

The Electrochemistry of Ag in Deep Eutectic Solvents

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By

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Abstract

A fundamental study in to the correlation of nucleation mechanism with deposit morphology using silver salts as a well behaved system has been carried out in deep eutectic solvents *i.e.* mixtures of choline chloride (ChCl) with firstly ethylene glycol and secondly urea in a 1:2 molar ratio. The nucleation and growth kinetics of silver deposition were measured as a function of liquid type, deposition potential and silver salt type. The effect of different additives including surfactants (SDS and CTAB) and aqueous brightener (cresyl fast violet-CFV and crystal violet-CV) on nucleation was determined using electrochemical techniques such as cyclic voltammetry and chronoamperometry. Electrogravimetric studies were carried out using electrochemical quartz crystal microbalance (EQCM) to correlate the deposited mass of silver with findings from the electrochemical studies in both solvents.

A qualitative evaluation of the nucleation and growth mechanism and quantitative estimation of the kinetic parameters of silver electrocrystallization process was carried out using the existing theoretical formalisms. A computer simulation was used to extract the nuclear number density, rate of nucleation, diffusion co-efficient and influence of the double layer charging by fitting the whole potentiostatic current transients using a ‘non-linear best fitting’ method. The analysis of the development of the surface by nucleation and growth of the silver deposition in real time was studied using the *ex-situ* AFM and *in-situ* DHM. The latter of these was the first demonstration of this technique for the study of nucleation and growth mechanism of metal deposition and the results showed good agreement with the *ex-situ* AFM findings.

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Abbreviations

DES	Deep Eutectic Solvents
EQCM	Electrochemical Quartz Crystal Microbalance
SEM	Scanning Electron Microscope
AFM	Atomic Force Microscope
DHM	Digital Holographic Microscope
EDX	Energy Dispersive X-ray
1:2 ChCl:EG	1:2 ChCl:Ethylene glycol / Ethaline
1:2 ChCl:urea	1:2 ChCl:Urea / Reline
EN	1:2 ChCl:EG + AgNO ₃
EC	1:2 ChCl:EG + AgCl
EO	1:2 ChCl:EG + Ag ₂ O
RN	1:2 ChCl:Urea + AgNO ₃
RC	1:2 ChCl:Urea + AgCl
RO	1:2 ChCl:Urea + Ag ₂ O
CTAB	Cetyl trimethylammonium bromide
SDS	Sodium dodecyl sulphate
CFV	Cresyl fast violet
CV	Crystal violet

Chapter 1 : Electrocristallization : Nucleation and Growth of New Phase

- 1.1 Introduction
- 1.2 Ionic liquids as novel electrochemical solvent
 - 1.2.1 *Aqueous System*
 - 1.2.2 *Non aqueous system*
 - 1.2.2.1 *Molecular solvents*
 - 1.2.2.2 *Ionic fluids*
 - 1.2.2.3 *Ionic liquids*
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1.1 Introduction

Surface finishing of metals on diverse substrates is essential for a variety of industries including electronics, optics, sensors, automotive and aerospace etc¹. The surface finishing is accomplished by the deposition of thin films or even thick layers of distinct materials on the surface of solid substrates. This process has been utilized as the premier technique for enhancing or changing the substrate's appearance and/ or attributes such as abrasion and wear resistance, corrosion protection, surface hardening, optical filters, microelectronic devices, integrated circuitry and improvement of aesthetic qualities etc. onto a surface lacking that property. Several approaches have been taken to the deposition of these metal films or layers include physical vapour deposition (PVD), chemical vapour deposition (CVD) and sputtering. These methods allow the coating of most substrates (metal, plastic, glass, ceramic etc.) not only with metal but also with alloys or compounds (oxide, nitride, carbide etc.). These techniques work well but they suffer from the disadvantages including high capital investment and slow deposition rates. Other techniques include electrochemical and electroless plating for depositing thick layers, and more recently thin films, on the surface of conducting or semiconducting substrates. The electrochemical approaches have the advantages of low production costs and the deposition under ambient temperature and pressure, but the technique is directly related to many academic challenges in material physics, biochemistry, biophysics and environment.

1.2 Ionic liquids as novel electrochemical solvents

1.2.1 Aqueous systems

Electrochemical deposition is the subject of significant interest in modern electrochemistry due to its technological importance and the main metals of interest include Cr, Ni, Cu, Au, Ag, Zn and Cd together with a number of copper and zinc-based alloys¹. The electroplating industry, which dates back well over 100 years, is based solely on aqueous solutions due to the high solubility of electrolytes and metal salts resulting in highly conducting solutions. Water does, however, suffer from the drawback that it has a relatively narrow potential window, and hence the deposition of metals with large negative reduction potentials such as Cr and Zn is hindered by poor current efficiencies and hydrogen embrittlement of the substrate¹, toxic cyanide based

plating baths that often contain additional organic additives which are both harmful and difficult to dispose of after the process is complete.

1.2.2 Non-aqueous systems

A current research focus is on the use of 'green' processes to reduce the environmental impact of existing technologies by waste minimisation and replacement of highly toxic and polluting deposition baths. At the same time numerous studies have attempted to achieve the deposition of new alloys and semiconductors and new coating methods for reactive metals, particularly to deposit the refractory metals such as Ti, Al and W which are difficult to extract in pure forms due to highly stable oxides of these metals.

1.2.2.1 Molecular Solvents

A range of non-aqueous solvents can be used as alternative electrolyte solutions. Polar molecules can ideally be used as electrolyte solutions due to having the pre-requisite properties for such processes, but they are good electron donors and coordinate strongly with the metals subsequently making their reduction difficult. Therefore their use is limited to only noble metals and the processes offer few advantages over aqueous processes. Non-polar organic solvents especially hydrocarbons have been studied and they have wide potential windows and metals like Al and Ti can be deposited. They suffer from the disadvantage that the dissolved electrolytes dissociate poorly and hence low conductivities. The first non aqueous commercial electroplating process (SIGL) for Al from toluene has been developed in late 1980s^{2,3}.

1.2.2.2 Ionic Fluids

High temperature molten salts have wide potential windows, high conductivities and high solubilities for metal salts. They have been used in the electrowinning of metals such as Li, Na, Ti and Al at temperatures up to 1000°C⁴⁻⁶. Their use is limited by the high temperature operational conditions and small range of substrates.

1.2.2.3 Ionic liquids

Ionic liquids are the salts that exist in its liquid state at room temperature and below 100 °C⁷. These are liquids that only contain ions and the cation is usually a large, bulky and non-centrosymmetric organic compound²⁷. By carefully selecting anions,

ionic liquids with melting point around and below room temperature can be prepared^{8, 9}. Generally the cation is more important in controlling the physical properties of the salt whereas the anion has a greater effect upon the stability and chemical reactivity. The ionic liquids can be tailored to meet the criteria for a specific application by selecting suitable cations and anions or can be fine tuned by modifying a single cation class by changing the nature of one or more substituent alkyl chains. For this reason they are often termed ‘designer solvents’⁸.

The proposed applications of ionic liquids range from fuel desulfurization⁹ to organic synthesis to catalysis to electrochemistry to precious metal processing. The use of ionic liquids show many advantages over conventional organic solvents but very few have come to practical fruition although several are at pilot scale.

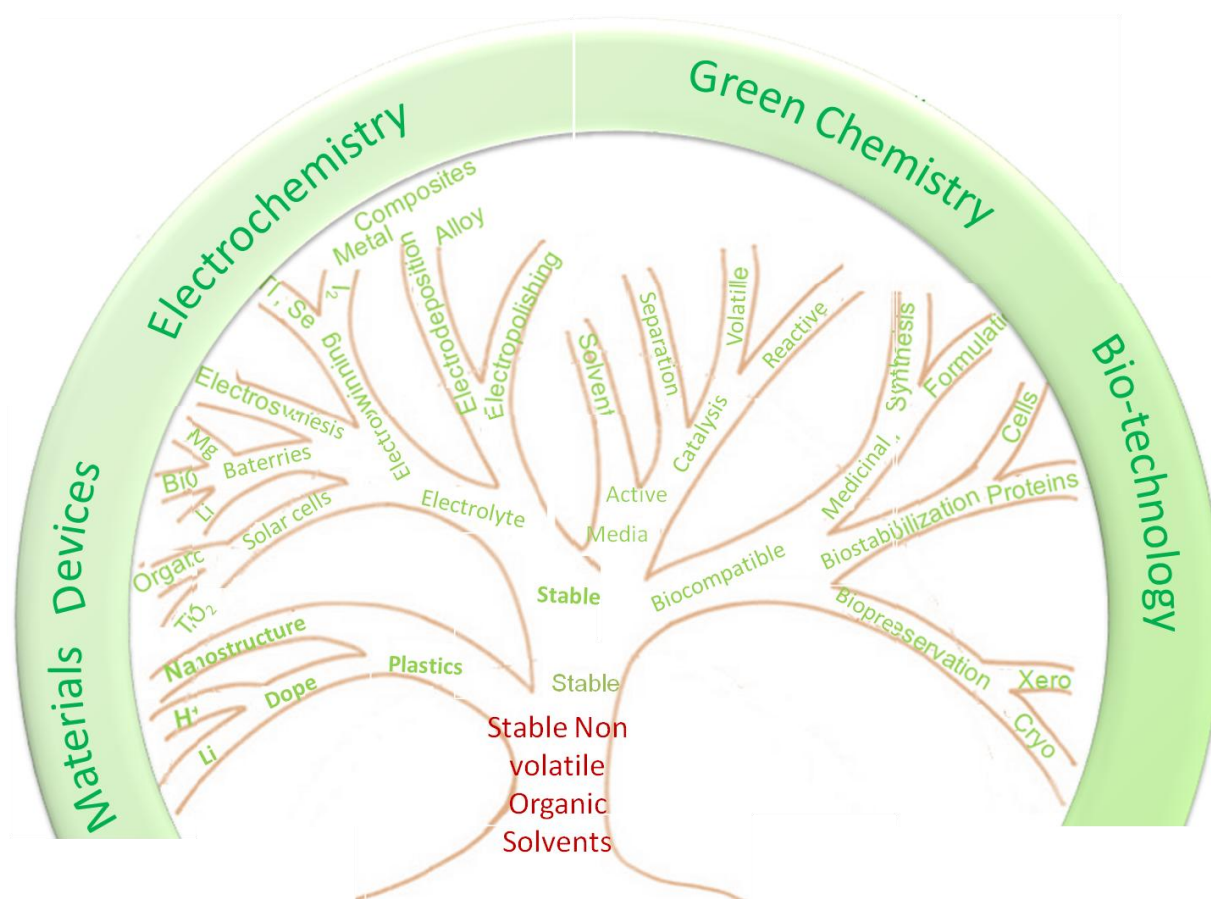
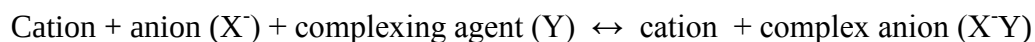


Figure 1.1 : Ionic liquids : Designer solvents for a cleaner world (Causeway of Future)

1.2.2.4 Deep Eutectic Solvents

Eutectic based ionic liquids have the general formula $R_1R_2R_3R_4N^+ X^- \cdot z Y$, where $R_1R_2R_3R_4N^+$ is for example a choline like cation such as $HOC_2H_4N^+(CH_3)_3$ X^- is generally halide anion (usually Cl^-). Y refers to a Lewis or Bronsted acid or complexing agent, z refers to the number of Y molecules which complex X^- . They are based on equilibria set up between X^- and Y and described as below



The ionic liquids can be subdivided into three types

Eutectic Type I $Y = MCl_x$, $M = Zn^{10}, Sn^{11}, Fe^{12}, Al^{13}, Ga^{14}$

Eutectic Type II $Y = MCl_x \cdot yH_2O$, $M = Cr^{15}, Co, Cu, Ni, Fe$

Eutectic Type III $Y = RZ$, $Z = CoNH_2^{16}, COOH^{17}, OH$

The relative proportions of anionic species depend on the ionic liquid composition. The ability to vary the composition of Lewis or Bronsted acid adds an additional dimension to the tuneability of the eutectic-based ionic liquids. The anionic species have been identified for Type I, II and III based eutectics where $Al^{18}, Sn^{19}, Zn^{19}, Cr^{15}$ and urea¹⁶ are the complexing agents and some studies have quantified the proportion of species present^{18, 19}. They are also clearly useful for electroplating if the metal of interest falls in the category defined above under Type I or Type II as the metal ion concentration can be as high as 10 mol dm^{-3} . The Abbott group, the first to pioneer this technology has focused on using metal halide salts, both hydrated and non-hydrated, quaternary ammonium salts and hydrogen bond donors. Deep eutectic solvents are an extension of the ionic liquid model and the term is coined as a means to differentiate them from ionic liquids with discrete anions. They are less expensive and easier to handle than other ionic liquids.

There is some controversy over the classification of complex anions as ionic liquids. It could, however, be argued that discrete anions are just a subset of complex anions where the Lewis acid and Lewis base are present in equimolar amounts and the equilibrium constant lies considerably over to the right.

1.2.3 Technological Potential of Ionic liquids

From an electrochemical perspective, many RTILs possess the archetypal properties such as high thermal stability, low volatility, high polarity, large viscosity, high intrinsic conductivity and wide electrochemical windows^{1, 20, 21}. These properties of RTILs commend their use for electrochemical processes.

Ionic liquids have a wide range of applications in electrochemistry including electrodeposition^{21, 22}, electrosynthesis and in electrochemical devices like lithium batteries, photoelectrochemical cells, fuel cells and capacitors⁷.

The advantages of the use of ionic liquids for electrodeposition of metals over the aqueous baths are as follow

- ❑ A series of transition and main group metals have been deposited using ionic liquids as shown in **Figure 1.2**.
- ❑ Electroplating of a range of metals impossible to deposit in water due to hydrolysis e.g. Al, Ta, Nb, Mo, W
- ❑ Direct electroplating of metals on water sensitive substrates e.g. Al, Mg
- ❑ Coatings with superior mechanical properties, crack free and more corrosion resistant can be obtained from ionic liquids while coatings from aqueous bath may suffer from hydrogen embrittlement.
- ❑ A large number of alloys can be electrodeposited .
- ❑ Ionic liquids complex metals and therefore offer the possibility to develop novel electroless plating bath for coating polymers (in electronics) without the need for the toxic and problematic organic complexants used in water.
- ❑ Present elctropolishing and electropickling processes produce large quantities of metal laden, corrosive effluent solution whereas in ionic liquid electrolytes, the metals precipitate and can readily be separated and recycled.
- ❑ Although the cost for ionic liquids will be greater than aqueous electrolytes, the capital costs will be much lower than the alternative techniques like PVD and CVD.
- ❑ The replacement of many hazardous and toxic materials currently used in aqueous systems, which have a strong negative impact on the environment,

e.g. toxic form of chromium (VI), cyanide, highly corrosive and caustic electrolytes.

- ❑ Nano-composite coatings of metals and alloys which confer good thermal and electrical conductivity, uniformity, low friction to the coatings.
- ❑ An increased range of metal coatings on polymers is accessible by electroless plating using ionic liquids containing reducing agents.

