as a function of frequency for a range of different

temperature measurements (5-60 °C) are presented in Fig. 8.6 with $T = 20\text{ °C}$ selected as the arbitrary reference temperature, T_0 ; the data shown here were taken from Fig. 8.4.

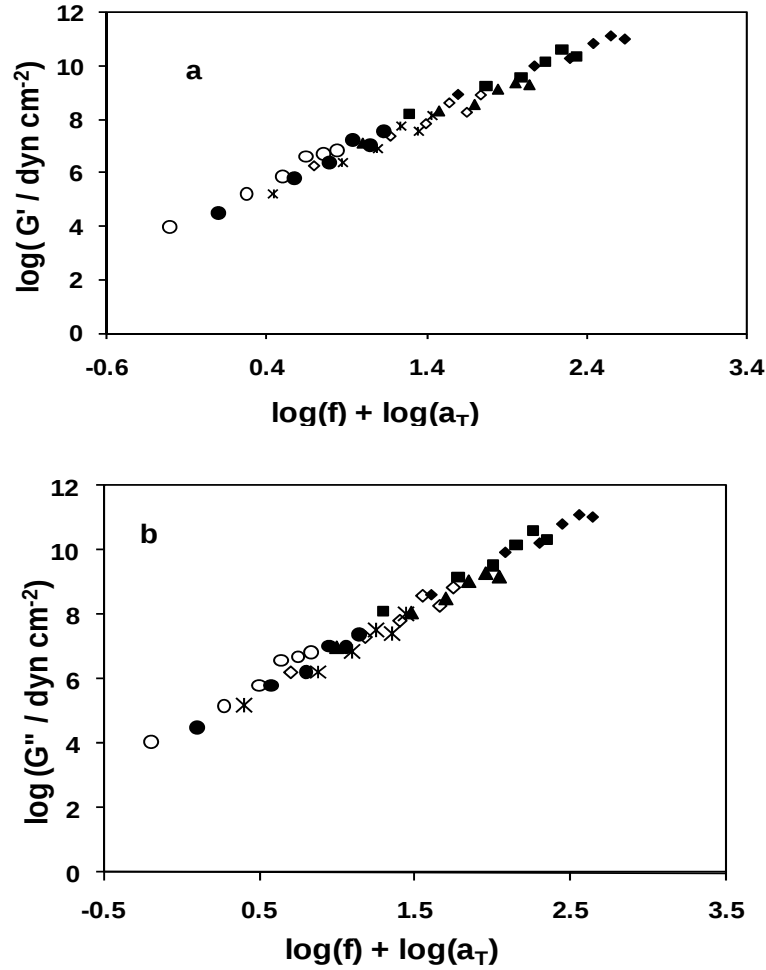


Fig. 8.6: Double logarithmic shear moduli values as functions of frequency, f , and temperature constructed on a common master relaxation curve according the shift factors explained in the text. In panel *a*, storage shear modulus data are shown and in panel *b*, loss shear modulus data are presented. Temperature is annotated. The data shown here are from Fig. 8.4.

For the construction of the master relaxation curves in Fig. 8.6, the data sets for each temperature were shifted on the logarithmic frequency scale from $\log(\omega)$ to “ $\log(\omega) + \log(a_T(T))$ ”; to do so, one requires to apply the same shift factors, $a_T(T)$, to both G' and

G'' values and their values are shown in Fig. 8.7. This is significant by itself for the principle of time-temperature correspondence to hold as explained above.

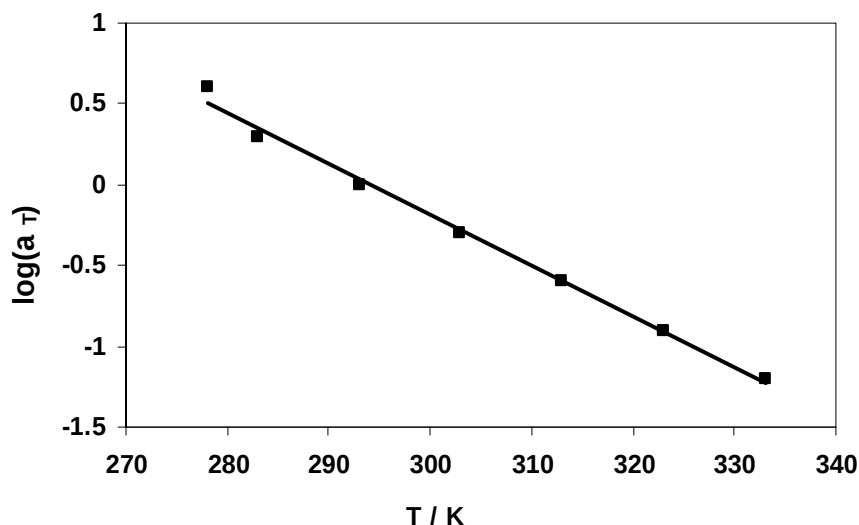


Fig. 8.7: Experimentally determined shift factors of polyaniline film data in aqueous solution of 1 M HClO₄. The logarithmic scale of shift factors is plotted against temperature at $E = -0.2$ V.

We now turn back to the WLF model to understand the physical significance of the *shift factors* in terms of the underlying molecular processes of polymer chain units. The model predicts temperature dependence of film viscoelastic responses through the experimentally determined shift factors as described below:

$$\log a_T(T) = \frac{-C_1(T - T_o)}{C_2 + T - T_o} \quad (8.3)$$

where T_o is the arbitrary reference temperature, and C_1 and C_2 are material-specific constants. When the reference temperature is set to be the glass transition temperature T_g , many viscoelastic polymers have nearly “*universal*” values for $C_1 = 17.4$ and $C_2 = 51.6$; this may be due to the suggestion that spinal motions of polymer chains are insensitive to the detailed structural characteristics of the polymer.

In terms of the theoretical rationalisation of WLF model, we need to consider the semi-empirical Doolittle equation [22, 23, 26]:

$$\ln \eta = \ln A + B \left(\frac{1}{f} - 1 \right) \quad (8.4)$$

where η is the viscosity, f is the fractional free volume (unoccupied space) of the system; $f = V_f/V$, where V_f and V are free volume and total volume, respectively. In Eq. 8.4, A and B are constants.

Above the glass transition temperature, the fractional free volume, $f = V_f/V$, increases linearly with temperature by [22, 23, 26]:

$$f = f_g + \alpha_T (T - T_g) \quad (8.5)$$

where f is the fractional free volume at T , any temperature above T_g , f_g is the fractional free volume at T_g , and α_T is the thermal coefficient of the fractional free volume above T_g . Inserting Eq. 8.5 into Eq. 8.4, the Doolittle equation becomes:

$$\ln \eta(T) = \ln A + B \left(\frac{1}{f_g + \alpha_T (T - T_g)} - 1 \right) \text{ at } T > T_g \quad (8.6)$$

and at T_g :

$$\ln \eta(T_g) = \ln A + B \left(\frac{1}{f_g} - 1 \right) \quad (8.7)$$

Subtracting Eq. 8.7 from Eq. 8.6 yields:

$$\ln \frac{\eta(T)}{\eta(T_g)} = B \left(\frac{1}{f_g + \alpha_T (T - T_g)} - \frac{1}{f_g} \right) \quad (8.8)$$

With a little algebraic rearrangement, Eq. 8.8 simplifies to a form identical to the WLF equation:

$$\log \frac{\eta(T)}{\eta(T_g)} = \log a_T = -\frac{B}{2.303 f_g} \left(\frac{T - T_g}{(f_g / \alpha_T) + T - T_g} \right) \quad (8.9)$$

where $C_1 = B/2.303f_g$ and $C_2 = f_g/\alpha_T$. From Eq. 8.9, one can recognise that WLF equation is simply a short-hand form of the empirical Doolittle equation. The glass transition temperature T_g , fractional free volume, f_g , at T_g , and the thermal expansion coefficient, α_T , above T_g are all useful parameters for polymer technology and can be determined from the master relaxation curve. Fitting Eq. 8.9 into the experimental data of Fig. 8.6 with an arbitrarily selected reference temperature of $T_o = 20$ °C yields polyaniline film parameters of $\alpha_T = 4.4 \times 10^{-4} \text{ K}^{-1}$, $f_g = 0.074$ and $T_g = 292.31 \text{ K}$. Conventionally, bulk polymers have a nearly universal value of $f_g = 0.025$ near the glass transition temperature. The relatively high value of the fractional free volume (a factor of 3 bigger) associated with the polyaniline data shown here indicates the existence of high solvent population within the film which has a direct effect on the thermal properties of the film (lowering the glass transition temperature). The value of T_g calculated is consistent with the values reported in the literature [16] for polyaniline films considering the effect of water on T_g ; the overwhelming majority of studies were conducted in either N-methylpyrrolidone (NMP) or m-cresol solvents in which polyaniline films can be processed. The difference is that we use thin films attached to electrode surfaces, whereas in the literature dissolved powder or fibres of polyaniline films were used. Furthermore, in most other cases, the film was prepared chemically whereas in our case the film is electrochemically deposited on electrode surface; the difference may be chain-chain cross-linking. Another difference is that in previous studies traditional thermogravimetric or differential scanning

calorimetry was employed; in our experiments a sophisticated combination of electrochemical and an acoustic wave device was used.

8.8.2 Activation Model

Plotting variations of shift factors with temperature in an “Arrhenius-like” format (Fig. 8.8), the associated activation enthalpy, ΔH_a , with film relaxation processes can be calculated according to:

$$\Delta H_a = 2.303R \frac{\partial \log a_T}{\partial (1/T)} \quad (8.10)$$

where R is the universal gas constant. From the slope of Fig. 8.8, one can find $\Delta H_a = 57.4 \text{ kJ mol}^{-1}$. In the literature, similar activation enthalpy ($\sim 65 \text{ kJ mol}^{-1}$ though for bulk polyaniline) has been calculated and attributed to water molecules acting as cross-linking units at temperatures lower than $\sim 70^\circ \text{C}$ [4]. Above this temperature, polyaniline films undergo chain-chain cross-linking with an effect of raising glass transition temperature (different values have been reported due to the nature of solvent used and the sensitivity of the technique employed).

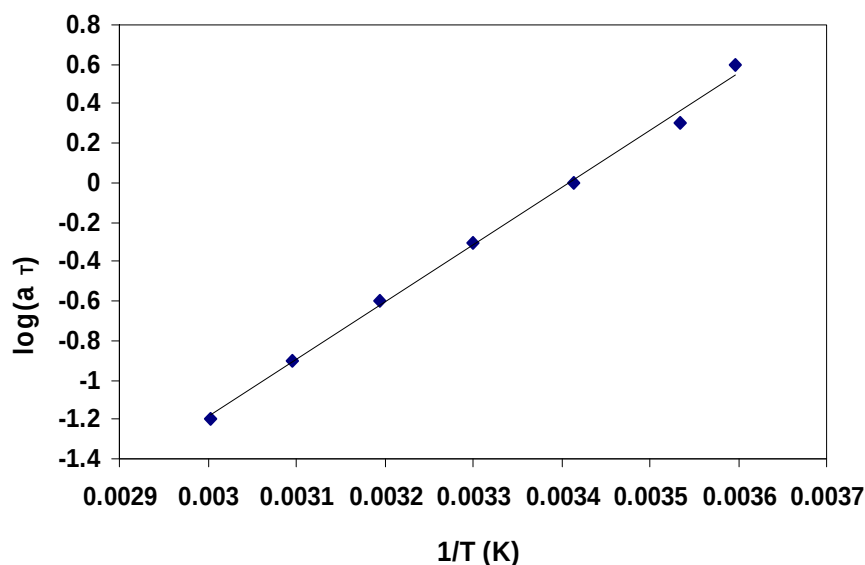


Fig. 8.8: Data of Fig. 8.7 plotted in an Arrhenius-type format. From the gradient of plot one can obtain the activation energy of film relaxation processes.