1	As Metals										As Alloy					As Metals and Alloy					18
H	2											13	14	15	16	17	He				
Li	Be											B	C	N	O	F	Ne				
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar				
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra	Ac																			
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu					
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr					

Figure 1.2: Summary of the elements deposited from the RTILs

1.3 Electrocrystallization

Metal electrodeposition takes place at electrode/electrolyte interfaces under the influence of an electric field and includes a number of phase formation phenomena. A typical electrochemical metal deposition process namely electrocrystallization has attracted much attention from both scientists and engineers. Electrocrystallization is a process in which mass transfer is accompanied by a charge transfer²³. The formation of new phase requires that the system is in a metastable phase. This condition of supersaturation is achieved by perturbing the equilibrium either through the applied potential or by changing the temperature and composition of the electrolyte bath. The applied potential plays a vital role in controlling the deposition and the applied potential influences the crystallization process by the following two ways:

- (i) Direct influence - it determines the type of nucleation and the growth kinetics for the electrodeposition of the metal.

- (ii) Indirect influence - due to the side reactions like decomposition of the solvent which changes the local reaction environment around the electrode subsequently altering the nature of the reaction product. e.g. hydrogen evolution in unbuffered electrolytes may results in the co-deposition of metal oxides / hydroxides in the metal deposit.

In many process, a significant combination of the above influences is observed.

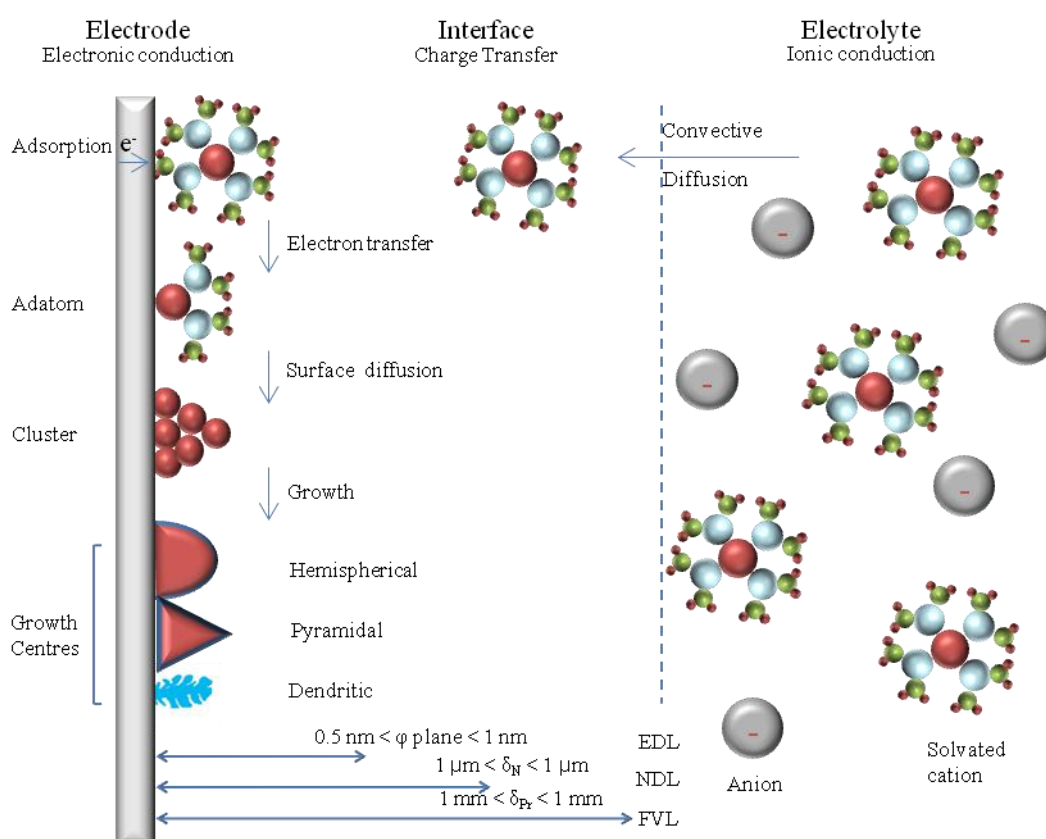


Figure 1.3: Simplified schematic representation of electrocrystallization of metal onto a substrate. Below are shown the broad ranges of the interfacial layers Electrical double layer, Nernstian diffusion layer and Fluid velocity layer

1.3.1 Steps in electrocrystallization process

Consider a heterogeneous charge transfer reaction at the interface between an electronic conductor (or semi conductor) and an ionic conductor. The steps involved

during this process are shown in **Figure 1.3**. The electrocrystallization process may include the following processes:

- (i) Anodic, cathodic or cell reaction,
- (ii) Chemical and electrochemical steps,
- (iii) Ions and uncharged species including the solvents,
- (iv) Disappearance, appearance or transformation of a solid phase and
- (v) Phases which remain on the electrode or which reside in the electrolyte.

1.3.2 Interface Region

Electrocrystallization processes may be affected by changes in interfacial layers near the electrode surface. In practice interactions occur between these layers giving rise to a complex environment and the concept of the reaction layer²⁴. The interface region is divided into following three zones.

1.3.2.1 Electrical double layer

This arises due to the charge separation resulting in a potential distribution near the surface in contact with solutions²⁵. The earliest model is proposed by Helmholtz²⁶ based on a single layer supposing that the solvated ions arrange themselves along the surface of the electrode but are held away from it by the molecules in their solvation spheres and treating it mathematically as a simple capacitor. Important approximations used in this model are:

- ☐ Ions are effectively point charges,
- ☐ The only significant interactions are coulombic,
- ☐ Electrical permittivity is constant throughout the double layer and
- ☐ The solvent is uniform at the atomic scale.

The limitation to this model is the exclusion of the disrupting effect of thermal motion, which tends to break up and disperse the rigid wall of charge.

The Gouy, Chapman and Stern^{27, 28} proposed a new model, according to which the ions closest to the electrode are constrained into a rigid Helmholtz plane while outside that plane the ions are dispersed as depicted in **Figure 1.4**. The interactions between the ions and the substrate surface depend on the balance between its chemical interaction with the substrate and the heat of solvation.

The ions having strongly bounded solvation shells interact with the electrode surface by electrostatic forces only and are called *non-specifically adsorbed*. These ions define the outer Helmholtz plane (OHP). The surface coverage of the non-specifically adsorbed ions rarely exceeds 0.1 – 0.2 of a full monolayer to establish (maximum) potential drops of about 1 V.

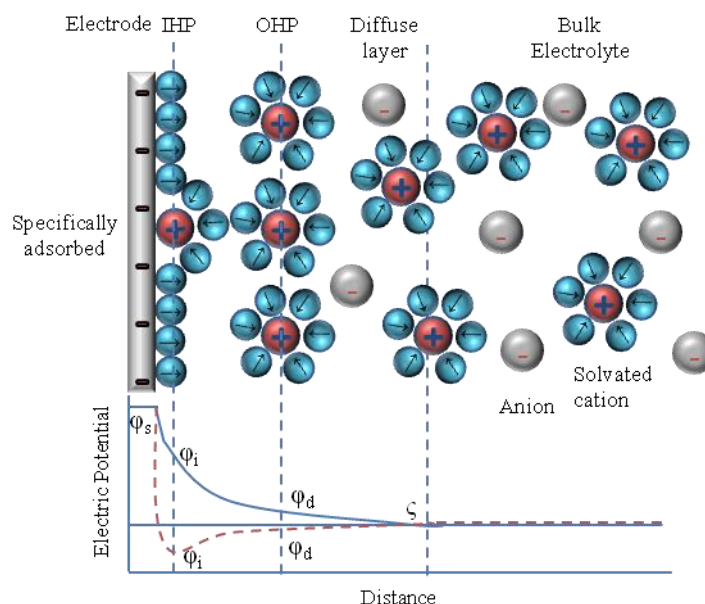


Figure 1.4: The Gouy-Chapman-Stern model of the electrical double layer and the resulting potential field of negatively charged surface. Solid line is the case of purely electrostatic interactions while dashed line show the case of specifically adsorbed ions.

The ions with weakly bounded solvation shells may partly strip their solvation shell in the double layer and undergo a direct chemical bond with the electrode surface. They are called *specifically adsorbed* and their location defines the inner Helmholtz plane (IHP). The coverage of specifically adsorbed ions can be up to close packing, however their ionic character is then strongly reduced. The substrate structure dictates the concentration of these ions and varies significantly between different crystallographic orientations.

1.3.2.2 Concentration profile Layer

It arises due to the depletion or build up of the electrolyte species near the electrode surface due to convective diffusion.^{29, 30} At the limiting current, the reaction is under

complete mass transport control and the surface concentration has reached zero. The Nernstian diffusion layer thickness may be defined by assuming (fictitious) linear diffusion profile by

$$K_L = \frac{D}{\delta_N}$$

where K_L is mass transport co-efficient, D is the diffusion co-efficient

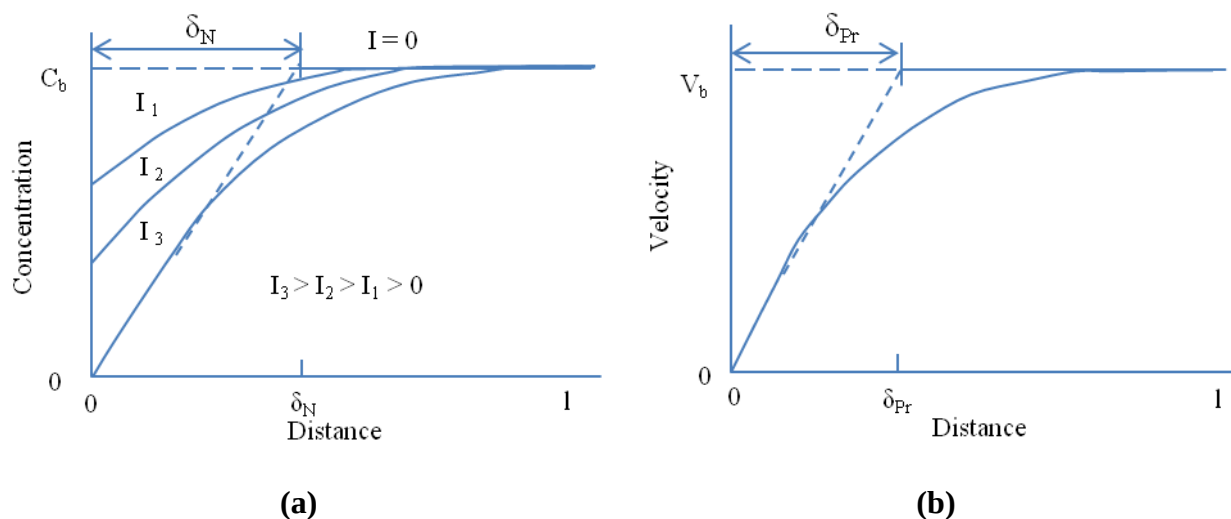


Figure 1.5: *Electrolyte layers near the electrode surface (a) The concentration boundary layer (b) The fluid boundary layer*

1.3.2.3 Fluid velocity layer

It arises due to the localized differences in electrolyte convection due to fluid shear and flow development. The bulk velocity is increasingly retarded as the electrode surface is approached. At the surface itself, the fluid is stationary relative to the electrode. Assumption of a linear profile allows the Prandtl (hydrodynamic) boundary layer δ_{pt} thickness to be obtained.

1.3.3 Complications in the electrocrystallization process

The electrocrystallization process is very sensitive to the applied electrode potential. Many complications may occur in the crystallization process due to the poor control of the applied potential or the nature and state of the electrode, the electrolyte composition, temperature and flow effects²⁴ and the major complications are:

- ❑ The nature of the solid phase e.g. alloy, metal/metal oxide composite, combined crystallographic phases.
- ❑ Chemical steps may be significant e.g. increasing pH encourage oxide / hydroxide formation or exceed a solubility limit leading to precipitation.
- ❑ ‘Under-potential’ deposition of a metallic monolayer resulting in the formation of essentially a two dimensional array of absorbed metal adatoms.
- ❑ Electrode participation may result in corrosion with the formation of intermetallic or other metal compounds.
- ❑ The surface state and composition affects the nature of the adsorption and nucleation processes.
- ❑ Roughened surfaces, electrocatalysis, enhanced surface area or improved mass transfer effects.
- ❑ Localized potential and current on the electrode change the morphology, chemical composition or phase composition of the products.
- ❑ Competitive electrochemical reactions.
- ❑ Time – dependent effects.

1.4 Formation of metal phase

The electrochemical metal (Me) phase formation on a foreign substrate (S) e.g. foreign metals, graphite, semiconductor, super conductors, membrane etc. involves the fundamental processes of nucleation and crystal growth.

The rates of these processes determine the granularity and morphology of the deposit. Higher rate of nucleation results in a finer crystal grained deposit. The direction of the growth determines the morphology and structure of the deposit. If the crystal growth rate is higher perpendicular to the substrate surface then a fibrous structure is obtained while higher growth rates along the substrate surface give a brighter deposit.

1.4.1 Nucleation

Nucleation and growth are the essentials of the kinetics of first order phase transitions, which occur always in the metastable region in the Frumkin isotherm illustrated in **Figure 1.6**. Nucleation, the initial stages of metal deposition, is kinetically limited by

the Gibbs formation energy which is linked with an increase of the Gibbs energy of the system.

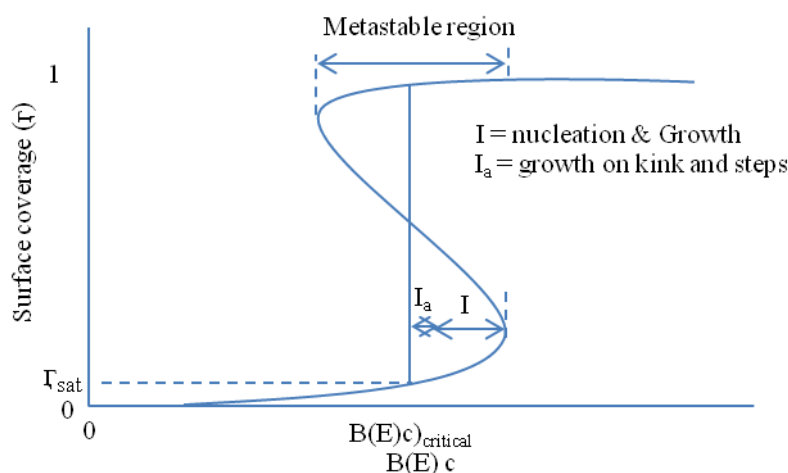


Figure 1.6: Schematic representation of the Frumkin isotherm. Concentrations of adsorbed species $B(E)c$ depending on the considered potential regions versus surface coverage. Within the metastable region signed by vertical dotted lines nucleation and growth occur.

1.4.1.1 Transfer of ions from electrolytes to substrate

The transfer of ions from the electrolytes to the substrate surface is strongly dependent on the dimensionality of the active sites. The probability of the deposition of metal ions is high on rough, high indexed surfaces or on stepped vicinal or planes with a high density of kink sites³¹ (**Figure 1.7**). Active sites represent not only surface imperfections, but may also be generated by surface oxidation / reduction, reconstruction processes or ad/desorption of anions or solvent molecules.

Surface reconstruction is the re-arrangement of the surface atoms' positions under the influence of temperature or *in situ* electrochemical conditions to reduce the surface energy³¹⁻³³. The reconstruction of Au(111) has been extensively studied and the reconstructed surface has 4 % higher atom density than the unreconstructed surface as shown in **Figure 1.8**. When the potential is positively charged, the reconstruction is lifted and the atoms relax back into the positions on the truncated 3D lattice, to form a hexagonal structure. Adsorbed anions (particularly halides) have a significant impact on the crystallography of the Au(111) electrode and cause the removal of a reconstructed surface³². During this process, the excess 4 % reconstructed atoms are

expelled resulting in a degree of roughness which might alter the electrochemical behaviour of the electrode.

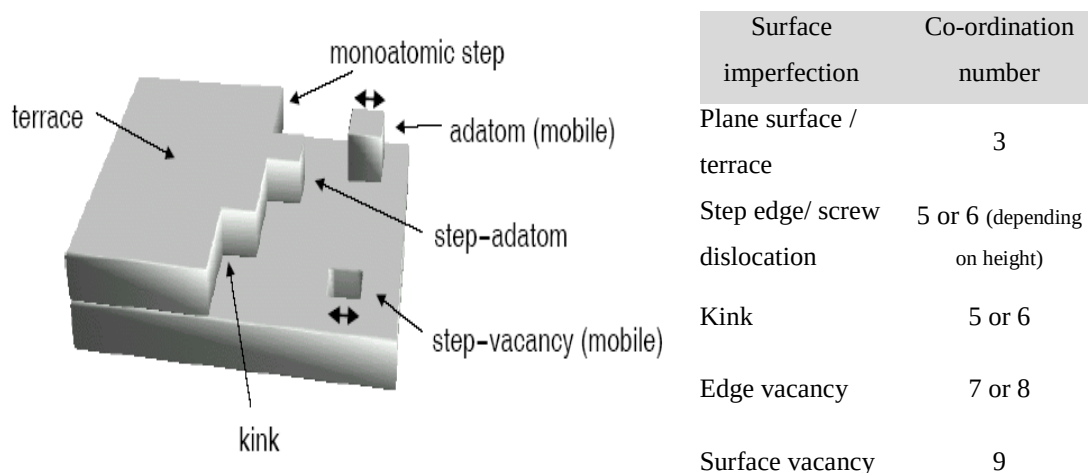


Figure 1.7: Different types of surface imperfections and corresponding co-ordination numbers and at constant super saturation, $J(\text{terrace}) < J(\text{step}) < J(\text{kink})$.

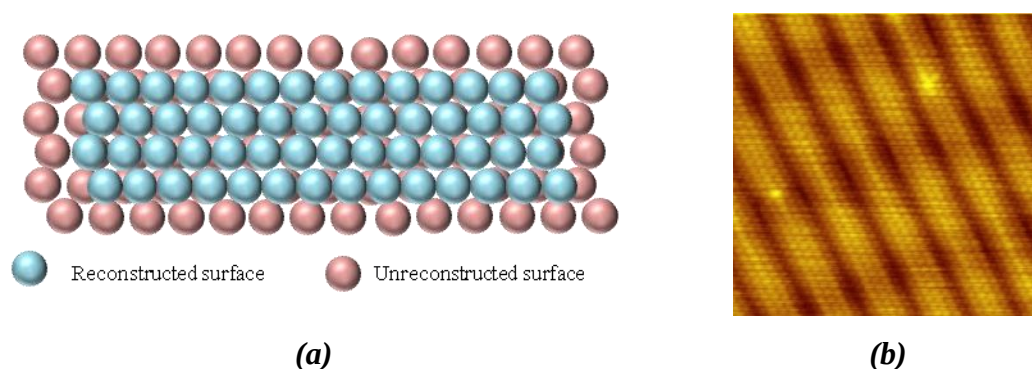


Figure 1.8: (a) The reconstructed Au(111) (b) Atomically resolved STM image of clean Au³³

1.4.1.2 Nuclear cluster size

The adsorption of an atom on the substrate results in the increase of the Gibbs' free energy of the system. This increase in energy is due to the formation of the bond of the atom with surface and the interaction of the adatom with the other atoms in the cluster due to the formation of new boundaries, internal strains, deviation from the bulk atom arrangements etc. and is termed as the surface energy.

The number of atoms in the nucleus cluster is kinetically limited by the Gibbs formation energy which is given by

$$\Delta G(N) = -NZe|\eta| + \phi(N)$$

Where the term $-NZe|\eta|$ is the energy associated with the transfer of ions from the electrolyte to the substrate surface and the binding energies of an atom to the cluster which include the interaction of atoms with the cluster atom and the substrate.

The term $\phi(N)$ represent the energy contributions derived from the deviation of the new phase from the bulk phase and represent the free energy of creation of new boundaries and is given by

$$\phi(N) = \varphi X(N)$$

Where X represent the surface area (A_{3D}) in case of 3D cluster while it is perimeter (P) in case of 2D cluster and φ is the specific boundary energy for each extension in the cluster size i.e. addition of new atom to the growing cluster.

1.5 Growth

The expansion of a supercritical nucleus through continued incorporation of monomers is called *growth*. The growth mode determines the film morphology and the structural properties such as perfection, flatness and interface abruptness of the layers, which are controlled by the kinetics of the transport and diffusion processes on the surface. The different atomistic processes taking place on the surface during new phase formation are shown in **Figure 1.9**.

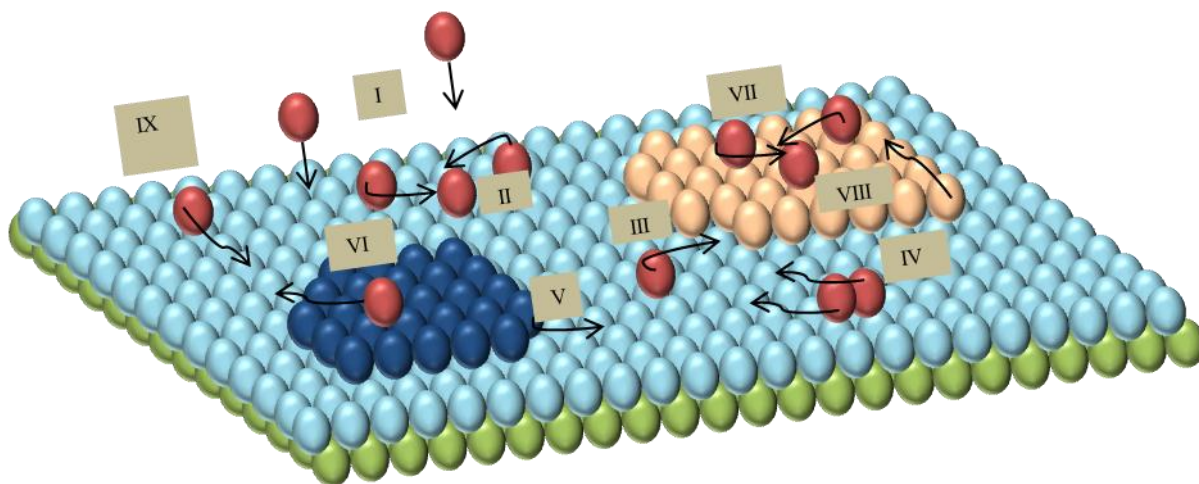


Figure 1.9: Schematic diagram of nucleation and growth, (I)Arrival (II)nucleation on island (III) attachment to island (IV)diffusion of dimer (V) detachment from an island (VI) diffusion to lower terrace (VII) binding and nucleation on second layer (VIII) diffusion along step edge (IX) diffusion on terrace

1.5.1 Types of growth

The rates of nucleation and growth are both functions of the applied supersaturation (e.g. electrode potential or difference in surface energy respectively). Three basic regimes may be distinguished:

- ❑ If the formation period of the critical cluster is much longer than the time required to cover the available electrode surface by its subsequent growth, the transformation involves just one nucleus and is called *mononucleation*.
- ❑ If the rate of nucleation is much faster than the subsequent growth process, many nuclei contribute to the creation of the new phase. This regime is known as *polynucleation*.
- ❑ The intermediate case which involves just a few nuclei is termed *oligonucleation*.

1.5.2 Propagation of the nucleus

The growth rate is controlled by the propagation rate of the growing nuclei. There are two ways to supply the atoms to the propagating step.

- (i) The deposition of an ion on any arbitrary site of the surface as an adatom then migrated to the growing site by surface diffusion. In this case, the growth is controlled by the surface diffusion coefficient. In this case the adatoms are added to the periphery of the island and hence contribute to the lateral growth.
- (ii) Direct deposition on the step edge. This type of attachment usually results in the vertical growth.

1.5.3 Modes of growth

The growth of epitaxial (homogenous or heterogeneous) thin films on a substrate depends critically on the interaction energy between adatom and the substrate surface and adatom-adatom interaction energy. Practically, there are three classical growth modes³¹ as described below and depicted in **Figure 1.10**.

1.5.3.1 Volmer Weber (VW) growth

In the case of stronger adatom-adatom interactions than adatom-substrate interactions the preferential adsorption of ions on the growing clusters results in the formation of 3D adatom clusters or islands. Growth of these islands coupled with coarsening gives rise to rough multi layer films which grow on the substrate surface³³. VW growth often results in a high moasicity of the material inside the layer.

1.5.3.2 Frank–van der Merwe (FM) growth

This is a two dimensional growth mode. If the adatom-substrate interactions are stronger, then adatoms preferentially attach to the growing surface sites (perimeter) resulting in atomically smooth, fully formed layers and growth is two dimensional^{33, 34}. A new layer is nucleated only after the completion of the subsequent growing layer. The optimum layer homogeneity can be achieved by one dimensional movement of steps in FV mode initiated by a precisely controlled small angle substrate misorientation.

In ideal cases this growth occurs over long distances but due to crystal imperfections like screw dislocations which act as a ‘sink’ for growth species and results in spiral growth mechanism. A cone, or in the anisotropic case, a pyramid is formed with its apex at the emergence point of the screw dislocation.

1.5.3.3 Stranski–Krastanov (SK) growth

The SK mode is an intermediary process characterized by both 2D layer and 3D island growth. It is caused by significant lattice misfit from film and substrate³³⁻³⁵. The first deposited layer is atomically smooth (FV growth mode), a compressively strained layer grows up to a certain thickness called critical thickness, which is highly dependent on the chemical and physical properties, such as surface energies and lattice parameters, of the substrate and film. Phase transition to island growth mechanism reduces the strain energy of the non-uniform strain field.

1.6 Kinetics of Nucleation and Growth

1.6.1 Nucleation overpotential

It is the critical potential corresponding to the onset of deposition of material on the substrate referenced to its equilibrium potential. The magnitude of the nucleation

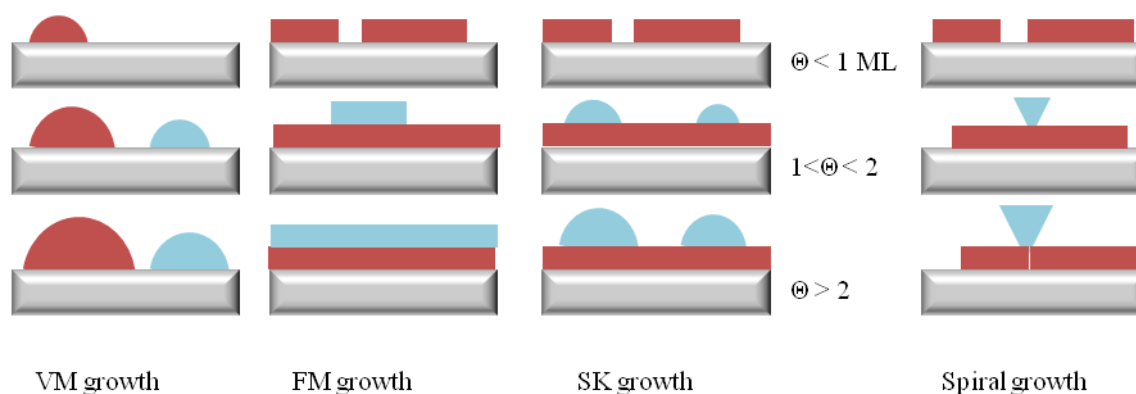


Figure 1.10:

Primary modes of thin-film growth, Volmer-Weber (VW: island formation), Frank-van der Merwe (FM: layer-by-layer), and Stranski-Krastanov (SK: layer-plus-island). Spiral growth in FM growth mode due to screw dislocations of the crystal face

overpotential which can be several hundred millivolts has important implications for island growth and the evolution of surface morphology and is dependent on the substrate surface area, time scale of the experiment and the atomic structure of the substrate. It sets the lower limit on the island growth rate which can be broadly classified into three regimes as shown in **Figure 1.11** and hence is critical in determining whether the kinetic island growth regime can be accessed³⁶.

1.6.2 Implications of the nucleation overpotential on island growth

In the electrocrystallization of metals, the island shape and orientation can be dictated to get the deposit for specific applications e.g arrays of islands for catalysis or coalesced islands (thin films) but this area has not received significant attention despite of its scientific and technological importance³⁶.

1.6.2.1 Island shape

Island shape is determined by the different surface energy of the different crystallographic planes in the electrocrystallization process^{37, 38}. This difference in surface energy can be used to tune the island shape. Generally the growth rates are faster on high energy facets than the facets with low energy. In the absence of specific adsorption, the low energy facets are the planes with highest density of atoms. In cubic Bravais lattices, these are usually the {111} planes. The energy of the crystallographic planes can be tuned by the selective adsorption of a molecule or ion

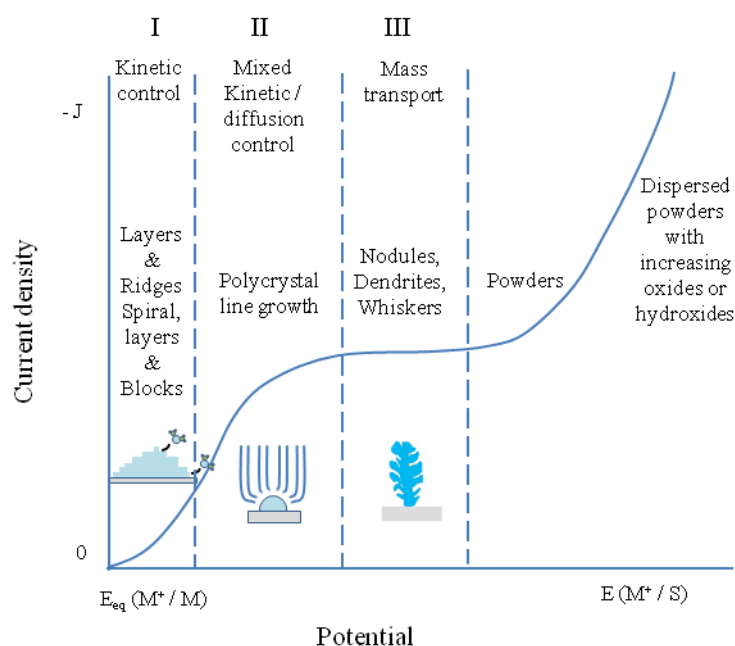


Figure 1.11: Steady state current – voltage curve for the deposition of metal on substrate (I) Small nucleation over potential regime ($>100\text{mV}$), island shape is dictated by the energy of different facets (II) Intermediate nucleation overpotential ($<100\text{ mV}$), radial diffusion leads to hemispherical island and (III) Large nucleation overpotential, growth instabilities result in aggregates, dense branching, dendrites.

thereby slowing the rate of growth on those planes. For the deposition of Cu_2O from nitrate solutions, the crystals are defined by $\{111\}$ ³⁹ plane as nitrate ions adsorb preferentially on the $\{100\}$ plane while in the presence of sodium dodecyl sulphate (SDS) the crystals are characterized by the $\{111\}$ plane due to the adsorption of SDS on $\{111\}$ planes and making them of lower energy than that of the $\{100\}$ planes⁴⁰⁻⁴².