8.8.3 Rouse-Zimm Model

In contrast to the WLF model, the Rouse-Zimm model attempts to gain a deeper understanding on a molecular level of polymer viscoelasticity based on the theory that assumes un-entangled polymer chains in a viscous medium [22, 23, 39]. With the use of Rouse-Zimm model, the prediction of relaxation spectra of polymer viscoelastic behaviour is possible.

In this model, the polymer chain is assumed to consist of a series of N subunits per unit volume. Each subunit is also assumed to behave like an entropy spring that realises a Gaussian distribution of segments (> 50 carbon atoms). The spring accounts for the polymer elasticity. On the other hand, the mass of the chain itself moving in the viscous medium, often represented as a bead, is responsible for the energy dissipation of the system.

Starting with a single isolated chain, the viscoelastic polymer adopts the most suitable conformation or segmental distribution. The application of stress to the system causes distortion that disturbs the equilibrium conformation to a less probable one. This results in a decrease in the entropy and thus a corresponding increase in the free energy of the system. Upon removal of the stress, polymer chain segments re-orient and diffuse back to their equilibrium position (unperturbed situation); in the meantime the whole chain may have changed its spatial position. However, if the applied stress is maintained the excess free energy is converted into heat via strain relief, thereby stimulating the thermal motion of the polymer chain segments back into their original state; this process is called “*stress relaxation*”.

In principle, overall motion of the polymer chain depends on the co-operative movements of all subunit segments. As a result, the stress relaxation of the system is associated with the number of ways the polymer chain can regain its most probable structural conformation. Therefore, each possible co-ordinated movement of chain segments can be treated as a mode of motion with characteristic relaxation time.

Schematically we can represent the polymer and the movement modes of a flexible chain in the cartoon depicted in Fig. 8.9. Simplistically the first mode, $p = 1$, represents a polymer chain translating as a whole in a viscous medium; this mode has the largest relaxation time, τ_1 , as it requires maximum co-ordination in segmental movement. In the second mode, $p = 2$, polymer chain ends move in opposite directions and in the third mode, $p = 3$, polymer chain ends move synchronously in the same direction whereas the centre moves in the opposite. Higher modes, $p = 4, 5, 6, \dots$, involve a progressively lower degree of segmental movement co-ordination. Correspondingly, the lesser segmental co-ordination results in lower polymer relaxation time, τ_p . In physical terms, this means that a single polymer chain can possess a wide distribution of viscoelastic relaxation times. With the help of Stokes-Einstein relationship (equilibrated viscous drag and diffusive forces), one can find the characteristic relaxation time, τ_p , of a perturbed polymer chain as follows:

$$\tau_p = \frac{6\eta}{Nk_B T \pi^2 p^2} \quad (8.11)$$

where η represents the viscosity of the medium in which chains are present, $p = 1 \dots z$ is particular movement modes of the chain and $Nk_B T$ is the modulus associated with each relaxation time; k_B is the Boltzmann constant. Eq. 8.11 suggests that polymer relaxation time, τ_p , is strongly dependent on temperature variation ($\tau_p \propto 1/T$) and hence the Rouse-Zimm model is in a qualitative agreement with experimental results [23].

Based on mechanical models to aid the elucidation of viscoelastic phenomena of polymer films, notably, the Maxwell-Wiechert model (explained in chapter two), the polymer relaxation process under dynamic experiments can be found via real, $G'(\omega)$, and imaginary, $G''(\omega)$, shear modulus components by:

$$G'(\omega) = Nk_B T \sum_{p=1}^z \frac{\omega^2 \tau_p^2}{1 + \omega^2 \tau_p^2} \quad (8.12)$$

$$G''(\omega) = Nk_B T \sum_{p=1}^z \frac{\omega \tau_p}{1 + \omega^2 \tau_p^2} \quad (8.13)$$

With the help of the Maple package (powerful mathematical software), one can predict using Eqs. 8.12 and 8.13 polymer viscoelastic behaviour as functions of both stress relaxation times of polymer chain conformations and the observational timescale (experimental frequency) in a 3D format. We can also relate the characteristic polymer relaxation time and temperature changes of the system; changes in film viscosity by temperature have a direct influence on film viscoelastic relaxation processes.

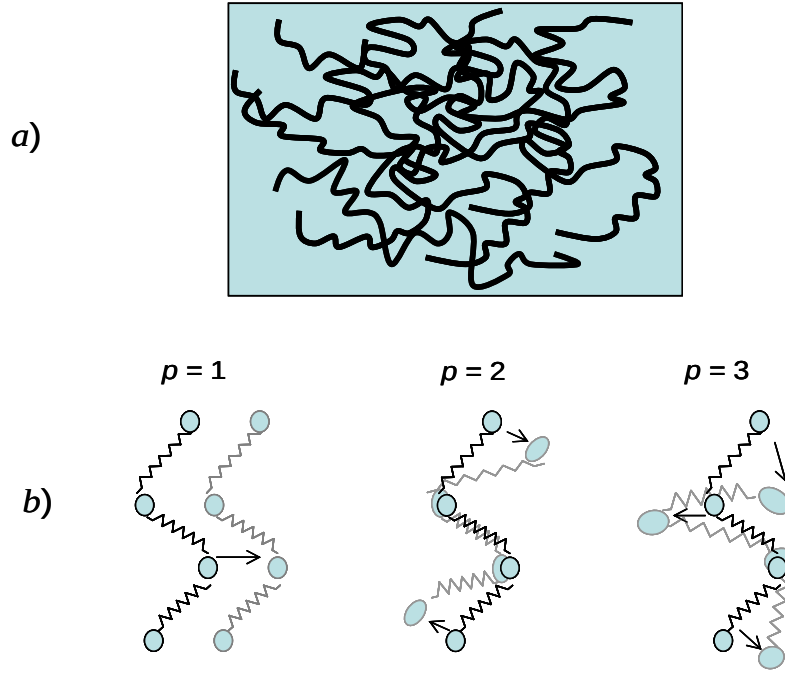


Fig. 8.9: Schematic representation of a polymer film; a) a polymer film with entangled multiple chains; b) representative modes of movement of a single flexible chain as simplified in Rouse-Zimm model are shown: in mode $p = 1$, the chain laterally translates with a full co-ordination of all subunit segments; in mode $p = 2$, chain ends move in opposite directions and in mode $p = 3$, both ends move in the same direction while the centre moves in the opposite direction.

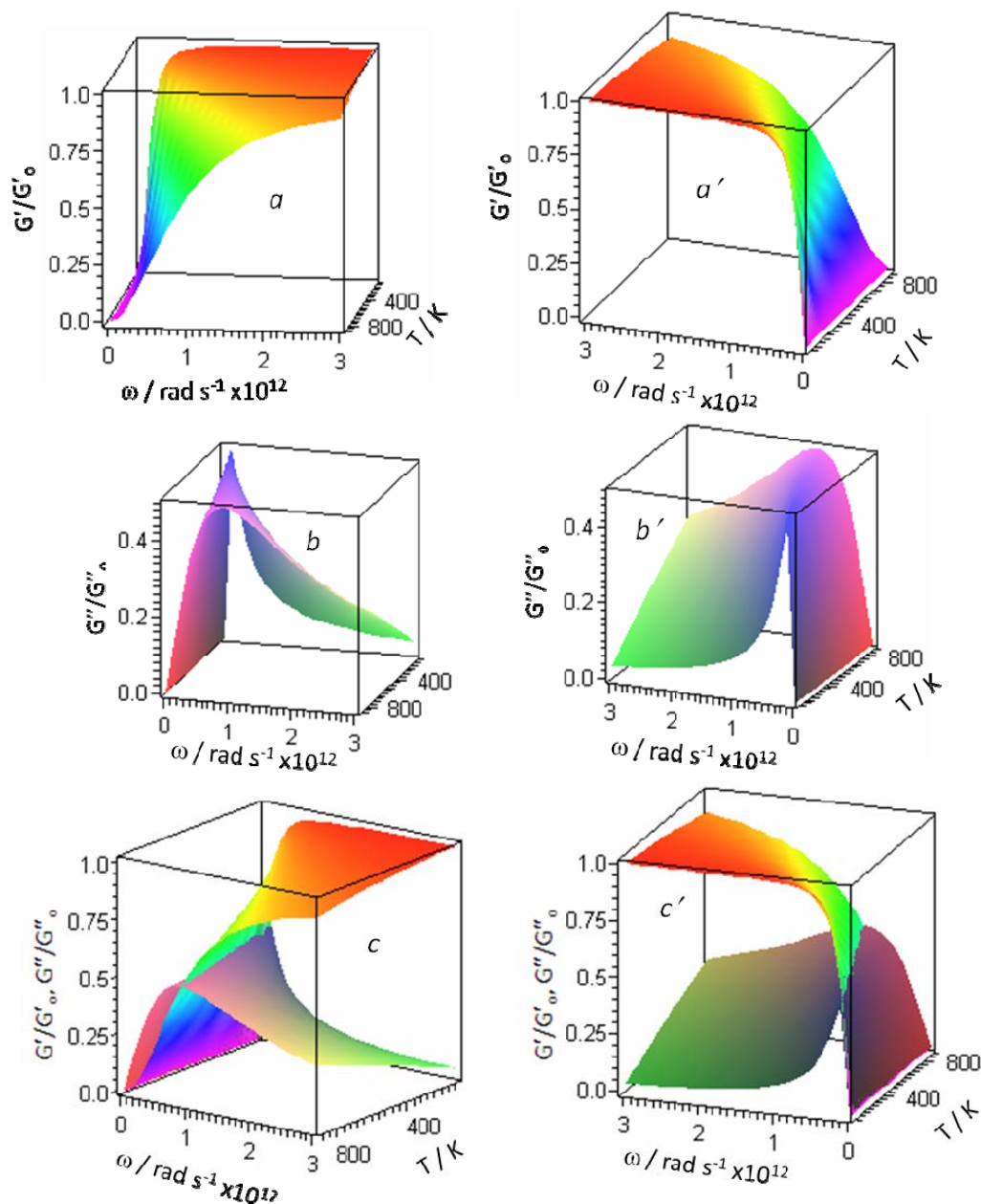


Fig. 8.10: Mathematically calculated models predicting film viscoelastic behaviour based on Maxwell-Wiechert model with the assumption of first relaxation mode, $p = 1$. Both shear modulus components are normalized by the typical limiting shear modulus value for most polymers where $G_0 = Nk_B T = 2.44 \times 10^{10}$ dyn cm⁻² at $T = 293$ K. The angular frequency values used were $\omega = 1-3 \times 10^{12}$ rad s⁻¹ and the temperature range was $T = 100-1000$ K. In this simulation, storage and loss shear modulus values are presented in panels *a* and *b*, respectively. Both figures are combined in panel *c*. Letters *a'*, *b'* and *c'* indicate different perspectives of their corresponding panels.

Considering realistic assumptions applicable to most polymer systems, we can mathematically simulate shear modulus values of typical polymer systems as shown in Fig. 8.10. In the model represented in Fig. 8.10, we removed the effect of the limiting shear modulus ($G_0 = Nk_B T$) value at short times (high frequencies); $G_0 = Nk_B T = c^* R T$ is typically equal to 2.44×10^{10} dyn cm⁻² at $T = 293$ K for the first relaxation mode, i.e. $p = 1$, where $c^* \sim 10^2$ mol cm⁻³ is the number of polymeric moles in unit volume and $R = 8.314 \times 10^5$ cm dyn K⁻¹ mol⁻¹ is the universal gas constant. The experimentally more practical target is to establish straightforward correlation between shear modulus components (measured film viscoelastic responses) and temperature variation (controlled variable). This goal can be achieved by first considering the effect of temperature on film relaxation time. At temperatures higher than the glass transition temperature, T_g , the Vogel-Fulcher-Tammann-Hesse (VFTH) equation, $\tau = \tau_0 \exp(1/\alpha T)$ can be used where α is the thermal expansion coefficient with a typical value of ca. 4×10^{-4} K⁻¹. At temperatures below T_g Arrhenius-type behaviour, $\tau = \tau_0 \exp(E_a/RT)$, governs sub-glass relaxation phenomena which are thermally activated. In the models presented in Fig. 8.10, the film relaxation time as predicted by Rouse-Zimm model was used. In this case, Eq. 8.11 simplifies to $\tau_p = \beta/T = 10^{-9}/T$ where $\beta = 6\eta/Nk_B \pi^2 p^2$ using the same assumptions as above for $Nk_B = c^* R$, $p = 1$ and $\eta = 1$ dyn cm⁻² s. Eq. 8.11 was chosen as it applies to all temperature ranges and for a polymer chain subjected to equilibrated diffusive and viscous drag forces (as described in Stokes-Einstein relationship).