1.6.2.2 Island orientation

The island shape and aspect ratio can be manipulated by the island orientation. If the nucleation results in low energy facets as the base i.e parallel to the substrate surface, then the top of the island will be a low energy plane, consequently the island will have a low aspect ratio. Conversely if the island nucleates with a high energy $\{100\}$ base plane then islands with a high aspect ratio (pyramidal) will be formed and the $\{111\}$ will be at an angle. This situation is shown in **Figure 1.12(b)**.

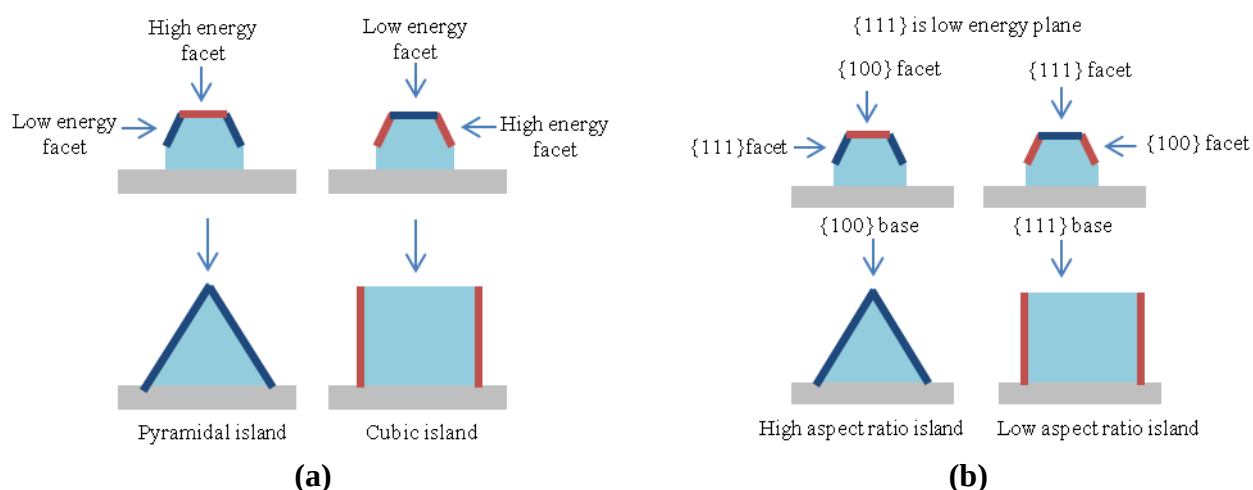


Figure 1.12: Schematic illustration of crystal growth in kinetic control regime (a) island shape (b) island orientation

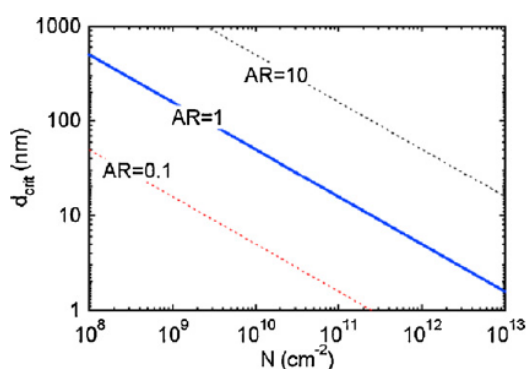
1.6.2.3 Thin film growth

In 3D island growth, the nuclear number density (N) is the key factor in controlling the critical film thickness (d_{cri}) at coalescence and the grain size. N is exponentially dependent on the overpotential. Coupling between the island density, critical film thickness and the grain size at coalescence may be problematic as many film properties are influenced by the grain size such as smaller grains result in a decrease in electric conductivity while the larger the nuclear density the less will be the thickness of the film at coalescence.

This coupling between the d_{cri} and N can be overcome by controlling the shape of the island and hence the island aspect ratio. **Figure 1.13** shows how the island aspect ratio and critical film thickness are linked. In general, at a given N , a one order decrease in the island aspect ratio results in an order of magnitude decrease in the critical thickness for coalescence and an order of magnitude increase in the grain size⁴³.

1.6.3 Manipulation of island growth dependence on the nucleation overpotential

The small nucleation potential (typically <1) referenced to the equilibrium potential (kinetic regime) is the key limitation for controlling the island shape and subsequently the properties of the deposit. There are many strategies to circumvent this limitation and summarized below



$$d_{cri} = (2\sqrt{N})^{-1}$$

AR = 0.1 for disk shaped islands

AR = 1 for hemispherical islands

AR = 10 for elongated islands

Figure 1.13: Island density vs. the critical thickness for film coalescence³⁶

1.6.3.1 Nucleation on self-assembled monolayers

This technique involves the modification of the surface with electrochemical reduction of a monolayer of precursor ions. This treatment leads to a coverage of metal atoms close to a complete close packed monolayer and effectively shifts the nucleation potential to more positive value⁴⁴.

1.6.3.2 Wetting layer

Under-potential deposition (UPD) is the deposition of monolayer of metal on the surface positive to its equilibrium potential and subsequently simple displacement

reaction to replace the UPD metal monolayer with a more noble metal⁴⁵. The number of M^+/S systems exhibiting this process is limited and various approaches have been developed to use this approach⁴⁶⁻⁴⁸.

1.6.3.3 Self-assembled monolayer as molecular resistors

Self assembled monolayers (SAM) act as a molecular resistor for electrodeposition of patterned structures and shift the nucleation potential to more negative values. The island develops at places of the breakdown of defect sites of molecular layers such as domain boundaries in the SAM. Further nucleation is suppressed due to the self assembled monolayer resulting in high island growth rates after nucleation^{49, 50}.

1.6.3.4 Suppressor complexes

The suppressor complexes are adsorbed on the surface and hence shift the onset potential to more negative values. The subsequent spatially dependent displacement of the suppressor complex results in the deposition of the metal.^{51, 52}

1.6.3.5 Potential modulation

This involves the double pulsed deposition in which an initial potential pulse is applied for a short time at a more negative potential which generates a high nuclear density and then the growth of the deposited nuclei at more positive potential under mixed diffusion/kinetic or kinetic control.^{53, 54}

1.7 Analysis of nucleation and growth

The nucleation and growth process can be studied using *in situ* methods such as quartz crystal microbalance measurements, scanning probe microscopy, chronoamperometry, voltammetry or by *ex situ* methods such as electron microscopy, scanning probe microscopy or surface microscopy (e.g. X-ray photoelectron spectroscopy). The electrochemical methods for studying the nucleation and growth have the advantages that the driving force for the process is the applied potential and can be varied simply by changing the applied potential. Nucleation and growth events at electrochemical interfaces can be observed in potential step experiments by monitoring current, charge or capacitance as a function of time.

The growth can be classified into two major categories:

- (i) Interfacial (or charge) controlled in which the nucleus growth rate is limited by the rapidity with which ions can be incorporated into the new phase. High concentration and low deposition overpotentials favour this process.
- (ii) Diffusion controlled in which the nucleus growth is limited by the rate at which material is transported through the solution to the electrode surface. Low concentrations and high overpotentials favour this process.

The current-time transients for these two processes are different from each other and are shown in **Figure 1.14**. In case of interfacial controlled growth the current transients show an initial brief spike due to double layer charging, then the current density rapidly drops to a low value and subsequently becomes progressively more negative with time. At sufficiently long times the current density tends to a constant, steady state value. At the higher overpotential values, the current increases at faster rate, a large steady state value and a shorter transition time to the plateau region.

In case of diffusion control the current transients show the initial rapid surge corresponding to double layer charging and then the current rises exponentially which culminates in a maximum then the current fades away slowly and continuously towards infinity corresponding to the planar diffusion to the whole electrode surface and for a longer time almost merges into a common curve.

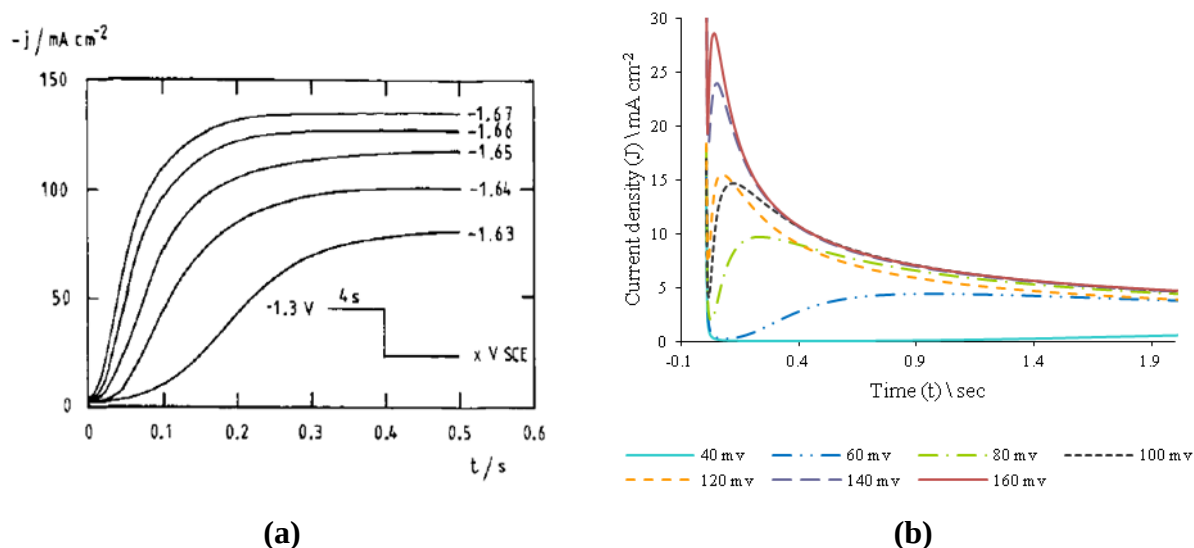


Figure 1.14: The current –time transients (a) interfacial controlled growth (manganese onto vitreous carbon⁵⁵) (b) diffusion controlled growth (silver on Platinum)

1.7.1 Treatment of the current transients

For the extraction of information about the nucleation and growth process from electrochemical data different theoretical models and simulations have been developed to explain the process, a brief review of different approaches is given here.

These analytical expressions describe the current as the product of charge density by velocity of ions. These models are based on the following two assumptions:

- i. For a real surface the rate of nucleation is given by⁵⁶

$$\frac{dN}{dt} = (N_o - N)A$$

Integration, with $N = 0$ at $t = 0$

$$N(t) = \frac{\partial N(t)}{\partial t} = N_o[1 - \exp(-At)]$$

Where A is the steady state nucleation rate per active site, N is the number of nuclei, N_o is the maximum possible number of nuclei in the absence of subsequent growth process. The two limiting cases of the exponential law of nucleation are of particular importance

- $A \gg 1$ instantaneous nucleation

$N(t) = N_o$ e.g. within the time all latently active centres are transformed into real nuclei at the very beginning of the condensation process.

- $A \ll 1$ progressive nucleation

$N(t) = AN_o t$ e.g. where the number of critical nuclei increases linearly with time.

The combination of active intermediates to form a critical nucleus at a specific site may lead to the power law of n step nucleation

$$N(t) = AN_o t^n$$

- ii. Planar diffusion zones are the projection of the cylindrical diffusion zones with a nucleus centred at the bottom, on the electrode surface. The overlap of these hypothetical planar diffusion zones is accounted for within the framework of

the Avrami theorem^{57, 58}, the individual centres can be assumed to grow rather independently of each other, (the concept of extended coverage is shown in **Figure 1.15**.)

1.7.1.1 Deposition with interfacial adsorption controlled growth

The current transients for the interfacial controlled growth can be explained by the ‘right regular cone’ model proposed by Abeneh and Fleischmann^{59, 60}. They explain the growth in terms of ‘Death’ and ‘Rebirth’ of the growing centres. In its simplest form the ‘rebirth’ of the growing centres is synchronised with the ‘death’ process, i.e.

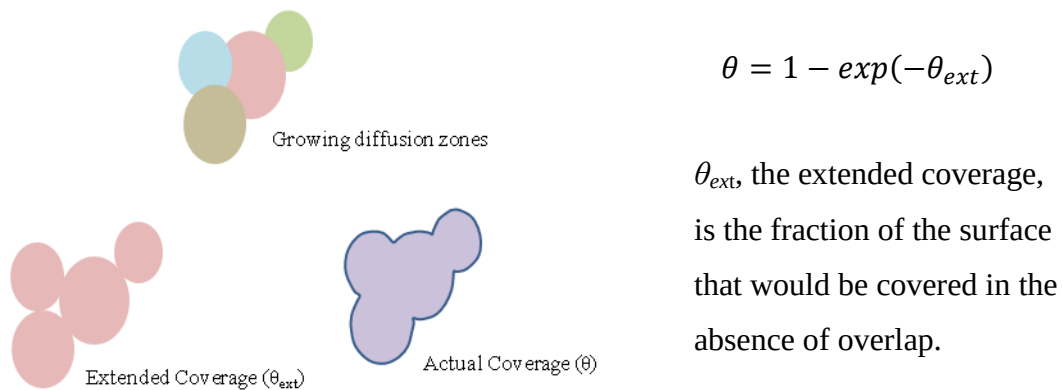


Figure 1.15: *The Avrami theorem : The relation of the true surface coverage and the extended surface coverage in case of overlap of the growth centers*

occurring with a defined time delay. The rate at which these secondary nuclei form is therefore the same as the rate at which the primary growth centres reach the age of maturity. This situation is shown in **Figure 1.16**.

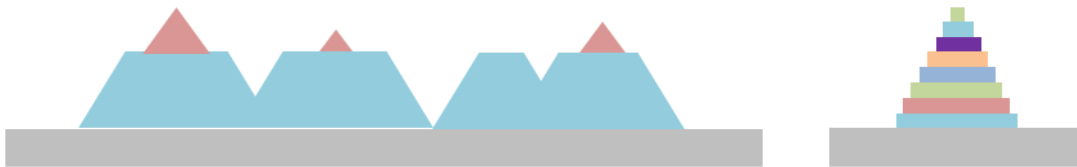


Figure 1.16: *Growth of right circular cones on surface, followed by ‘death’ of crystal growth and synchronized ‘rebirth’ of growth centres*

1.7.2 Deposition with diffusion controlled growth

1.7.2.1 Treatment of nuclei without overlap of diffusion zones

Fleischmann, Thirsk and coworkers^{56, 61, 62} used a potential step method and suggested that the nuclei were formed according to the equation⁵⁶ which is the basis for an entire family of more sophisticated models.

$$N(t) = N_o[1 - \exp(-At)]$$

Where A is the steady state nucleation rate per active site (nuclei s^{-1}), N is the number of nuclei, N_o is the maximum possible number of nuclei in the absence of subsequent growth process (number of active sites) and t is the time since the potential step.

Later in 1967, Astley *et al.*⁶³ investigated the deposition of metals using single potential step and double potential experiments. They found for mercury deposition on a glassy carbon that the current transients follow $J \propto t^{3/2}$ at short time without initial pulse and $J \propto t^{1/2}$ when initial pulse is applied. They modelled this situation by considering a growing hemispherical nucleus which is fed by planar diffusion and then integrated to give a total current using

$$\int_0^t I(u) \left(\frac{dN(t)}{dt} \right)_{t=(t-u)} du$$

Where $I(u)$ is the current resulting from a single nucleus at the time after the appearance of that nucleus (u).

Hills *et al.*⁶⁴ modified the model by introducing the concept of hemispherical diffusion instead of planar diffusion and the validity of the model is checked for single nucleus (microelectrode studies).^{65, 66}

The above models describe well the growth of the single nuclei growing independently but fail to reproduce correctly the overlap of diffusion zones in case of multiple nucleations on a macroelectrode (**Figure 1.17(b)**). These models predict very high current values at a longer time.^{67, 68}

1.7.2.2 Treatment of nuclei with overlap of diffusion zones

The nucleus growth and diffusion of depositing material extends into the bulk electrolyte and generates a situation somewhere between a two and three dimensional problem that is difficult to analyze mathematically.

1.7.2.2.1 Scharifker and Hills model

Scharifker, Hills and coworkers^{69, 70} attempted to tackle this problem by using the Avrami theorem to relate the radial flux density through the real diffusion zones to an equivalent diffusive flux towards electrode area.

$$J(\text{instantaneous}) = \frac{nFD^{1/2}c}{\pi^{1/2}t^{1/2}} [1 - \exp(-N_o\pi kFt)] \quad (\text{Instantaneous})$$

$$J(\text{progressive}) = \frac{nFD^{1/2}c}{\pi^{1/2}t^{1/2}} \left[1 - \exp\left(-\frac{AN_o\pi k'Dt^2}{2}\right) \right] \quad (\text{Progressive})$$

$$k' = \frac{4}{3}[8\pi cM]^{\frac{1}{2}} \quad \text{and} \quad k = [8\pi cM]^{\frac{1}{2}}$$

Where n = equivalent mole⁻¹, F = Faraday constant, (Coulomb equivalent⁻¹), D = diffusion coefficient (cm²sec⁻¹), c = bulk concentration (mol cm⁻³), M = Molar mass, ρ = density of the deposited material, t = time (s), J = current density (A cm⁻²)

These equations are usually used in the form of dimensionless curves and have a characteristic shape for instantaneous and progressive nucleation as shown in **Figure 1.17(a)**.

$$\left[\frac{J}{J_{max}}\right]^2 = 1.9542 \left[\frac{t}{t_{max}}\right]^{-1} \left\{ 1 - \exp\left[-1.2564 \left[\frac{t}{t_{max}}\right]\right] \right\}^2 \quad (\text{Instantaneous})$$

$$\left[\frac{J}{J_{max}}\right]^2 = 1.2254 \left[\frac{t}{t_{max}}\right]^{-1} \left\{ 1 - \exp\left[-2.3367 \left[\frac{t}{t_{max}}\right]^2\right] \right\}^2 \quad (\text{Progressive})$$

It is difficult to extract useful parameters like N , A from this model, and it suffers from the requirement that progressive and instantaneous cases be treated separately.

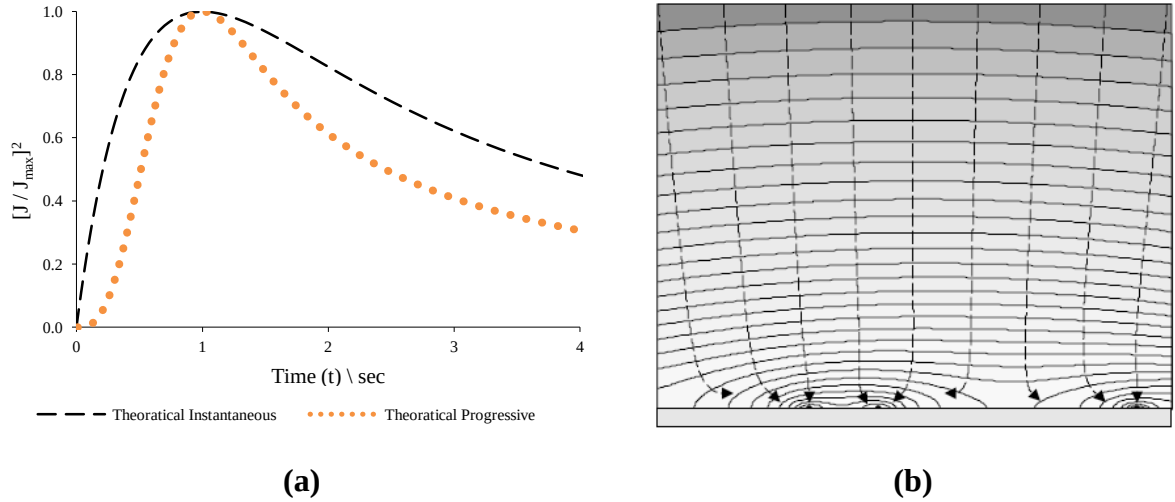


Figure 1.17: (a) Theoretical non-dimensional plots of diffusion zones around growing nuclei on an electrode surface, showing the eventual overlap inhibiting the total amount of material available to a given nucleus⁷¹.

1.7.2.2.2 Scharifker and Mostany Model (SM model)^{72, 73}

They introduce the apriori definition of K , $k = \left[\frac{8\pi cM}{\rho} \right]^{1/2}$ and eliminate the need for classification of two cases of nucleation. An expression is derived for the total current considering hemispherical diffusion towards a growing nucleus and circular diffusion zones having time dependent radii as shown in **Figure 1.18(a)**. The time variable for considering the size of the diffusion zone at time 't' is the time since the appearance of t nucleus, (t - u), and hence the expression for the radial flux is given by

$$\pi \delta_{SM}^2 = (2\pi)^{3/2} D \left(\frac{cM}{\rho} \right)^{1/2} (t - u)$$

Applying Avrami's theorem gives the result

$$I_{SM} = \frac{1}{\alpha (At)^{1/2}} \{1 - \exp[-\alpha(At - 1 + e^{-At})]\}$$

Where $\alpha = (2\pi)^{3/2} D \left(\frac{cM}{\rho} \right)^{3/2} \frac{N_o}{A}$

The above equation is widely used as it can be directly compared to experimental data to extract the parameters N_o and A .

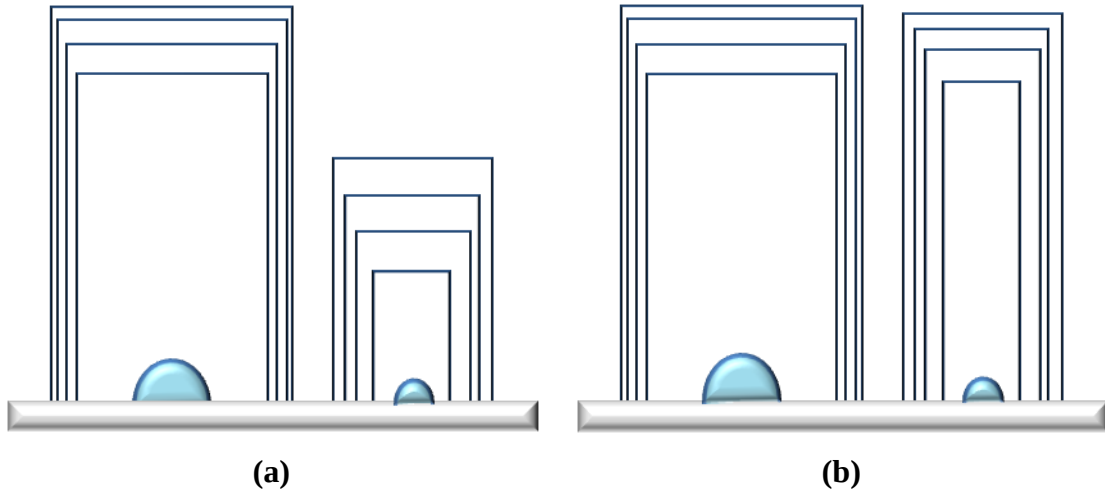


Figure 1.18: Schematic views of the hypothetical diffusion cylinders around established and newly appeared nucleus (small nucleus) at successive time interval⁷¹ (a) SM approach (b) SRWBS model

1.7.2.2.3 Sluyters – Rehbach, Wijenberg, Bosco and Sluyters (‘SRWBS’) Model⁷³

It was argued that SM model is inconsistent with the exact result in the limit of no overlap. They modified the model by considering planar diffusion zones of uniform thickness with the result that the concentration gradients are uniform over the substrate surface as shown in **Figure 1.18(b)**. The hypothetical radial flux is then a function of both $(t - u)$ and t itself

$$\pi \delta_{SM}^2 = (2\pi)^{3/2} D \left(\frac{cM}{\rho} \right)^{3/2} (t - u)^{1/2} t^{1/2}$$

$$I_{SRWBS} = \frac{1}{\alpha (At)^{1/2}} \left\{ 1 - \exp \left[-\alpha (At)^{1/2} \left\{ (At)^{1/2} - e^{-At} \int_0^{\sqrt{At}} e^{\lambda^2} d\lambda \right\} \right] \right\}$$

in which λ is a dummy variable. This expression correctly reduces to the exact expression in the limit of no nuclear overlap and the Cottrell equation as $t \rightarrow \infty$

This model is criticized as expressing the radial flux in terms of $(t - u)$ and that t is ‘unphysical’ in the sense that it implies later appearing nuclei will grow faster than early appearing ones.

1.7.2.2.4 Heerman and Tarallo (HT) model ⁷⁴

Heerman and Tarallo reconcile the two approaches (SM & SRWBS) and argue that the expansion of the diffusion layer should be a function of the nucleation rate constant as well as time and therefore it is inappropriate to use Cottrell's equation to describe the current density. They introduce new parameter δ' , the thickness of the uniform diffusion layer in the case of overlap and it should be introduced via a generalization of the reasoning of SRWBS's method. When treated as before using Avrami's theorem this generates the result

$$I_{MN/HT} = \frac{(At)^{1/2} - e^{-At} \int_0^{\sqrt{At}} e^{\lambda^2} d\lambda}{\alpha(At - 1 + e^{-At})} \times \{1 - \exp[-\alpha(At - 1 + e^{-At})]\}$$

It is notable for including terms from both SM and SRWBS expressions for the current.

Heerman *et al.* improved Heernam and Tarallo's theory ⁷⁵ which shows that the HT model gives arguably correct results but its derivation is wrongly based on the principle of a flux balance. They suggest an improvement by applying the concept of planar diffusion zones to an ensemble of growing nuclei, rather than a single nucleus. This approach leads elegantly to the definition of HT's diffusion layer thickness which is related to the 'mean concentration field' approximation used by Bobbert *et al* ⁷⁶.

These models allow the estimation of the number of active sites and nucleation rate as a function of experimental conditions and were successfully attempted by many authors. It has been noted for a variety of systems that both N_o and A are functions of applied potential ⁷⁷⁻⁷⁹.

1.7.2.2.5 Stochastic approach

D'Ajello *et al.* ^{80, 81} developed a model based on the stochastic approach which is based on Langevin formulation. They introduce a new entity, the reaction radius, which is directly related to the region where the concentration of electrolyte changes, which can easily be correlated with experimental current transients. The assumptions of this model are:

- (i) Ions with a solvation sphere migrate in the bulk solution describing a Brownian motion (absence of an external field of force).

- (ii) Ions which randomly cross a hemispherical surface, defined by a radius R , will lose their solvation shells (region II).
- (iii) Inside the first reaction surface ions migrate towards an electroactive site by performing a diffusive motion assisted by an electric field.
- (iv) At the electroactive site, ions are reduced and form a nucleus, 3D hemispherical, initiating the deposition process.

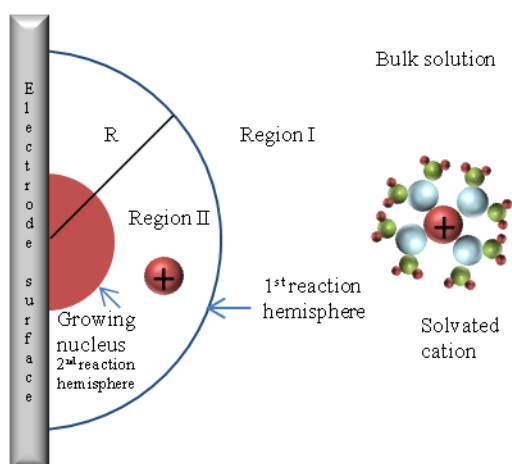


Figure 1.19: *Stochastic model: schematic representation of the different regions and surface near electrode*

The ‘reaction radius’ may be related to experimental variables such as the deposition potential and approaches the Scharifker and Hills model as a limiting case. It appears to describe experimental transients well but has not been extensively tested.

1.7.2.2.6 Treatment of overlap without Avrami theorem

The above methods rely on Avrami theorem to treat the overlap of diffusion zones. Bobbert *et al.*^{76 55} suggested a new approach in which diffusion to an assembly of hemispheres on a substrate is replaced by diffusion to an assembly of spheres in free space, with their centres on a plane. The spherical nuclei are considered as point ‘sinks’ (a good approximation as long as nuclei are relatively widely spaced) and introduce the term ‘*mean concentration field*’ instead of the individual concentration fields of the nuclei at a small distance from each nucleus. They then compared the results from using the approximation with a numerical simulation and observed that errors due to nucleus correlation effects were fairly small. The results were similar to

those of the Scharifker and Hills model but Bobbert's model is only applied to instantaneous nucleation.

1.8 Summary

Electrochemical deposition is the most economical and most widely used technique for surface finishing. Presently the whole sector relies on aqueous deposition baths. This can be associated with hazardous vapours and highly corrosive acidic / alkaline solutions and can have a strong negative impact on the environment. The stringent legislation shifts the focus to find alternative deposition baths to achieve more environmentally compatible deposition systems. Ionic liquids have potential for this purpose due to their unique electrochemical properties but research is at a fundamental stage. A lot of issues have not been addressed yet such as life cycle analysis and their greenness, coating qualities, economic impacts and improved quality over the existing products.