As predicted by Eqs. 8.12 and 8.13, the storage, $G'(\omega, T)$, shear modulus values (panels a and a') increases quadratically with the decrease of the experimental timescale until it reaches the limiting value (2.44×10^{10} dyn cm⁻²). Conversely, the values of $G'(\omega, T)$ increase as the temperature is lowered through the decrease in film relaxation time, τ .

Interestingly, the effects of the two variables (ω, T) are constructively coupled at two regions of the shear modulus surface spectrum: i) either at higher temperatures and long experimental timescale ($\omega\tau < 1$) or ii) lower temperature scales and short observational time ($\omega\tau > 1$). Similar behaviour applies to loss shear modulus except that the $G''(\omega, T)$

values go through a maximum point (panels *b* and *b'* of Fig. 8.10) at $\omega\tau = 1$. This means that at long observational times compared with the relaxation time for segmental chain motion, the applied stress is taken up by inter-chain movements (i.e. chains slip past one another); this results in viscous domination. On the other hand, at very short times, polymer chains do not have time sufficient to reorient substantially and move past one another. In this case, the strain is taken up by the individual polymer chains resulting in high modulus, i.e. elastic storage dominating film viscoelastic responses.

Between these extrema, i.e. comparable film relaxation time (temperature effect) and observational timescale (device frequency), the elastic and viscous components of film viscoelastic behaviour are comparable. This is where $G''(\omega, T)$ is maximum at $\omega\tau = 1$ (panels *b* and *b'* of Fig. 8.10).

The extent at which these models apply to our data is an open question. Overall, the effects of temperature and timescale on film structural dynamics in both systems (bulk vs thin) have similar behaviour. The difference is that in classical models, bulk polymer is considered in contrast to the thin surface-confined film we characterise. In addition, these models are based on low-frequency devices, whereas the thickness shear mode (TSM) resonator we use operates in high frequency region. Interestingly, the effective timescale, a ratio of the characteristic timescale, τ , of the diffusion-like motions in the polymer and the experimental timescales, t , of both systems (bulk vs thin) is the same even though the absolute timescales of the film relaxation process in the bulk and thin polymer systems are very different. For example, we consider a bulk polymer film with a thickness of $l = 10^3 \mu\text{m}$, i.e. 1 mm and a thin film with a thickness of $l = 1 \mu\text{m}$ both subjected to a dynamic modulation at very low frequency of $f = 10 \text{ Hz}$ and a high frequency of $f = 10 \text{ MHz} = 10^7 \text{ Hz}$, respectively. The effective timescale, τ/t , of each system can be evaluated as described in Eq. 8.14:

$$\frac{\tau}{t} = \frac{l^2}{D} \bigg/ \frac{1}{\omega} \quad 8.14$$

where D is the diffusion coefficient of mobile species transport within the polymer film and $\omega = 2\pi f$. Comparing between the effective timescales of the two systems, we find:

$$\begin{aligned} \left(\frac{\tau}{t}\right)_{bulk} / \left(\frac{\tau}{t}\right)_{thin} &= (\omega l^2)_{bulk} / (\omega l^2)_{thin} \\ &= [(2\pi)(10)(10^{-1})^2 \text{ cm}^2 \text{ s}^{-1}]_{bulk} / [(2\pi)(10^7)(10^{-4})^2 \text{ cm}^2 \text{ s}^{-1}]_{thin} = 1 \end{aligned} \quad 8.15$$

where the diffusion coefficients, D , cancel out. From this comparison, one can deduce that classic viscoelastic models can be applied to thin electroactive films via device frequency control, i.e. the decrease in film thickness can be compensated by an increase in device frequency.

8.9 The effect of temperature variation on film composition

Since solvent content of the film affects its thermal behaviour (viscoelastic properties), we now focus on the variation of film composition with temperature and potential in electrochemical characterisation experiments. Fig. 8.11 presents the variation of solvent mole fraction, X_S , with temperature as the potential is cycled. The data presented here was analysed gravimetrically though collected in viscoelastic regime (acoustically thick film regime); there was no direct way of extracting the absolute solvent content of the film in the limitation of the technique we employ here (TSM) resonator. Solvent population changes of the film was calculated by simply correlating resonant frequent changes and charge density of film during redox cycling as explained in chapter five. This was achieved by the use of Sauerbrey equation and Faraday law.

In panel *a*, film composition variation as a function of temperature was shown at the extreme ends of film redox states; this figure clearly shows that film solvent content is 20% higher in the oxidised form of the film than the reduced across all the temperature range explored. In panel *b*, the molar fraction changes with potential are presented for individual temperature measurements. By the application of the van't Hoff equation to the data in panel *b*, one can find the enthalpy of solvent and anion transfer as a function of potential; interestingly, the logarithmic nature of the van't Hoff equation allows us

focus on the changes, but not the absolute values of solvent content of the film to obtain the energetics of the system.

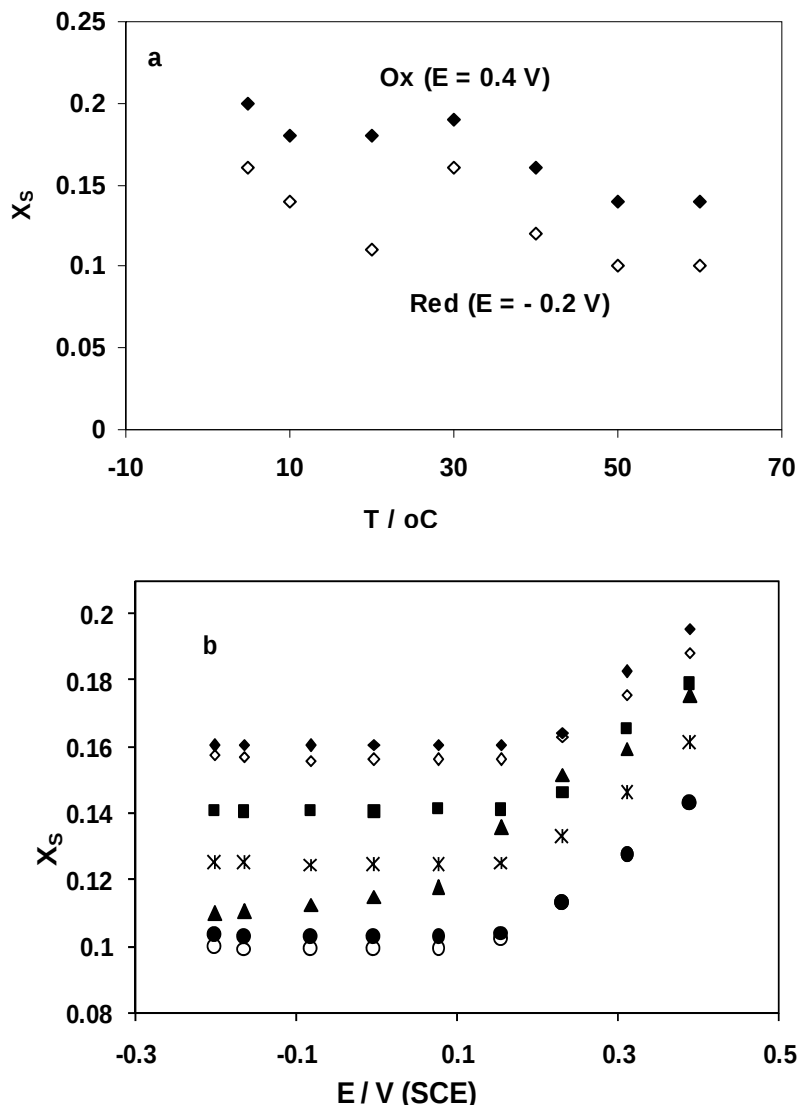


Fig. 8.11: Mole fraction of film solvent content extracted via correlation of resonant frequency changes and film charge density during first redox cycling; the film was deposited and redox-cycled in 1 M HClO_4 . In panel *a*, solvent mole fractions as a function of temperature for the two extrema of film polarisation were shown; $E = -0.2 \text{ V}$ for the reduced film and $E = 0.4 \text{ V}$ for the oxidised. In panel *b*, solvent mole fractions of the system as a function of potential and temperature variation were shown; the symbols $\diamond$, $\blacksquare$, $\blacktriangle$, $\diamond$, $\times$, $\bullet$, and $\circ$ indicate the temperature values of 5, 10, 20, 30, 40, 50, and 60 $^\circ\text{C}$, respectively. From the gradients of the vertical points of panel *b*, one can acquire solvation energetics of the system (Fig. 8.12) at each potential point using van't Hoff's equation as discussed in the text.

The results of solvation enthalpy as a function of potential from the gradients are shown in Fig. 8.12. Surprisingly, the values of solvation enthalpy are exothermic ($-6 \leq \Delta H$ kJ/mol ≤ -3.5) throughout with a little variation with potential, but small in magnitude; similar values of solvation energy, but of opposite sign (endothermic) was found for polyethyldioxythiophene (PEDOT) films though characterised in non-aqueous system (acetonitrile) [17].

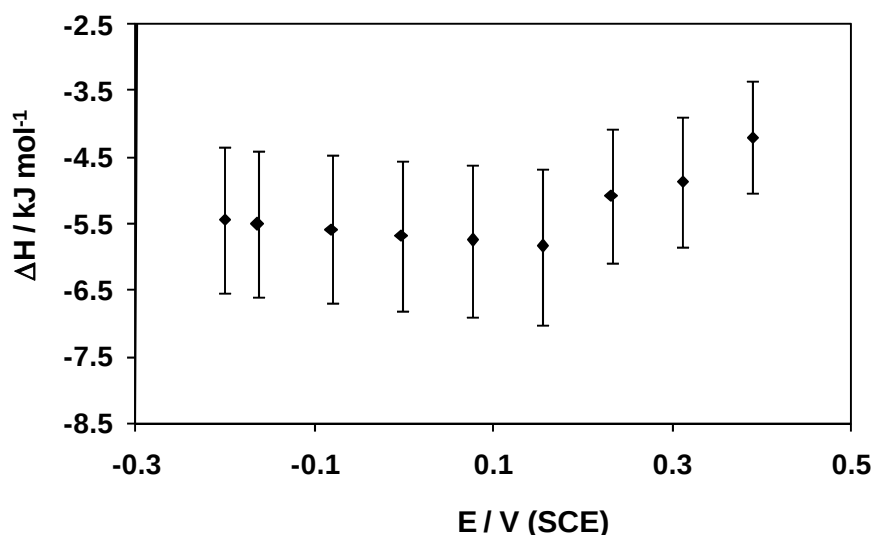


Fig. 8.12: Solvation enthalpy of polyaniline films in aqueous electrochemical systems of 1 M HClO_4 solution. Error bars provide visual guide for the extent of enthalpy variation across the potential scale.

8.10 Summary

In this chapter, viscoelastic behaviour of polyaniline films has been described in unprecedented detail using a combination of potential, temperature and timescale effects. The film was characterised using higher harmonics ($f = 10\text{--}110$ MHz) of a thickness shear mode resonator in potentiodynamic and potentiostatic electrochemical experiments ($-0.2 \leq E/V \leq 0.4$). For the temperature variation, the electrochemical cell was immersed in a thermostat bath. Experiments were performed in an aqueous perchloric acid medium (1 M HClO_4). From qualitative observation of the raw data, the effects of potential,

temperature and experimental timescale were found to be small, medium and dramatic, respectively.