New metal phase formation on the substrate surface occurs by an island growth mechanism that is a strong function of the nucleation over-potential. The nucleation over-potential can be used to tailor the shape and orientation of a growing island and hence the morphology and the properties of the deposited film by artificial manipulation of the nucleation over-potential using self assembled monolayers or adsorbed complexes. The ability to predict the nucleation over-potential for a specific system requires significant advances in our understanding of the growth process, the influence of the substrate, surface structure and solution chemistry.

In the present work a fundamental study into the correlation of nucleation mechanism with deposit morphology using silver (Ag^+) as a well behaved system has been carried out in 1:2 ChCl:EG and 1:2 ChCl:urea. The influence of the liquid, the effect of deposition potential, different types of silver salts and different additives including surfactants (SDS and CTAB) and aqueous brightener (cresyl fast violet-CFV and crystal violet-CV) are studied using electrochemical techniques such as cyclic voltammetry and chronoamperometry. The *in situ* and *ex situ* visual examination of the nucleation and growth process using atomic force microscopy (AFM), digital holography microscopy (DHM) and scanning electron microscopy (SEM) has also

been tried. The effect of these additives on the physical properties of liquid like surface tension, density and viscosity has also been investigated.

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Chapter 2 : Experimental Procedures

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 - 2.7.3 *Chronoamperometry*
 - 2.7.4 *Surface analysis*
-

This chapter contains the standard experimental conditions and protocols used throughout this thesis. The theories underlying standard electrochemical techniques are not described in detail.

2.1. Materials

Table 2.1:	<i>List of compounds used in the project. All the chemicals were used as obtained.</i>		
Compound	Abbreviation	Molecular Weight	Purity
Choline chloride (ChCl)	$\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)^+\text{Cl}^-$	139.63	Aldrich, >98%
Ethylene glycol (EG)	$\text{C}_2\text{H}_4(\text{OH})_2$	62.07	Aldrich, >99%
Urea	NH_2CONH_2	60.06	Aldrich, >99%
Silver Chloride	AgCl	143.32	Aldrich, >99%
Silver Nitrate	AgNO_3	169.87	Aldrich, >99%
Silver Oxide	Ag_2O	231.74	Aldrich, >99%
Cetyltrimethylammonium bromide (CTAB)omide	$\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{Br})(\text{CH}_3)_3$	364.45	Aldrich, >99%
Sodium dodecyl sulphate (SDS)	$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$	288.38	Aldrich, >99%
Cresyl fast violet (CFV)	$\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_3$	321.33	Aldrich, technical grade
Crystal violet (CV)	$\text{C}_{25}\text{H}_{30}\text{N}_3\text{Cl}$	407.98	Aldrich, >9%

2.2. Preparation of solutions

2.2.1 Deep eutectic solvents

The ionic liquids used in this study were 1:2 ChCl:EG and 1:2 ChCl:urea. The H-bond donors for the complex anions of the two liquids were: ethylene glycol (EG) and urea respectively. The deep eutectic mixtures were formed by continuous stirring of the two components at 60°C until a homogeneous, colourless liquid was formed.

2.2.2. Silver salts of solution

Three silver salts AgCl, AgNO₃ and Ag₂O were used in this study. The concentration of Ag(I) in these solutions was 15, 25, 50, 75 and 100 mmol dm⁻³ unless otherwise stated.

2.2.3 Additive solutions

Surfactants Hexacetylammoniumbromide (CTAB), sodium dodecyl sulphate (SDS) and aqueous brightener dyes Cresyl fast violet (CFV) and Crystal violet (CV) were used as additive to study their effect on the nucleation and growth mechanism. The concentration of these additives used was 1, 3 and 5 mmol dm⁻³ i.e. 2, 6 and 10 % of the concentration of Ag(I) in the solution.

2.3 Physical properties

The physical properties of the above solutions i.e conductivity, viscosity, surface tension and density were measured.

2.3.1 Viscosity Measurements

The viscosity of eutectic mixtures was measured using a Brookfield DV-E Viscometer fitted with a thermostated jacket. The viscometer jacket was connected to a thermostated water bath. The readings were taken at different temperatures ranging from 25 to 50 °C with an increment of 5 °C after 15-20 min. The measurements are conducted using the spindle attachment and spindles S61 and S64 were used for viscosity measurements of solutions of 1:2 ChCl:EG and 1:2 ChCl:urea respectively.

2.3.2 Surface Tension measurements

The surface tension of the mixtures was measured using a Kruss Tensiometer K9 with a platinum plate. The plate was thoroughly washed with deionised water followed by heating to red hot in a Bunsen flame to ensure the removal of any adherent material and then cooled to room temperature. Readings were taken at 25 °C.

2.3.3 Density Measurements

The densities of the systems were also measured on the Kruss Tensiometer K9 using the density probe. The density probe was submerged into the liquid for 5 minutes so

the apparatus reached equilibrium and then the reading on the tensiometer was taken at 25 °C.

2.3.4 Conductivity Measurements

The conductivity of the different systems was measured using a Jenway 4071 conductivity meter probe. The conductivity values were measured at temperature ranging from 25 to 70 °C with an increment of 10 °C. The temperature was controlled by using the jacket connected with the water bath. Readings were taken after 25-30 min. for each temperature to ensure good equilibration of temperature between the water bath and the sample.

2.4 Electrochemical Measurements

All electrochemical procedures e.g. cyclic voltammetry and chronoamperometry were carried out using an Autolab PGSTAT20 potentiostat (Ecochemie. Holland) controlled by GPES software. A 3-electrode system consisting of a working electrode (platinum disc electrode; 1mm diameter), counter electrode (platinum flag; area 1cm²) and pseudo-reference electrode (silver wire) was used. The working electrode was first cleaned electrochemically and then mechanically polished with 0.3 µm alumina paste to diminish the memory effect followed by rinsing with deionised water and dried before each measurement. The measurements were carried out at 40 °C.

2.4.1 Cyclic Voltammetry

Cyclic voltammetric study was performed in the potential window of +0.3 to -0.3 V and at scan rates of 0.005, 0.01, 0.02, 0.03, 0.04, 0.05 and 0.1 Vs⁻¹. The sweep potential was initiated at +0.3V and proceeded in the negative direction and reversed at -0.3V (E_{λ}).

2.4.2 Potential step Experiment

The chronoamperometric data have been obtained by stepping the potential of the platinum working electrode positive to equilibrium potential where no silver reduction takes place (+0.2 volt) to sufficiently negative values (-0.04, -0.06, -0.08, -0.1, -0.12, -0.14, -0.16, -0.18, -0.2, -0.22 V) where the nucleation and growth process take place after a short induction period against silver wire quasi reference. The working electrode was cleaned electrochemically and mechanically polishing with Buehler

micropolish II (0.05 micron Deagglomerated gamma alumina) after each measurement.

2.5 Electrochemical Quartz Crystal Microbalance

The crystal impedance spectra were recorded using a Hewlett Packard 87512A transmission/ reflectance unit via a 50 Ω coaxial cable such that the centre of the recorded spectra was close to the resonant frequency, f_0 , of the crystal (*ca.* 10 MHz). To improve the temporal resolution, network analyser data acquisition was controlled by a computer running HP VEE. This program was capable of recording admittance spectra every 2-3 s.

In this study, 10MHz AT-cut polished (flat mirror) finish quartz crystal with a gold film thickness of 900 Å, deposited in a keyhole shape on both sides with central disc active area of 0.211 cm² was used (International Crystal Manufacturing Co., Oklahoma City, USA.). The crystal was placed into a Teflon cell such that one face of the crystal was exposed to the solution and one face was exposed to air. The three electrode electrochemical cell was completed with a Pt mesh counter electrode. EQCM experiments were carried out at room temperature (typically 20-23 °C). The measurements were conducted at -500 mV and -600 mV against a silver wire as a quasi reference electrode and a platinum flag was used as a counter electrode and the spectra were recorded for time period of 20 minutes.

2.6 Surface Analysis

The surface analysis was divided into three groups;

- i. The study of the morphology and chemical composition of the bulk deposits. The silver was deposited potentiostatically on the platinum flag (area 0.25 cm²) at -500 mV and -600 mV for a period of between ½ and 1 hour from solutions containing Ag(I) 100 mmol dm⁻³ from 1:2 ChCl:EG and 1:2 ChCl:urea respectively.
- ii. An *ex-situ* study of the initial stages of the nucleation and growth was conducted on a platinum disc electrode (5 mm diameter) from a solution of AgNO₃ in 1:2 ChCl:EG (Ag(I) 100 mmol dm⁻³). The surface was analysed using AFM.
- iii. An *in-situ* study of the initial stages of the nucleation and growth was performed by digital holographic microscopy. The deposition was carried out

from a solution of AgNO_3 in 1:2 CHCl_3 :EG (Ag(I) 100 mmol dm^{-3}) on a polished gold quartz crystal at -100 mV for 100 s.

2.6.1 AFM

Atomic force micrographs were acquired using a Digital Instruments (DI) Nanoscope IV, Dimension 3100 instrument using resonant tapping mode and the controlling software is nanoscope version 6.13.

2.6.2 SEM and EDAX

Surface analysis with SEM and elemental analysis by EDAX were carried out using a Phillips XL30 ESEM instrument with an accelerator voltage of between 20 and 25 keV, giving an average beam current of ca. 120 μA .

2.6.3 DHM

A digital holography microscope of series R1000 series Lyncee Tec SA controlled by Koala V4 software was used. The detailed principle and operation of DHM is discussed in chapter 5.

2.7 Analysis of data

2.7.1 Cyclic voltammetry

The peak analysis of the voltammograms was performed by using the GPES ver. 4.9.

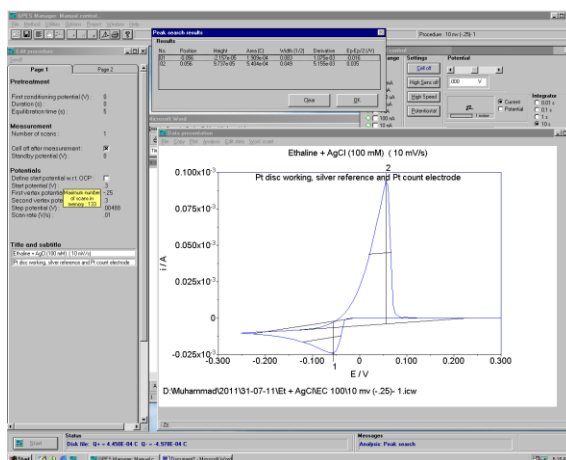


Figure 2.1:

'GPES' version 4.95

2.7.2 EQCM analysis

By this technique the deposited mass of Ag^0 at the electrode was studied through the variation in resonant frequency (Δf) of the gold coated quartz crystal working as cathode and the response of the quartz crystal's resonance frequency from its base value (f_0) was monitored as a function of time during potentiostatic deposition. A full resonance spectrum of the in situ mass loaded crystal at any point in time was acquired and the resonance curves were conventionally presented as admittance (reciprocal of impedance, Z / Ω), U / Siemens and frequency plot.

The measured data were fitted to a Lorentzian equivalent circuit model, **Equation 2.1**, incorporating the in-phase impedance, inductance and centre frequency, with an iterative difference method. The fitting was performed by using the fitting software developed by Dr. K. S. Ryder in Microsoft Excel using the Visual Basic for applications (**Figure2.2**)

$$U(f) = a + \left(\frac{R}{R^2 + 16\pi^2 L^2 (f - f_0)^2} \right) \quad \text{Equation 2.1}$$

Where $U(f)/\Omega^{-1}$ is the measured admittance curve as a function of applied frequency f Hz (and $U(f) = 1/Z(f)$), R/Ω is the real component of the impedance (Z), L Henry is the inductance, f_0/Hz is the centre frequency and a/Ω^{-1} is the baseline offset. The latter was used during fitting to compensate for variations in the static calibration of the network analyser.

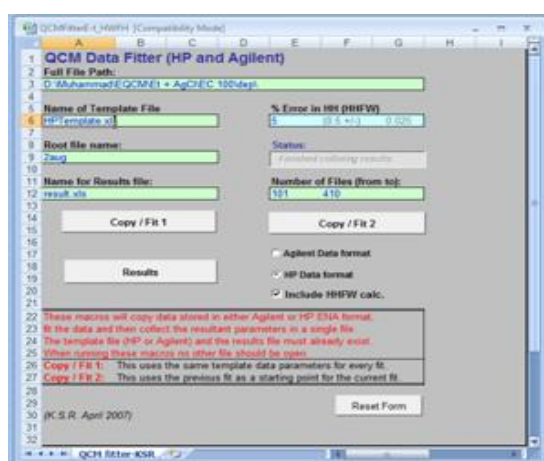
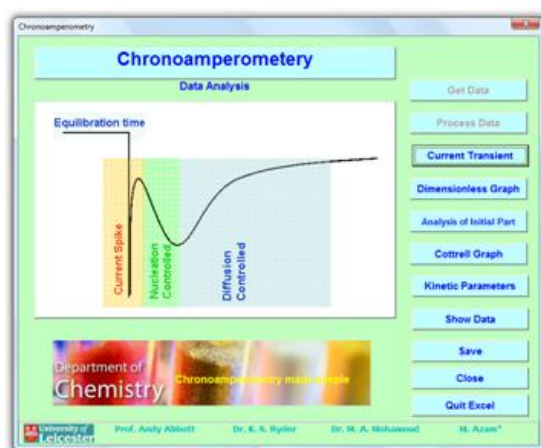


Figure 2.2: 'QCM Data Fitter (HP and Agilent) for the fitting of the QCM data developed by Dr. K. S. Ryder.

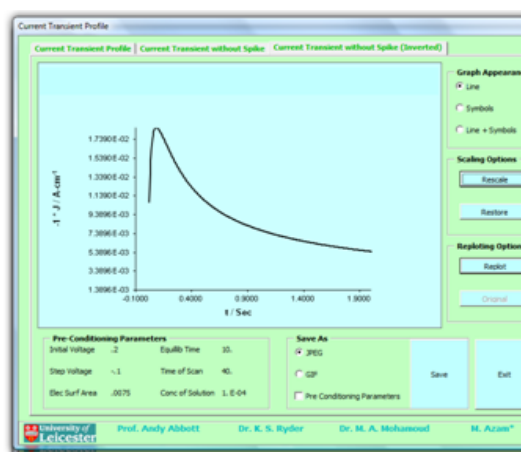
2.7.3 Chronoamperometry analysis

The raw data obtained from the Autolab PGSTAT20 potentiostat was processed to extract information about the nucleation and growth mechanism and the kinetic parameters using the self developed software ('Chronosolver') in Microsoft Excel using Visual Basic for application. The different types of analysis which can be performed by using this software are shown in **Figure 2.3**.