Using WLF and Rouse-Zimm models, we were able to elucidate macroscopic properties of film viscoelastic responses on the basis of molecular level interpretations. These models were developed to explain low-frequency motions of bulk polymers, but underexplored in the context of thin films deposited on electrode surfaces. A master relaxation curve was constructed by shifting isothermal individual data on a logarithmic timescale using the principle of “*time-temperature superimposition*”. Experimentally determined shift factors enabled the extraction of the activation energy associated with film relaxation processes. By fitting experimental data to WLF equation we were also able to calculate the glass transition temperature, T_g , of polyaniline films under electrochemical conditions, the fractional free volume, f_g , of the film near the glass transition, and the thermal expansion coefficient, α_T , above the glass transition temperature. In an attempt to acquire the solvation enthalpy of polyaniline film, solvent mole fractions (gravimetrically calculated) and temperature variation were correlated. With help of the van’t Hoff equation, we extracted the solvation energy of the system, $\Delta H = -3$ to -6 kJ mol⁻¹. In contrast to PEDOT films, the solvation energy of polyaniline films was found to be exothermic. Though PEDOT experiments were performed in acetonitrile solutions, and polyaniline in aqueous media, the solvation energetics (endothermic vs. exothermic) of the two systems indicate that film composition has a greater effect on film structural dynamics in PEDOT than polyaniline films, i.e. more energy input is needed.

In a novel approach, we have mathematically modelled polymer relaxation processes based on Maxwell-Wiechert physical models. The Rouse-Zimm model was used to describe the underpinning aspects of film viscoelastic responses at a molecular level. Although these models were initially developed for bulk polymers we use them to elucidate viscoelastic responses of thin polymer films deposited on electrode surfaces. The effects of temperature and timescales are coupled in two ways. At longer timescale or higher temperature, viscous behaviour of the film is predominant. At very short times

or lower temperatures, elastic behaviour of the film is predominant. Between these extrema both viscous and elastic behaviours of the film are comparable; this where the maximum peak of $G''(\omega, T)$ was observed. The activation model was also applied to the polyaniline data. This application requires very high activation energy for film relaxational processes and was attributed to cross-linking effect of water between polymer chains.

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Chapter Nine**Electrode Surface Modification of Flavin-Functionalised SAMs****9.1 Overview**

In contrast to previous chapters, the study is shifted in this chapter to the surface modification of electrodes with self-assembled monolayers (SAMs) using multivalent supramolecules. The application of supramolecular chemistry as a tool for the formation of smart surfaces with switchable properties and function is a fast growing field [1]. In particular, versatile properties of supramolecules such as reversibility, directionality and specificity *via* non-covalent surface modification provide an attractive bottom-up means of creating novel molecular machines and devices [2]. In recent years, it has been proven that the use of multivalent guest species is one particular promising method of surface modification [3-5]. In this regard, the multivalent nature of guest species improves the relatively weak binding events associated with monovalent supramolecular interactions; the multiple binding capabilities of the guests promote their incorporation into robust devices [3-5]. The concept of molecular printboards was developed by Reinhoudt and Huskens whereby well-ordered cyclodextrin-functionalised SAMs have the propensity to bind to appropriately functionalized multivalent dendrimer species (ferrocene-terminated dendrimers) [6-9].

In collaboration with the group of Graeme Cooke (Glasgow University), we carry out in this research gravimetric studies of the adsorption/desorption of 2,6-diamidopyridine dendrimer (16-branch dendrimer) on flavin-functionalised SAMs immobilized on electrode surfaces and the energetics associated with these systems. The idea is to

explore the adsorption of the dendrimer on flavin derivative surface via non-covalent hydrogen bonding followed by the desorption of the DAP dendrimer from the surface by the action of a small molecule “thymine”. The strategy here is to investigate the “*lock and key mechanism*” of these systems which mimic the behaviour of the ubiquitous flavoenzymes in biological processes [10, 11].

9.2 Experimental Procedures and Instrumentation

The solvent used throughout was CH₂Cl₂ (Fisher Scientific, 99%; used as received). Solutions for preparation of monolayer flavin-modified surfaces contained 1 mM each of flavin disulfide and butyl disulfide (both of these materials were provided by Graeme Cooke). Solutions for studying dendrimer adsorption contained 0.051, 0.0691, 0.0923, 0.11 and 0.144 mM DAP. Solutions for removal of surface-bound dendrimer contained 0.95, 3.8, 8.1, 13.8 and 19.5 mM thymine.

The QCM instrumentation and cell have been described in detail in chapter three. The quartz resonators were unpolished AT-cut 10 MHz quartz crystals (International Crystal Manufacturing Co., Oklahoma City, USA) sandwiched between two gold electrodes with a piezoelectrically active area of 0.21 cm². Acoustic wave device data collection (crystal admittance spectra and frequency shift) were controlled via a computer running the HP VEE program and connected to the network analyser as described in chapter three.

Adsorption and desorption of the dendrimer were determined via the resonant frequency shift of the quartz crystal, Δf (Hz). For such extremely thin (acoustically thin) films, the resonator responds gravimetrically [12-14]. Thus, the measured frequency shifts were converted to areal mass density changes, Δm (g cm⁻²), using the Sauerbrey equation [12-14]:

$$\Delta f = -\left(\frac{2f_0^2}{\rho_q V_q}\right)\Delta m = -C_1\Delta m \quad (9.1)$$

where ρ_q is the density of quartz, v_q is the wave velocity within the quartz crystal, f_0 is the base frequency (here, nominally 10 MHz), and C_1 represents the collected (known) constants of the quartz crystal.

Deposition of flavin monolayers was accomplished by exposing the Au electrode to a solution containing both flavin disulfide and butyl disulfide (each 1 mM) for 18 - 24 h. Gravimetric assays of DAP dendrimer adsorption and thymine-induced desorption were obtained by monitoring the resonant frequency shift and admittance spectra at 30 s time intervals. The absence of resonant admittance changes confirms the absence of film viscoelastic effects (stacking complications observed for this system). The frequency responses to changes in solution composition reached equilibrium values after a few minutes (see Fig. 9.2, below); we do not address transient kinetic or mass transfer effects.

9.3 Adsorption and Desorption Processes of the DAP dendrimer

QCM frequency response data were obtained for the binding to flavin-functionalised Au electrodes of DAP dendrimer and its subsequent desorption via binding to solution phase thymine; the structure and chemical formula of these materials are shown in Fig. 9.1. The effects of concentration of both the dendrimer (0.051 – 0.144 mM) and thymine (1 – 20 mM) were explored. These generated isotherms allowed evaluation of equilibrium constants and energetics for adsorption/desorption. The bulky and multifunctional nature of the dendrimer suggests that ideal (Langmuirian) adsorption would be unlikely; exploration of a range of isotherm models revealed that site-site interactions are significant, particularly at high coverage.

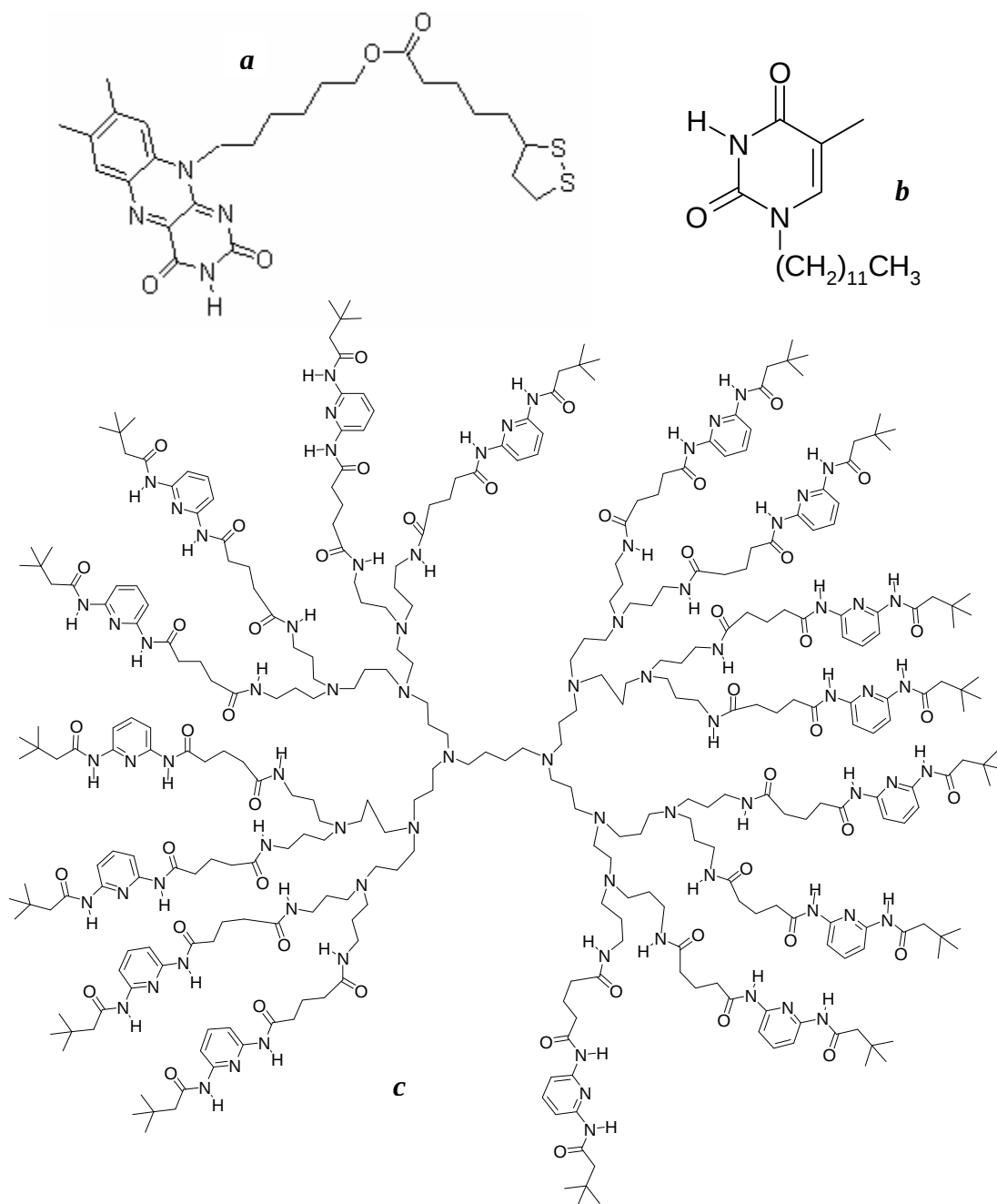


Fig. 9.1: The chemical structure of flavin disulfide (a), thymine derivative (b), and 2,6-diamidopyridine dendrimer (c).

Fig. 9.2 shows the gravimetric response to binding to the flavin-modified surface of DAP dendrimer present at various concentrations in solution, and subsequently to its removal from the surface by solution-phase thymine at progressively higher concentration. The experiment essentially provides progressively more favourable environments for the dendrimer: free in solution, bound to the surface-attached flavin, and bound to the solution-phase thymine. Thus, the first half of the experiment probes the energetics of DAP free in solution vs. flavin-bound on the surface, and the second half of the experiment probes the energetics of DAP flavin bound on the surface vs. thymine-bound in solution. The movement of dendrimer molecules between these environments is assayed by the changing inertial mass of the electrode: it increases progressively as more flavins acquire DAP, then decreases progressively as thymine molecules pick off the DAP from the surface. We now proceed to quantify these processes. The first important observation is that the efficiency of thymine-driven stripping of the DAP from the surface is 98.8%.

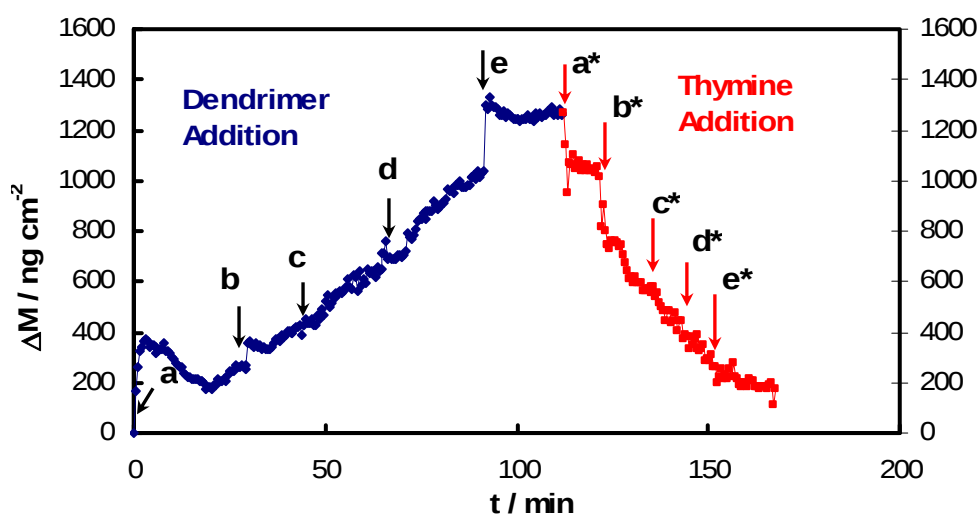


Fig. 9.2: QCM resonant frequency response to adsorption and desorption of DAP dendrimer on flavin-functionalised Au. During adsorption, thymine concentration was zero and dendrimer concentration (μM) was: a: 0; b: 51; c: 69.1; d: 111; e: 144. During desorption, dendrimer concentration was zero and thymine concentration (mM) was: a*: 0.95; b*: 3.8; c*: 8.1; d*: 13.8; e*: 19.5.

Fig. 9.3 shows the equilibrium surface coverage (θ) of DAP at various points during the experiment of Fig. 9.2. Panel *a* shows this as a function of dendrimer concentration during DAP adsorption from solution. Panel *b* shows this as a function of thymine concentration during DAP desorption from solution. The fractional coverage was determined gravimetrically (see Eq. 9.1) by taking the ratio of the mass change (Δm) at any given concentration, c , with respect to the limiting mass change (Δm_∞) at high concentration (here, $c = 1.44$ mM). In applying this procedure to the DAP adsorption process, we avoid very high concentrations ($c \gg 2$ mM), where multi-layer formation might complicate the issue.

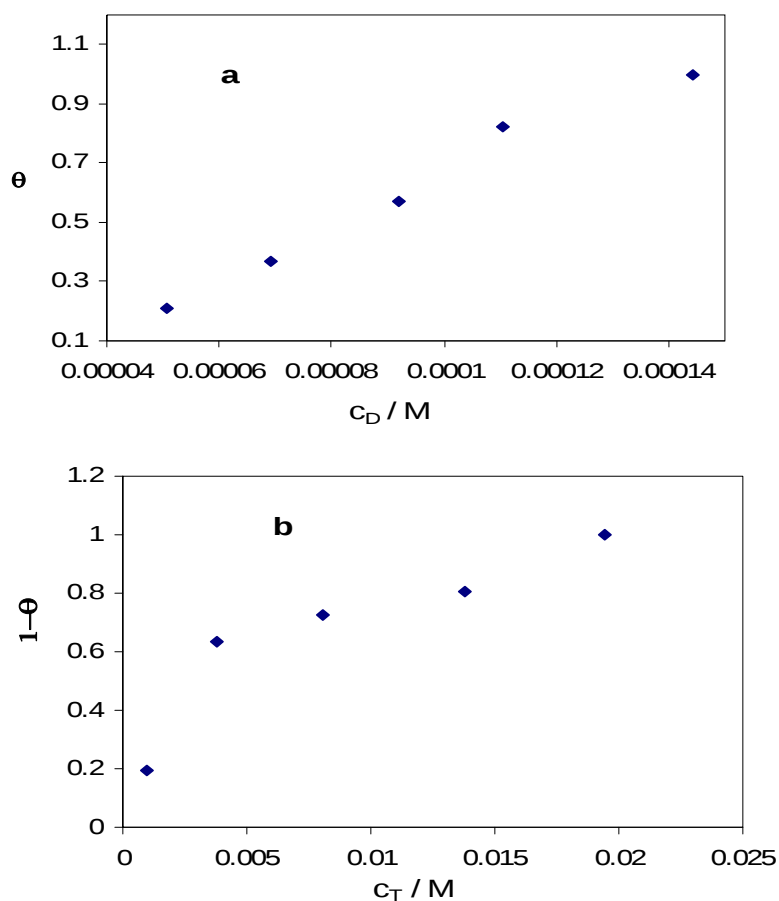
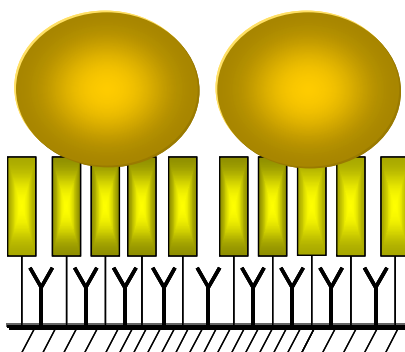


Fig. 9.3: Changes in surface coverage of dendrimer during adsorption (panel a) and desorption (panel b) as functions of solution concentration of dendrimer (c_D) and thymine (c_T), respectively. Data from fig. 1.

At the highest concentration of dendrimer used, the maximum increase in electrode mass (1.26 μg) corresponds to a limiting surface population density of $\Gamma_D = 0.2 \text{ nmol cm}^{-2}$. Converting the electrode mass change associated with flavin immobilization (4.84 μg) to a surface population density (based on the known butyl disulfide / flavin disulfide stoichiometry) gives $\Gamma_F = 6.45 \text{ nmol cm}^{-2}$. The ratio of these two populations is $\Gamma_D / \Gamma_F = 0.03$, i.e. one dendrimer for every ca. 30 bound flavin units. Taking a simple geometrical model (see scheme 9.1) of the dendrimer as a sphere of approximately unit density, the projected area of a single dendrimer unit is 6.09 nm^2 . Taking the analogously simple geometric view of the flavin units as edge-on rectangular slabs, their projected area is 0.27 nm^2 . The ratio of these two predicts that Γ_D / Γ_F should be ca. 0.04. In reality, the packing arrangements are not constrained to be highly regular, but it is clear that a simple model based on the relative sizes of the flavin binding site and the target dendrimer can explain their relative surface populations. It should be emphasised that the relative populations do not provide an estimate of the number of dendrimer-flavin interactions; geometric constraints suggest that there are probably around five per dendrimer unit.



Scheme 9.1: Representation of DAP dendrimer interaction with flavin/butyl disulfide self-assembly on electrode surface.

9.4 Coverage Dependence of Binding Processes

We now turn to the concentration dependence of the binding process, represented by the QCM response at lower concentrations. For the purpose of investigating the binding capability of the flavin-functionalised SAMs towards the dendrimer as well as the erasure efficiency of thymine, the data of Fig. 9.3 were fitted to a variety of model isotherms.

The simplest model, in which everything behaves in an ideal (non-interacting) manner is the Langmuir isotherm. The conventional (θ^{-1} vs. c^{-1}) linearised plot for this model is shown in Fig. 9.4, panel *a* for adsorption and panel *b* for desorption. While the plot works reasonably well at low concentration (i.e. low coverage, where adsorbates are far apart), it is a poor representation at high concentration (i.e. high coverage, where adsorbates are in close proximity); the model requires an intercept of 1 which is not the case here. We deduce that there are interactions between adsorbate molecules, the significance of which increase with concentration.

We therefore explored the effectiveness of a range of isotherms that, in various ways, relax the stringent constraints of the Langmuir isotherm. These included the Frumkin, Temkin, Freundlich, Flory-Huggins and El-Awady isotherms, of which the Frumkin model, represented in Fig. 9.5, proved to give the best empirical fits.

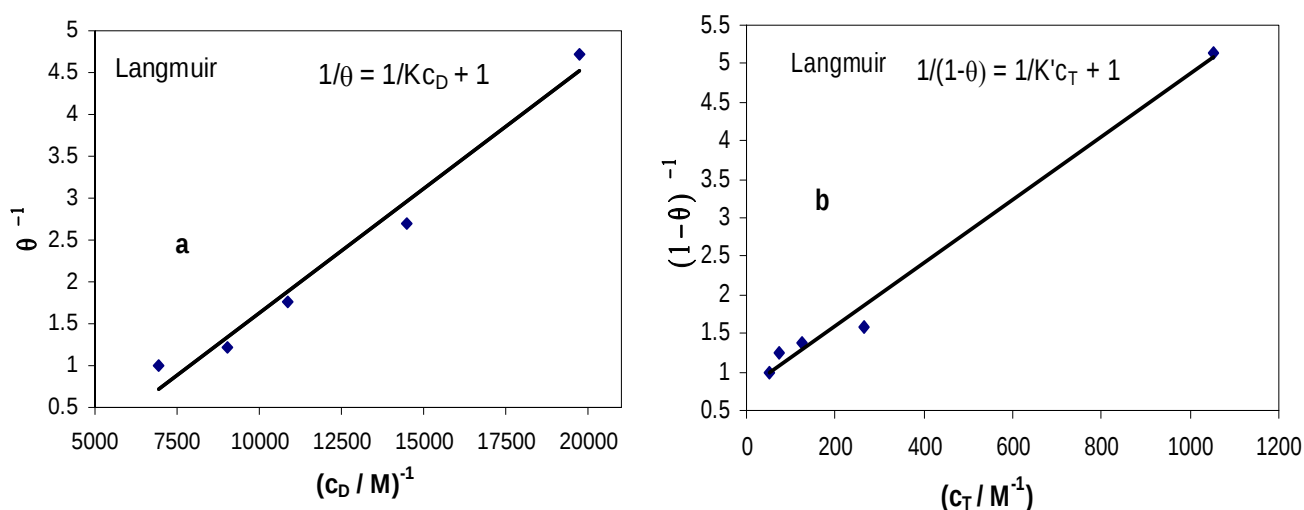


Fig. 9.4: Langmuir isotherms for adsorption (panel *a*) and subsequent thymine-induced desorption (panel *b*) of dendrimer.

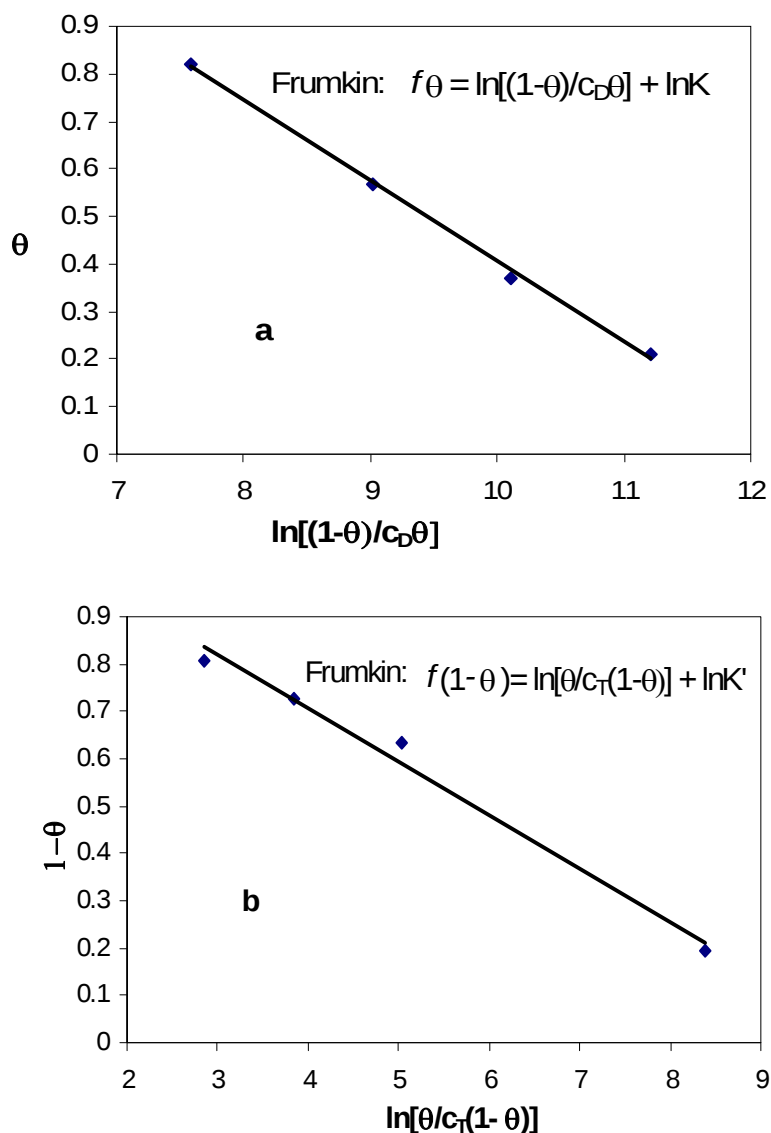


Fig. 9.5: Frumkin isotherms for adsorption (panel a) and subsequent thymine-induced desorption (panel b) of dendrimer.