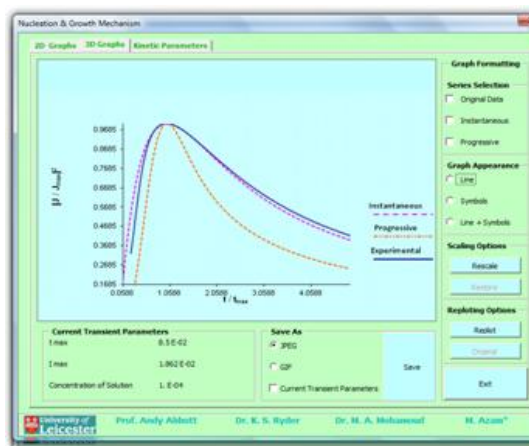
The non linear best fitting of the whole current-time transients using Scharifker and Mostany and Heerman and Tarallo theoretical models were performed in Microsoft Excel by manually simulating the kinetic parameters (N_0 , A , D , K_1 and K_2).



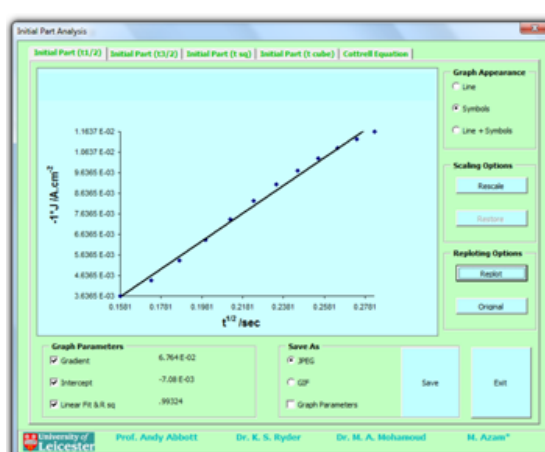
The Main switchboard of 'Chronosolver'



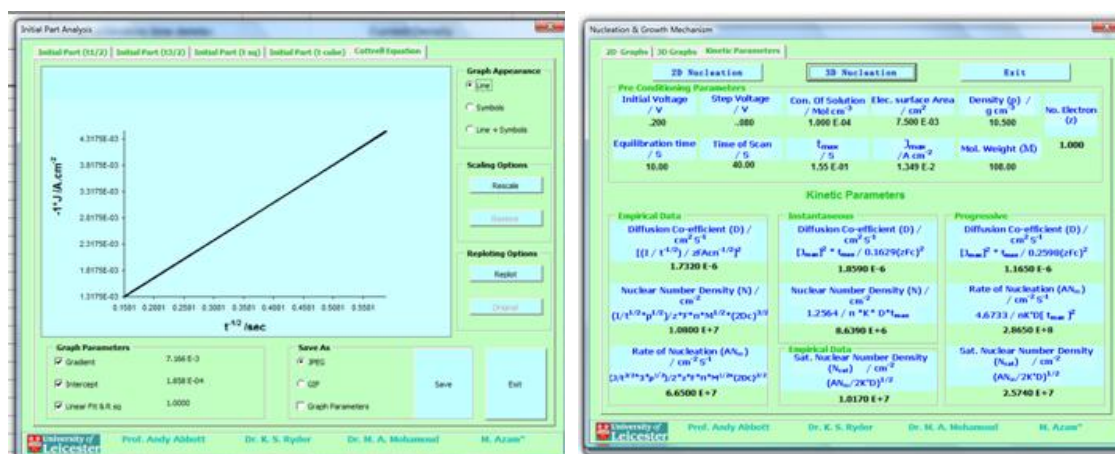
The current-time curve without initial currentspike and the rest step data



3D Dimensionless curve fitting to two limiting cases



Analysis of the initial rising part of the current transient



Cottrell analysis

Kinetic parameters obtained from the $t_{\max}$ and $J_{\max}$ co-ordinates of the current transients

Figure 2.3: 'Chronosolver' for the analysis of the chronoamperometric data developed by Muhammad Azam in Microsoft Excel using Visual Basic for applications.

2.7.4 Surface Analysis

The micrographs obtained from AFM in the *ex-situ* study of the early stages of nucleation and growth were analyzed by the commercial image analysis software 'Digimizer' developed by MedCalc Software.

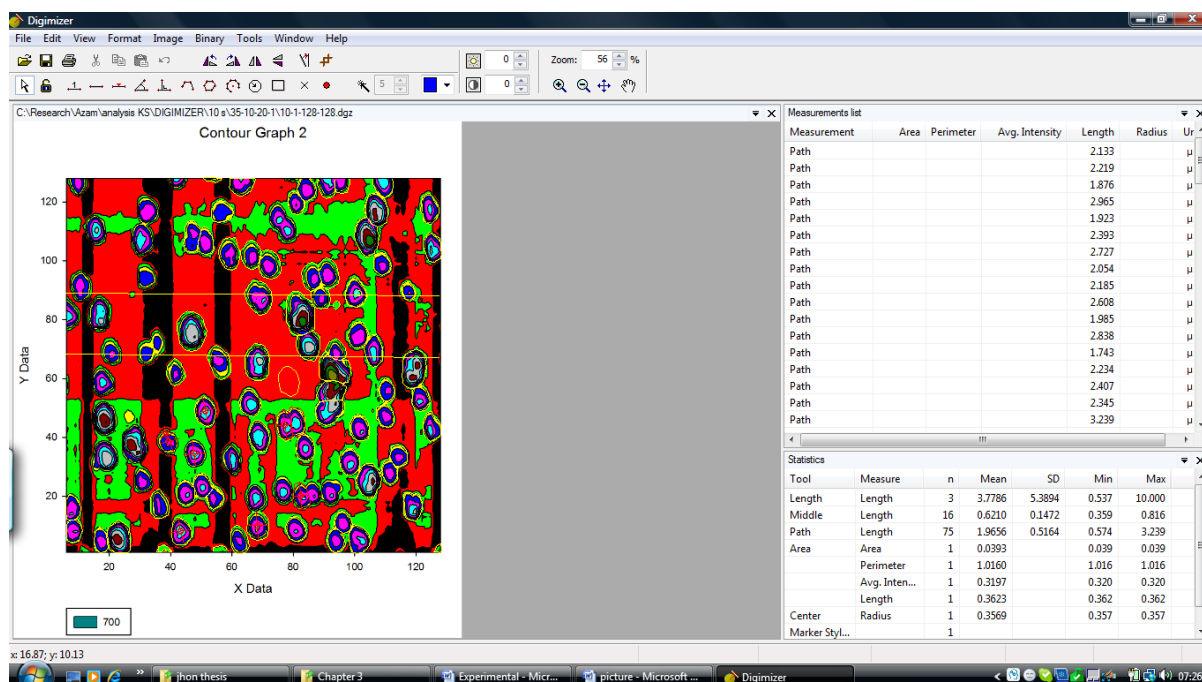


Figure 2.4: 'Digimizer' image analysis software developed by MedCalc software

Chapter 3 : The Electrodeposition of Silver from Deep Eutectic Solvents

3.1 Introduction

Results and Discussion

3.2 Physical Properties

3.2.1 *Viscosity and conductivity*

3.2.2 *Effect of temperature on viscosity and conductivity*

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3.2.4 *Density*

3.3 Potentiodynamic study

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3.3.2 *Cyclic voltammograms*

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3.4 Gravimetric Analysis

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3.7 Conclusion

3.8 References

3.1 Introduction

Metal deposition on to diverse substrates is a subject of significant interest for coatings and microelectronics industries. It is mainly conducted for corrosion protection, to give aesthetic appeal to the substrate and to produce integrated circuitry. Silver metal has been more intensively used for coatings because it exhibits excellent physicochemical and antibacterial properties, fairly good corrosion resistance, high bulk conductivity and excellent features for decorative purposes¹⁻⁵. Electrodeposited silver applications in the field of microelectronics, aerospace, automotive and jewellery require homogeneous, thin and good looking silver layers.

Silver can be deposited onto a less noble substrate electrolytically, electrolessly and with various vacuum techniques. Among all these methods electroplating is the simplest and cheapest technique to produce homogeneous, good looking and very thin silver deposits. The physical and chemical vapour deposition methods present several drawbacks like slow deposition rate, expensive equipments and difficulties in controlling the product quality. All the present commercial aqueous methods used for silver electroplating either use the strong inorganic acids (e.g. HNO_3) or highly toxic salts (e.g. cyanide). Large cyanide content not only threatens the operator's health but at the same time the disposal of the exhausted plating bath and waste water treatment make the process expensive. A current research focus is on the use of 'green' processes which aim at waste minimisation and replacement of highly toxic and polluting organic solvents with more benign room temperature ionic liquids (RTILs)⁶⁻⁹. RTILs have attracted extensive attention in many applications due to their unique properties as alternative solvents¹⁰⁻¹² and many organic and inorganic synthesis, nanomaterial fabrication and catalysis¹³⁻¹⁶ have been investigated in RTILs. The advantageous properties of RTILs like thermal stability, good conductivity, low toxicity and wide electrochemical window^{17, 18} make them suitable for electrodeposition of metals¹⁹⁻²¹ and novel electrolytes for lithium ion batteries²². In principle all the metals and alloys which can be electrodeposited from aqueous solutions can also be electrodeposited from ionic liquids, in addition crystalline metals and semiconductor can also be electrodeposited directly at elevated temperature instead of conventional high temperature molten salts.

Silver electrodeposition from RTILs alone^{23, 24} or as an alloy with other metals²⁵ and electroless deposition onto copper substrate²⁶ has been reported. Silver can be electrodeposited from water sensitive chloroaluminate ionic liquids²⁷ which requires handling under an inert atmosphere. Very thin, bright, adherent, mirror like deposits of silver have been reported on commercial grade copper from air-stable 1-butyl-3-methylimidazolium tetrafluoroborate [BMIm]BF₄²⁸ and silver nanowires in 1-butyl-3-methylimidazolium hexafluorophosphate [BMIm]PF₆²⁹ have also been reported. Although these systems are more or less water insensitive, long exposure to moisture causes hydrolysis with the generation of HF. Endres *et al.*³⁰ have reported the electrodeposition of nanocrystalline films and nanowires of silver from 1-ethyl-3-methylimidazolium trifluoromethyl sulfonate [EMIm] TfO which is based on the more stable anion.

Many examples of electrochemical processes in RTILs have been reported in the literature but relatively little is known about the underlying science in contrast to the corresponding aqueous system. The recent efforts on the electrodeposition from ionic liquids, are reviewed in the book ‘Electrodeposition from Ionic Liquids’³¹. The main challenges such as impurities, cation/anion effects or viscosity/conductivity need to be considered for the use of ionic liquids as an alternative electrodeposition bath. The study of the electrochemical processes range in scope from fundamental academic investigation, for example into the structure of solid/liquid and liquid/liquid interfaces, the double layer structure and its variation with changes in potential, metal speciation and current density and the detailed mechanisms of nucleation and growth and into the mechanisms of ion diffusion. Here the results of an in-depth study on silver electrodeposition from ionic liquids based on eutectic mixtures of choline chloride (ChCl) with either ethylene glycol or urea is presented.

These liquids are relatively new class of ILs based on the eutectic mixtures of the large, unsymmetrical, choline cation and a complex anion formed between [Cl⁻] and a hydrogen bond donor. A wide range of such liquids have been reported using diverse H-bond donors such as amides, alcohols and carboxylic acids^{32, 33}. These liquids are not only more air and moisture stable^{26, 34} as compared to conventional ionic liquids e.g. chloroaluminate salts but can also be prepared at low cost and with high purity. These liquids are promising solvents and have been used for the deposition of a range of metal coatings including Zn, Cr, Sn, Cu and Ag^{26, 35-38} at high current efficiency

and also for metal dissolution processes such as electropolishing replacing the current aqueous processes using strong inorganic acids or toxic ligands.²⁶ In previous studies Abbott *et al.* have characterised the physical properties of these liquids, *e.g.* viscosity and conductivity^{39, 40} and more recently have expanded their research to the characterisation of alloys electrodeposited from mixed systems⁴¹. The electrodeposition of metals in this type of ionic liquids has been recently reviewed¹⁹.

The focus of this study has been the deposition of silver coatings, from moisture stable ionic liquids aimed at replacement technologies for current aqueous electrolytes (note that the terms ionic liquid and deep eutectic solvents (DES) will be used interchangeably throughout this thesis). The choline chloride based ionic liquids contain a high concentration of $[\text{Cl}^-]$ that tends to minimise the role of ambient moisture such that even relatively high water content (from aerobic absorption) does not noticeably effect the electrolytic deposition process of metals. Whilst the liquids are formulated at a temperature of 70°C the subsequent metal deposition is carried out at lower temperatures (50°C) where water content is < 3 wt %. These conditions can easily be maintained for a commercial or technical metal deposition process, consequently rigorous drying of the starting material is not required.

This chapter focuses on the fundamental aspects of silver nucleation and growth under these conditions in choline chloride based ionic liquids using electrochemical methods (cyclic voltammetry, chronoamperometry) together with surface probe microscopy and acoustic impedance spectroscopy using an electrochemical quartz crystal microbalance (EQCM).

3.2 Physical Properties

The physical properties of 1:2 ChCl:EG and 1:2 ChCl:Urea such as viscosity, conductivity, density and surface tension are measured as a function of Ag(I) concentration, different silver salts and temperature.

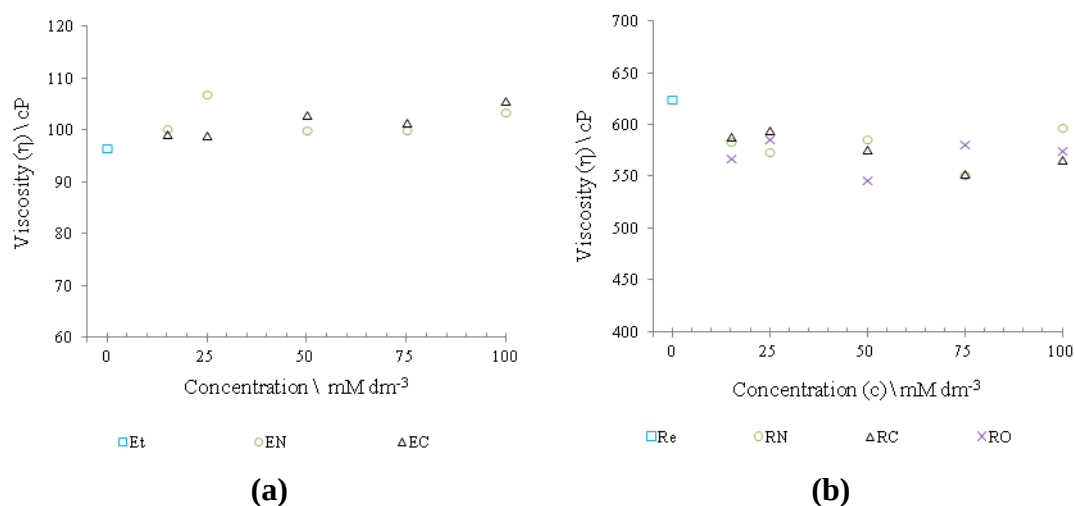


Figure 3.1: The viscosity of (a) 1:2 ChCl:EG and (b) 1:2 ChCl:urea as a function of Ag(I) concentration of different salts of silver, at 25°C

3.2.1 Viscosity and Conductivity

Figures 3.1 shows the viscosity of the 1:2 ChCl:EG and 1:2 ChCl:urea with different silver salts AgNO_3 , AgCl and Ag_2O as a function of Ag(I) concentration. The viscosity of 1:2 ChCl:EG is 93 cP at 25°C and the addition of silver salts has little or no effect on the viscosity. The viscosity of 1:2 ChCl:urea is 620 cP at 25°C and the addition of the silver slightly decreases the viscosity. In both the solvents the viscosity is insensitive to Ag(I) concentration and the different silver salts and counter ions of the salts. This is in contrast to the work of Barron⁴² who found that the addition of ZnCl_2 had a much more marked effect on the viscosity of the 1:2 ChCl:urea system.