9.5 Energetics Associated with Adsorption and Desorption DAP Dendrimers

For the adsorption of DAP onto the flavin surface, the intercept and slope, respectively, of Fig. 9.5 (panel a) yield an adsorption equilibrium constant, $K = 2.3 \times 10^5 \text{ M}^{-1}$ and interaction parameter (also known as Frumkin parameter), $f = -0.17$. Analogously, the desorption from the flavin surface onto the thymine in solution is characterized by $K = 2.9 \times 10^4 \text{ M}^{-1}$ and $f = -0.11$. The negative sign associated with the f -value signals

repulsive interactions between adsorbates. This is consistent with the direction of curvature in the Langmuir plot (Fig. 9.4), where the concentration required to achieve a given coverage is higher than predicted for the case of zero interaction energy.

The associated Gibbs adsorption (or desorption) energies can be calculated from:

$$\Delta G_{ADS}^o = \Delta G_{\theta \rightarrow 0}^o - 2RTf\theta \quad (9.2)$$

where the first term on the right hand side of Eq. 9.2 represents the adsorption Gibbs energy in the absence of site-site interactions and

$$\Delta G_{\theta \rightarrow 0}^o = -RT \ln K \quad (9.3)$$

The second term in Eq. 9.2 provides the contribution to the overall Gibbs energy from the adsorbate-adsorbate interactions. In the present example, the negative value of f means that the Gibbs energy is made more positive (i.e. less favourable), so that the apparent value of K is progressively decreased with increasing adsorption. Applying Eq. 9.3 to the data of Fig. 9.5, we find that the low-coverage limit of the Gibbs energy for dendrimer adsorption is $-30.1 \text{ kJ mol}^{-1}$; the corresponding Gibbs energy for thymine-induced desorption is $-25.0 \text{ kJ mol}^{-1}$.

9.6 Summary

In this chapter, we have studied the surface modification of flavin-functionalised self-assembled monolayers and their interaction with DAP dendrimer. The hypothesis is to explore the “*lock and key*” mechanism of the system as dendrimer is adsorbed on the electrode surface via non-covalent hydrogen bonding and subsequently detached by the action of thymine-induced desorption process. Through gravimetric measurements and visual geometrical model, surface populations of flavin derivative SAMs and the DAP dendrimer were calculated. This allowed us to estimate the number of dendrimer-flavin interactions which was estimated to be ca. five per dendrimer unit.

For the purpose of binding capability of flavin-functionalised SAMs towards the dendrimer, a variety of adsorption isotherm models were investigated. In contrast to the predictions of the Langmuir model (in which everything behaves in an ideal manner), fitting experimental data deduced interactions between adsorbate molecules significantly increasing with concentration (surface coverage). Among the number of models explored, the Frumkin model was found to give the best empirical fit to the experimental data. Quantitatively, the adsorption equilibrium constant and the interaction parameter (Frumkin parameter) of DAP dendrimer on flavin surface were $K = 2.3 \times 10^5 \text{ M}^{-1}$ and $f = -0.17$, respectively. For the desorption process via thymine in the solution phase, the system was characterised by $K = 2.9 \times 10^4$ and $f = -0.11$. Consistent to the deviation of the system from Langmuir model, the negative signal of Frumkin parameter signifies that the nature of adsorbate-adsorbate interactions is in a repulsive mode. With respect to the energetics associated with the surface coverage of DAP dendrimer on flavin surface and its subsequent desorption, it was found that the Gibbs energy for dendrimer adsorption to be $\Delta G = -30 \text{ kJ mol}^{-1}$. Analogously, the Gibbs energy associated with corresponding thymine-induced desorption process was calculated to be $\Delta G = -25 \text{ kJ mol}^{-1}$.

9.7 References

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Chapter Ten

General Conclusions and Future Work

10.1 Conclusions

10.1.1 Overview

In this thesis, the central theme of the research undertaken has focused on the broad issue of modified electrodes with both self-assembled monolayers (SAMs) and electroactive polymer multilayers. Potential applications of modified electrodes in a range of physico-chemical disciplines were reviewed in chapter one. The novelties of the work carried out here are demonstrated in two areas: i) gravimetric investigations of thin polymer films and self-assembled monolayers (SAMs), and ii) viscoelastic studies of conducting polymers at an unprecedented depth of analysis and interpretation.

In gravimetric studies, the aspects explored include: i) the mechanistic interpretation of mobile species (ions, solvent and/or neutral species) exchange between surface immobilised electroactive films and adjoining electrolyte solutions in electrochemical systems, ii) theoretical modelling of ion and solvent population within electroactive films under separate and/or combined thermodynamic and kinetic controls, and iii) the adsorption/desorption mechanisms of dendrimer species on/from surface-confined self-assembled supramolecules and their associated energetics. For mobile species transfer studies, the system explored was thin polyaniline films in 1 M HClO₄ solutions. The techniques used were combined electrochemical quartz crystal microbalance (EQCM) and cyclic voltammetry. Correlation between the resonant frequency changes of EQCM and the charge density of cyclic voltammetry enabled one to separate ion and solvent

dynamics. For the adsorption/desorption process, 2,4-diamidopyridine dendrimer in dichloromethane solution was adsorbed/desorbed on/from flavin-functionalised self-assembled monolayers on gold electrodes. The dendrimer was stripped off the surface by the action of the small molecule thymine. The quartz crystal microbalance (QCM) was employed for the characterisation of the system and the outcome was quantitative interpretation of flavin-dendrimer interaction data.

In viscoelastic investigations, the focus was: i) the study of the evolution of film viscoelastic properties during electrochemical deposition (as the polymer film progressively grows in potentiodynamic experiments); shear moduli data were used as quantifying parameters of film structural dynamics and appraised against potential and film thickness; ii) the effects of anion identity on polymer viscoelastic behaviour during electrochemical deposition of films and during film redox cycling in monomer-free electrolyte solutions. In a further characterisation approach, film viscoelastic response to a medium different to that of deposition was tested. In this regard, viscoelastic properties of thin polyaniline films were investigated for the first time. The effects of different anions on polyaniline mechanical properties during deposition and redox cycling were discovered to be substantial. The outcome was consistent with the results reported for the effects of the same electrolytes on film morphological features [1].

In a new approach, film structural dynamics were explored via shear modulus measurements as a function of interfacial potential, temperature and experimental timescale. Electrochemical methods coupled with the *in situ* thickness shear mode (TSM) resonator operating at high frequencies (both fundamental and odd harmonics) were exploited for the characterisation of the system. The data collected by using these combined techniques enabled us to explore, for the first time, the fundamental aspects underpinning the macroscopic behaviour of polymer film viscoelastic responses. Molecular level interpretations were elucidated with help of molecular theory models initially developed for bulk polymers, namely Rouse-Zimm, WLF, and activation models. The principle of “time-temperature superimposition” was applied to polyaniline

viscoelastic data and the master relaxation curve was constructed. The outcome was the determination of temperature and timescale dependent parameters of polyaniline films.

10.1.2 General Outcomes

The visualisation and diagnostics of mobile species dynamics across the film/solution interface in electrochemical systems were theoretically modelled on the basis of gravimetric studies; but other techniques could be used to provide film composition. Redox-driven ion and solvent composition of electroactive films were represented in 3D (E, Q, Γ_s) compositional space. In this 3D representation, the variables controlled (E) and observed (Q, Γ_s) represent the interfacial potential, charge response and mass response in EQCM experiments. The strategy adopted was to identify different behavioural patterns of mobile species transfers on the basis of experimental data.

It was found that the 3D representation provides immediate visual recognition of theoretically distinct conditions, i.e. the separation between thermodynamic and kinetic cases. In the thermodynamic case, the direction and extent of curvature (or otherwise) in Γ_s - Q plots provides insight into solvation non-idealities. In the simple ideal scenario, film solvent content is linearly related to charge density, i.e. single-valued, obeying Nernst equation. In the kinetic cases, comparison of hysteresis in the Q - and Γ_s -responses allows one to distinguish slow coupled electron/counter ion transfer and slow solvent transfer (timescale effects). In addition, the appearance of hysteresis in the Q - Γ_s plane was used as a diagnostic between kinetic effects and non-ideal thermodynamic curvature. The more practically plausible scenarios of complex interplay of non-ideal thermodynamics and kinetics in chemical systems were represented in unified models. Thermodynamic non-idealities may be associated with electrostatic interactions of mobile species and film redox sites. Under kinetic conditions, the temporal resolution of mobile species transfers and the mechanistic routes competing to bring the system to a new equilibrium state were studied. The outcome was the optimisation of EQCM experiments; at high scan rates, solvent entry/exit is the slowest step and at slow scan rates, the electrode dynamics are the rate limiting step, i.e. the coupled ion/electron determine the kinetics of the system.

For the identification of changes in behaviour at partial conversion during film redox transformations, more sensitive differential ion:solvent flux ratio, ρ , representations were introduced. These models provide immediate identification of the mobile species (solvent and counterion) that dominates film compositional changes at any given potential point in the transient. In the specific case of EQCM experiments, the “ion:solvent” flux ratio, ρ , representation can identify the dominant instantaneous contributor to mass flux; for $\rho > 1$, ion transfer is dominant and for $\rho < 1$, solvent transfer is dominant. This approach has the general utility in mechanistic diagnosis of the rate limiting step.

Gravimetric studies of polyaniline films in perchloric acid solutions were carried out. The data acquired were applied to the theoretical models. This revealed that considerably more information is contained within EQCM responses than commonly extracted. By simply plotting raw experimental data in 3D format one can distinguish thermodynamic from kinetic control for the individual transfers of ion and solvent. In the case of solvent transfer, it was possible to use experimental data to identify and quantify non-ideal behaviour of thermodynamic complexities. Application of the model’s diagnostic criteria has indicated that film solvent population was in equilibrium on the timescale of slow scan voltammetry, but showed thermodynamic non-idealities. Hysteresis in the film ion population was attributed to signal failure of the film redox state to maintain equilibrium with the applied potential.

For the first redox process of polyaniline films in 1 M HClO₄ solution, electroneutrality maintenance was assumed to be satisfied by a mixed transfer of anion and proton; anion exchange alone would require a non-monotonic transfer of solvent. In order to compensate for electroneutrality, film mass and charge responses were best described by a mechanism in which the early stages of film oxidation were associated with proton movement (exit) and the latter stages with perchlorate anion transfer (entry); perselectivity fails at high electrolyte concentration and low charge density. This elucidation was consistent with the more physically realistic scenario of monotonic

solvent transfer in a given switching direction, namely entry throughout film oxidation and exit throughout film reduction.

For the first time, viscoelastic studies of electrochemically deposited polyaniline films have been investigated using a high frequency thickness shear mode (TSM) resonator. Admittance spectra of the TSM resonator were used to follow the extent of film electrodeposition and film viscoelastic properties during polyaniline electrodeposition. The transition from acoustically thin films at low deposition charge to acoustically thick films at high deposition charge was observed by the acquisition of polyaniline admittance spectra. This means that frequency responses within the acoustically thick film associated with significant energy dissipation (decreased peak admittance) were interpreted viscoelastically. The acoustic admittance spectra were recorded simultaneously with voltammetric data for multiple deposition cycles. Full data analyses resulted in a set of film storage and loss shear moduli as a function of potential (within a given deposition cycle) and number of deposition cycles (thickness dependence). Values of the acoustic decay length (a material property) and the acoustic phase shift (a function of film properties and film thickness) were calculated using shear moduli data; these values were utilised to validate the semi-infinite regime in which viscoelastic properties of the film were determined. The decay length was always significantly larger than the film thickness and the acoustic phase shift was found to be below the value of $\pi/2$ associated with film resonance (appendix A) throughout the experiments performed; the model and analysis used were therefore appropriate.

The effects of anion identity on polyaniline viscoelastic responses were examined. The range of dopants considered was perchlorate, sulphate and chloride anions. It was found that the shear modulus components are largest (i.e. the films are stiffest and have greatest loss) in perchlorate medium; the values of shear modulus components in sulphate and chloride media were similar to each other, but smaller in perchlorate medium. This was consistent with a previous empirical classification of polyaniline dopants placing perchlorate anion in one category ("class 1") that is characteristic of compact films with

slow ion transport rates, and sulphate and chloride anions in another category (“class 2”) that is characteristic of more diffuse films with fast ion transport rates.

Film “memory” of deposition condition (e.g. via templating or other structural feature of anion/film combination) was tested by changing the anion present during film redox cycling from that used during film deposition. Through one test case involving chloride-prepared films subsequently exposed to sulphate, it was found that redox cycling in an electrolyte containing a different anion to that used for film deposition resulted in a rapid shift in viscoelastic properties towards those of the ambient medium. This behaviour of film viscoelastic response can be associated with rapid and complete exchange of dopant within a redox cycle.

In an unprecedented novel approach, polyaniline viscoelastic properties were characterised as functions of potential, temperature and timescale using both the fundamental resonance and higher harmonics of the acoustic wave resonator. The use of the time-temperature superimposition principle has enabled us to construct a master relaxation curve for polyaniline. On the basis of WLF, Rouse-Zimm, and activation models, macroscopic properties of film rheological dynamics were rationalised at the molecular level. Experimentally determined “*shift factors*” enabled extraction of the activation energy associated with film relaxation processes. By fitting data to the WLF equation (combined with its empirical variant of the Doolittle equation), the glass transition temperature, T_g , fractional free volume, f_g , at T_g and the thermal expansion coefficient, α_T , of polyaniline films in 1 M HClO_4 aqueous solution were determined. It was found that the fractional free volume, $f_g = 0.074$, of polyaniline was high (cf. universal value of most polymers, $f_g = 0.025$). This was attributed to the direct effect of film composition on the microscopic behaviour of viscoelastic responses. It was also found that the thermal expansion coefficient, $\alpha_T = 4 \times 10^{-4} \text{ K}^{-1}$, of the polyaniline film was relatively smaller than the typical value of $\alpha_T = 6\text{--}10 \times 10^{-4} \text{ K}^{-1}$ for most bulk polymers. This shows that polyaniline structural dynamics are not strongly influenced by thermally activated processes in the temperature range studied. Using the van’t Hoff equation, the solvation energy of the system was also calculated. In contrast to PEDOT films, the

solvation enthalpy of polyaniline films was found to be exothermic across the first redox conversion for all states.

Gravimetric measurements of 2,4-N-diamidopyridine dendrimer adsorption/desorption on/from flavin-functionalised surfaces were made. The experimental data were fitted to a variety of isotherm models of which Frumkin model was found to give the best empirical fit. Through the use of this model, the adsorption/desorption equilibrium constants and the interaction parameter were calculated. In addition, the associated energetics of the system were obtained from the equilibrium constants and the Frumkin parameter. The high value of the adsorption constant, $K_{ad} = 2.3 \times 10^5 \text{ M}^{-1}$, proved the strong interaction between the 2,4-N-diamidopyridine dendrimer and flavin-functionalised surfaces. Analogously, the desorption constant, $K_{des} = 3.0 \times 10^4 \text{ M}^{-1}$, was found to be high; this was measured by the action of thymine. The interaction parameter associated with the adsorption processes was small in magnitude, but negative ($f_M = -0.11$); this showed repulsive adsorbate-adsorbate interaction consistent with the deviation observed in the application of Langmuir model to the data. The chemical insight is that the system can be used as a tool for the formation of smart surfaces with switchable properties and function. The ultimate goal is to mimic the ubiquitous enzymoflavin behaviour in biological systems.

10.2 Future Work

For the future work, we recommend the extension of the work carried out in this research project to further understand the direct relationship between structure and composition of electroactive films. Sophisticated analysis and rigorous explanation of both experimental and theoretical modelling of structure-composition relationship are required. Among the aspects to be explored is the establishment of quantitative association between solvent compositional changes and film structural dynamics. The effects of different anions (both small and polymeric) on film solvent content and matrix dynamics need to be investigated. The determination of absolute solvent population associated with the nature of anion present during film electrodeposition and/or redox cycling is equally important for the improved understanding of the mechanical modulation of thin polymer films. The

latter problem can be unravelled by the use of neutron reflectivity (NR). NR is also capable of exploring the spatial (in)-homogeneity of redox active sites within electroactive films. Correlation between NR experiments and thickness shear mode (TSM) resonator operating in high frequency mode can yield quantitative correspondence of film structural dynamics (shear moduli measurements) and film solvent content. By using AFM, one can correlate surface morphological changes with swelling/de-swelling of the film due to film composition and thickness.

The determination of these aspects is crucial for the sensor/acoustic wave device performance and prerequisite to the practical applications of conducting thin polymer films. To be more specific, biomedical sensor behaviour is known to be strongly influenced by the morphology and the surface geometry of the bilayer film [2]. In electrocatalysis, the redox sites of the conducting polymer act as clean catalyst where reagents diffuse into the bulk of the film instead of the reaction taking place at the film/solution boundary [3-5]. Without full insight of the material behaviour, the applicability of their use may thus turn out to be difficult.

10.3 References

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Appendix A: Film Resonance

Film resonance is a dramatic phenomenon that occurs for specific combination of film properties, sample size and observational frequency. This behaviour of film dynamics is observed when the phase shift of the film reaches $\pi/2$ radian (i.e. 90°) resulting in constructive acoustic wave propagation across the film and the underlying quartz crystal; the round trip of phase shift between outgoing and reflected waves becomes 2π . The manipulation of the phase shift can be achieved by changing film rheological properties via control of film thickness or temperature variation. The data shown below was collected for polyaniline film deposited in 1 M HCl solution. The interpretation of the figures and the details of the experiment performed will appear in later publications.

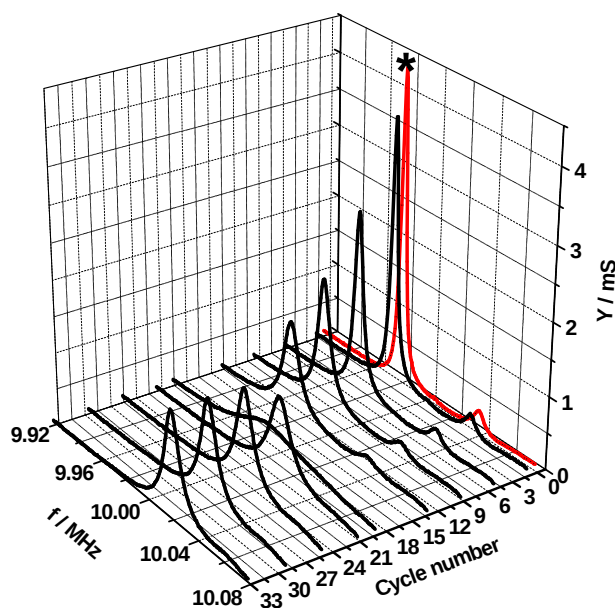


Fig. A1: The admittance spectra of potentiodynamically deposited polyaniline film in 1 M HCl solution at resonator fundamental frequency (10 MHz) with a potential range of $-0.2 \leq E/V \leq 0.9$ and scan rate of $\nu = 10 \text{ mV s}^{-1}$. The admittance spectrum of the bare electrode in solution is shown and marked with asterisk. As the film thickness increases in successive deposition cycles the peak admittance diminishes progressively and shifts to the lower frequency region. After cycle eighteen the amplitude of peak admittance re-emerges and dramatically shifts to higher region of the frequency. This is when film resonance occurs.

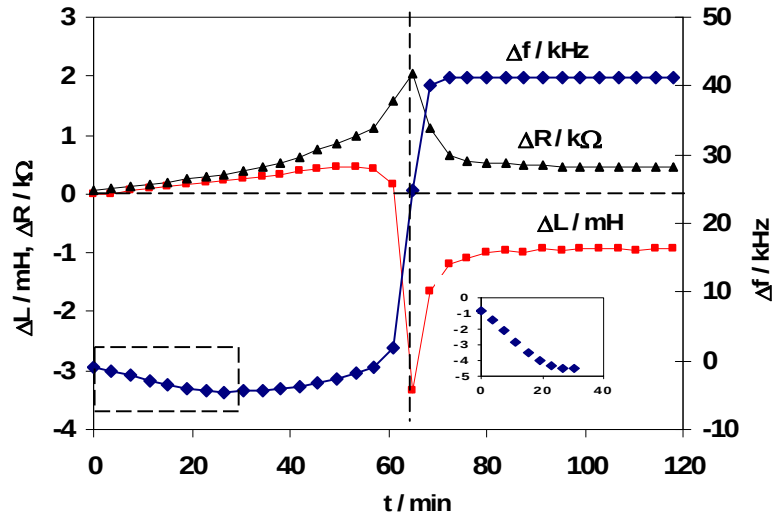


Fig. A2: Film parameters of inductance, resistance and changes in film resonance frequency as a function of experimental time (deposition timescale) are shown. These parameters were extracted by applying lumped element electrical equivalent model (also termed Butterworth van Dyke model) to the raw experimental data shown in Fig. A1.

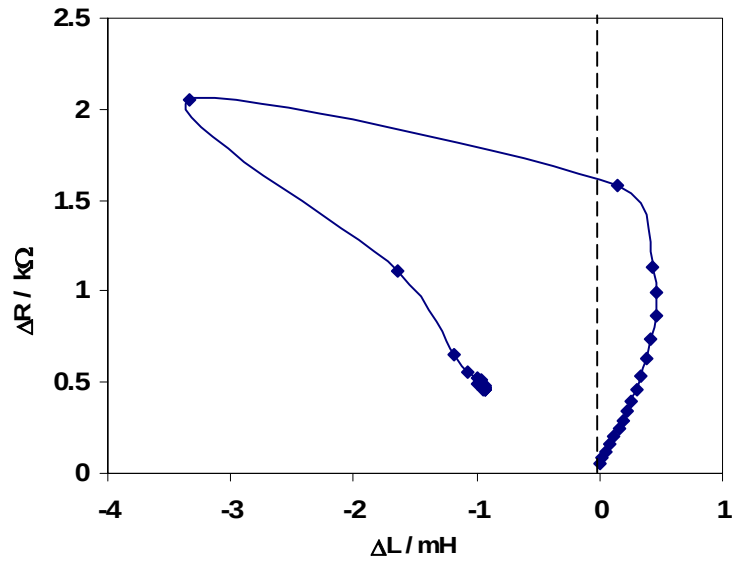


Fig. A3: The plot of resistance values, ΔR , of the film deposition (dissipation parameter) against the corresponding inductance, ΔL , of the film (mass accumulation). Obvious correlation of ΔR and ΔL were observed as the film thickness increases after each deposition cycle. At film resonance, dramatic increase of film resistance and decrease of inductance occur.

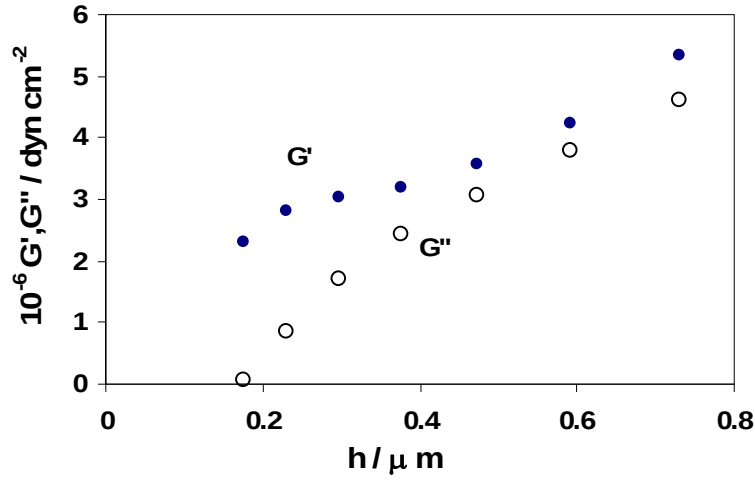


Fig. A4: Shear modulus data of the film before film resonance as a function of the progressively growing film thickness. The procedures of shear modulus extraction and film thickness calculation were explained in the experimental chapter (chapter three).

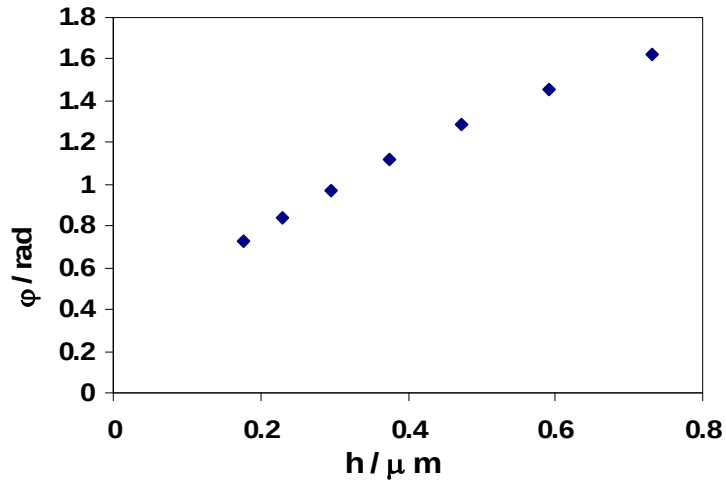


Fig. A5: Phase shift of the acoustic wave propagating across the film plotted vs film thickness. The phase shift reaches 90° ($\pi/2$ rad) significantly showing the dramatic behaviour of film resonance. The phase shift data (a function of both film properties and thickness) were calculated using the shear modulus values of Fig. A4 and the film thickness.

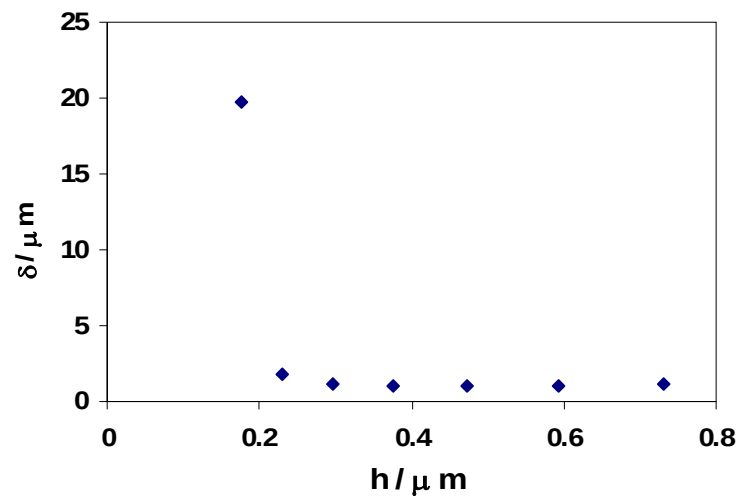


Fig. A6: The decay length of the acoustic wave across the film as a function of film thickness. The decay length (a function of film properties) was evaluated using the shear modulus data in Fig. A4.

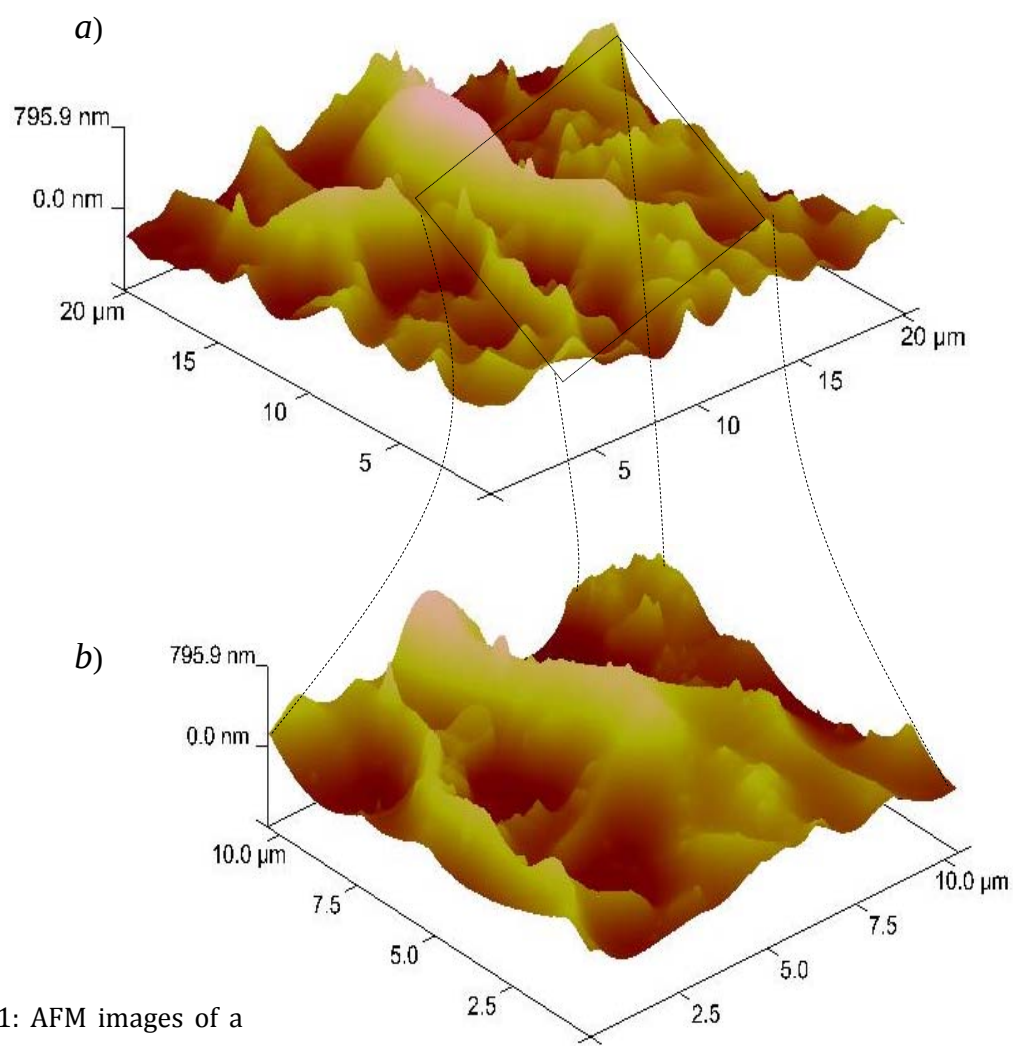
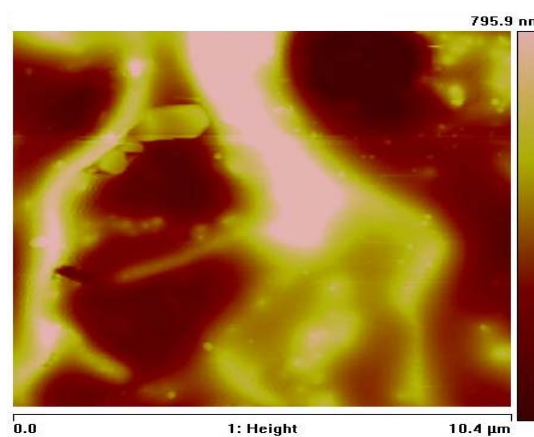


Fig. B1: AFM images of a polyaniline film grown potentiodynamically in 1 M H_2SO_4 . Panel c is 2D representation of panel b.

c)



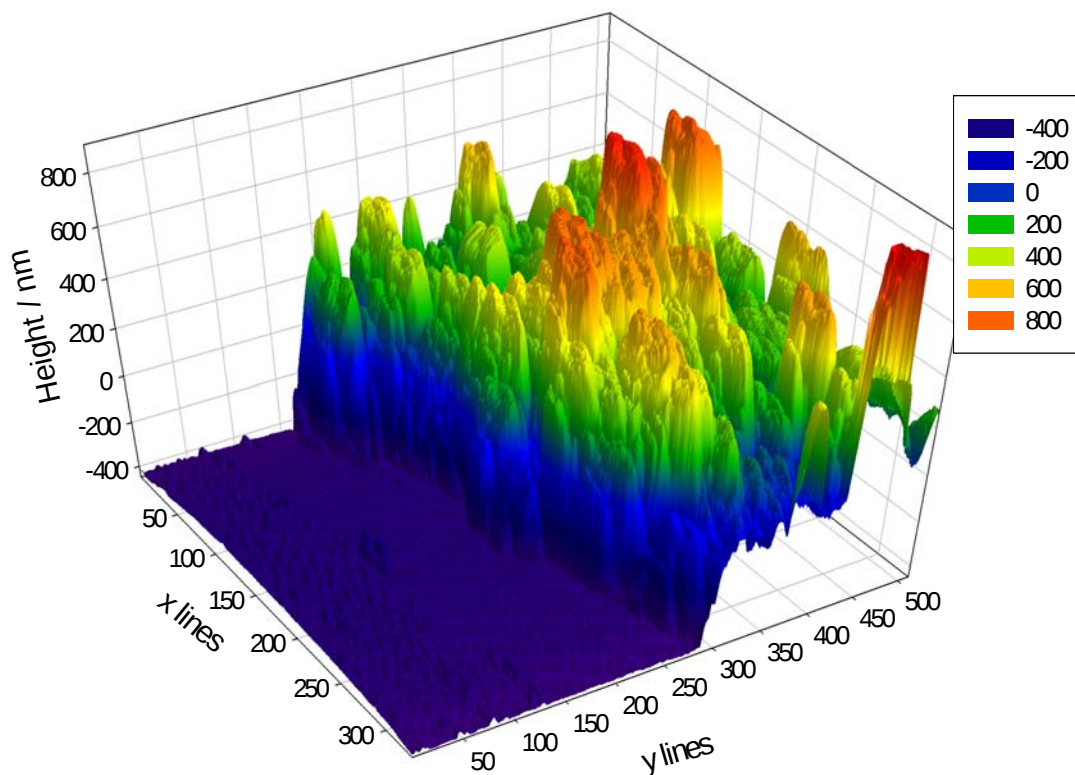


Fig. B2: AFM images of a polyaniline film grown potentiodynamically in 1 M HClO_4 . The film shows an average surface roughness of ~ 100 nm in the z direction. Interestingly, the film thickness measured by AFM agrees the values of thickness obtained by using the optimisation method explained in chapter three.