Figure 3.2 show the conductivity of both the solvents as a function of Ag(I) concentration and different silver salts. The conductivity of 1:2 ChCl:EG is found to be $2000 \mu\text{S}$ at 25°C and it slightly decreases on the addition of silver salts to it. The conductivity of 1:2 ChCl:urea is found to be $120 \mu\text{S}$ at 25°C and the addition of silver salts has no effect on it. In an analogous manner like viscosity, the different Ag(I) concentration and the different silver salts show no effect on the conductivity.

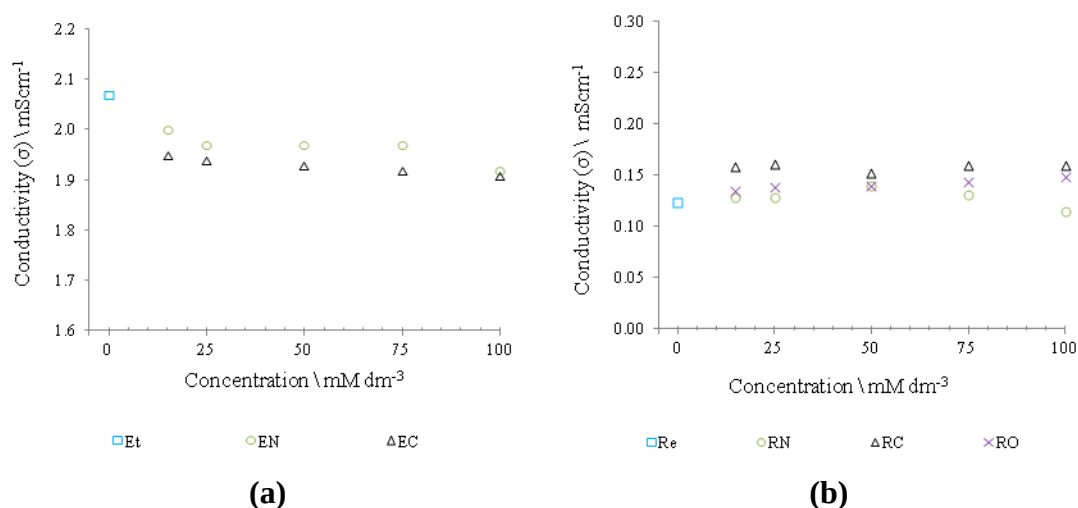


Figure 3.2: The conductivity of (a) 1:2 ChCl:EG and (b) 1:2 ChCl:urea as a function of Ag(I) concentration of different salts of silver, at 25 °C

3.2.2. Effect of Temperature on viscosity and conductivity

The variation of conductivity and the viscosity with temperature over the range of 25 °C-70 °C and 25 °C-50 °C respectively is shown in **Figure 3.3**. The viscosity and conductivity in both the solvents is affected significantly with temperature. The viscosity is decreased 60 % at 50°C as compared to room temperature in 1:2 ChCl:EG while more than 80 % decrease is observed over the same range in the 1:2 ChCl:urea. The increase in conductivity of 1:2 ChCl:EG and 1:2 ChCl:urea is about 2 and 10 times respectively at 70 °C as compare to room temperature. This higher magnitude of effect on change in temperature in 1:2 ChCl:urea compared to 1:2 ChCl:EG may be attributed to the strong hydrogen bonding in the former.

The viscosity and the conductivity of the solvents are related to the temperature by the equations 3.1 and 3.2 respectively⁴³.

$$\ln \eta = \ln \eta_o + \frac{E_\eta}{RT} \quad (3.1)$$

$$\ln \sigma = \ln \sigma_o - \frac{E_\Lambda}{RT} \quad (3.2)$$

Where η_o and σ_o are constants, E_η is the energy of activation of viscous flow and E_Λ is the energy of activation for conduction.

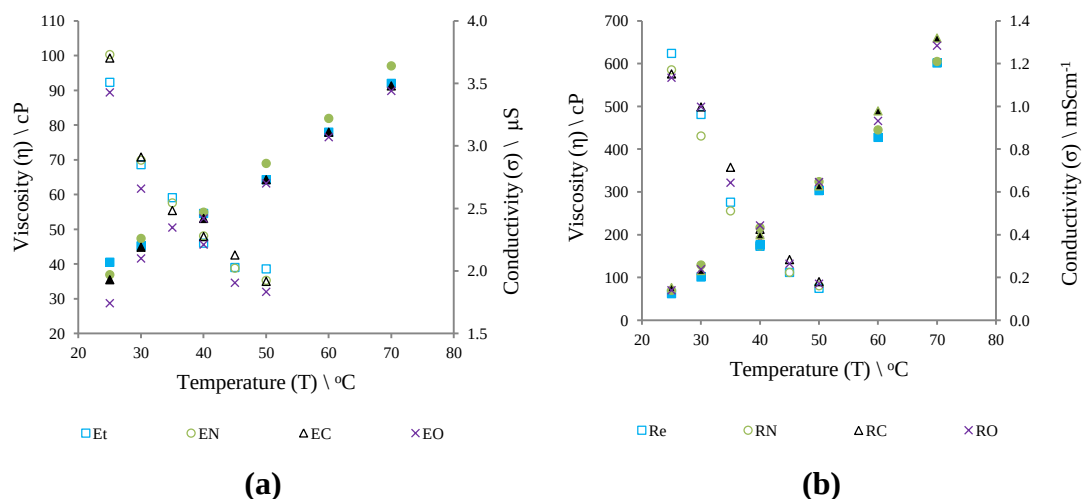


Figure 3.3 : The viscosity (open symbols) and conductivity (solid symbols) of (a) 1:2 ChCl:EG and (b) 1:2 ChCl:urea containing different Ag(I) concentration of different salts of silver as a function of temperature.

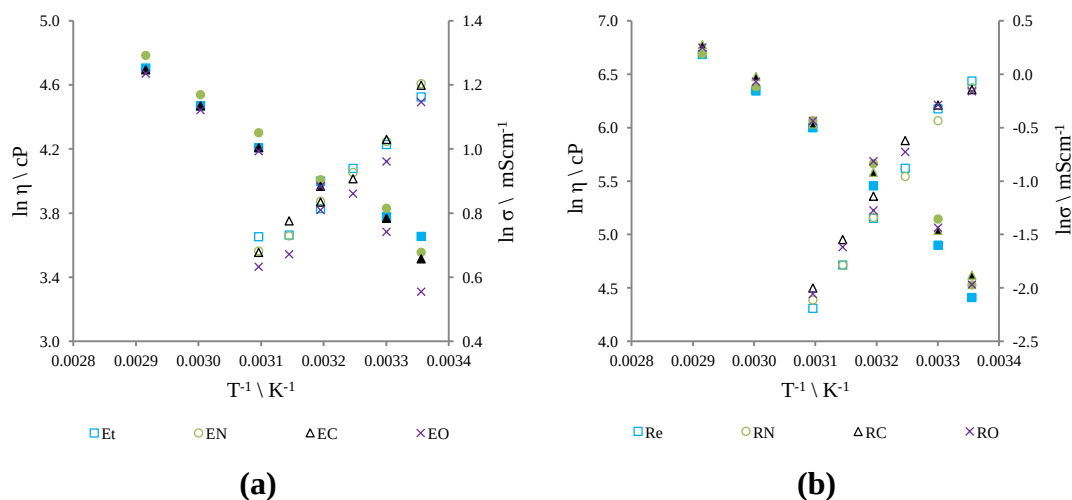


Figure 3.4: Plot of logarithm of viscosity (open symbols) and conductivity (solid symbols) vs. reciprocal of temperature for different silver salts containing different concentration in (a) 1:2 ChCl:EG (b) 1:2 ChCl:urea

Figure 3.4 shows that the data fits well to the equation 3.1 and equation 3.2 in both cases and the energy of activation is calculated using the slope of these graphs and are tabulated in **table 3.1**

Table 3.1:	<i>Activation energies for viscous flow (E_η) and conductivity (E_A) of silver salts for 50 mmol dm³ Ag(I)</i>						
	1:2 ChCl:EG	Ethaline + AgNO ₃	Ethaline + AgCl	1:2 ChCl: urea	Reline + AgNO ₃	Reline + AgCl	Reline + Ag ₂ O
E_η (kJ mole ⁻¹)	28.95	29.08	29.88	70.76	65.68	61.89	63.10
E_A (kJ mole ⁻¹)	10.43	11.08	10.67	42.08	38.49	40.37	40.23
Avg. void radius (Å)	1.415	1.42	1.43	1.178	1.185	1.174	1.185

The E_η and E_A values of 1:2 ChCl:EG are comparable to those of high temperature molten salts (typically group I halides have values of 5-20 kJ mole⁻¹)⁴⁴ while the values of 1:2 ChCl:urea are significantly larger than the high temperature molten salts but are comparable to ChCl/CrCl₃.6H₂O³³ and for most of the imidazolium based ionic liquids⁶.

A model which has been demonstrated to accurately predict the viscosities and conductivities of ionic liquids and deep eutectic solvents is the hole theory³⁹⁻⁴¹. The central assumption of the hole theory is that as a solid melts, voids of random size and orientation are formed. The ability of an ion to move is therefore considered to be dependent upon the presence of an adjacent void of an equal or greater size than the ion. The probability of ion motion can therefore be considered to be dependent on the size of the ions and the relative abundance of suitable sized holes.

The mass transport properties of a range of ionic liquids and deep eutectic solvents have been calculated using the hole theory and show a strong degree of correlation with experimentally obtained values³⁹. This correlation suggests that mass transport in ionic liquids, which contain bulky asymmetric ions, is primarily controlled by the availability of suitably sized holes. This is in contrast to the classical high temperature molten salts, which are generally composed of small symmetric ions, where mass transport is principally controlled by the concentration of charge carriers³⁹

A strong linear correlation between conductivity and the reciprocal of viscosity **Figure 3.5** indicates that the conductivity is governed by the ionic mobility rather than the number of charge carrier. The slopes in both the systems are approximately the same indicating that the charge carrying species are the same in all the cases in spite of the fact of the presence of the different anions.

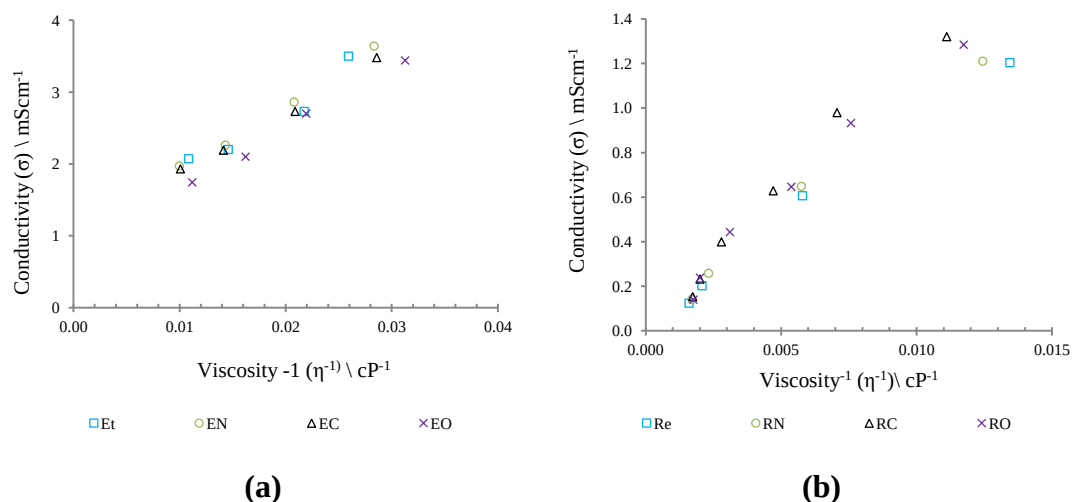


Figure 3.5: Conductivity as a function of fluidity (a) 1:2 ChCl:EG (b) 1:2 ChCl:urea

3.2.3. Surface tension

The surface tension of 1:2 ChCl:EG is found to be 56 mNm^{-1} which is less than water but is comparable to the imidazolium based ionic liquids while the viscosity of 1:2 ChCl:urea is found to be 82 mNm^{-1} at 25°C which is higher than water and comparable to the high temperature molten salts ($\text{KBr } \gamma = 77.3 \text{ mNm}^{-1}$ at 900°C)⁴⁴. The surface tension in both the solvents is independent of the silver concentration and the salt anions as shown in **Figure 3.6**.

The surface tension of the liquid can be related to the radius of the average size of void through following equation 3.3⁴³.

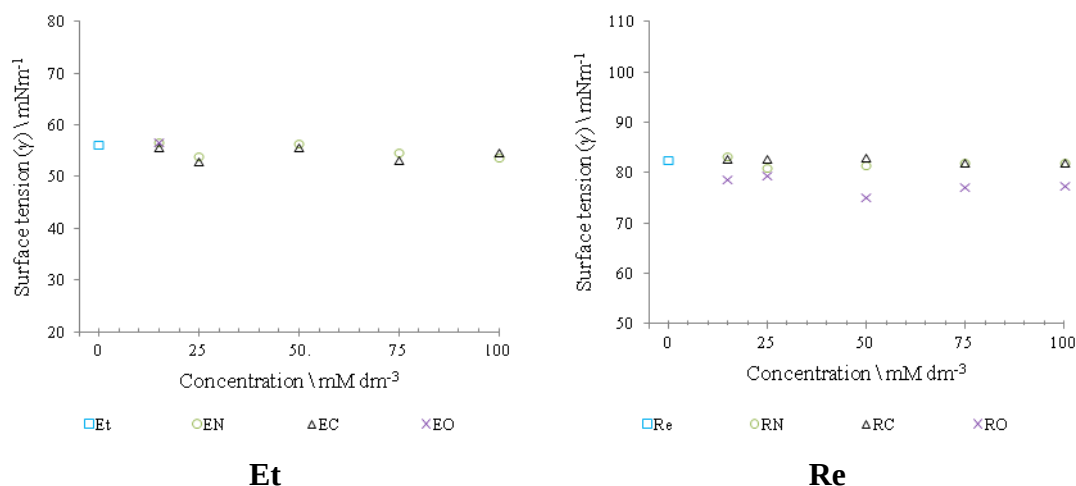


Figure 3.6: The surface tension of (a) 1:2 ChCl:EG and (b) 1:2 ChCl:urea as a function of silver salts and concentration, at 25°C

$$4 \pi \langle r^2 \rangle = 3.5 \frac{kT}{\gamma} \quad (3.3)$$

Where k is the Boltzmann's constant and T is the absolute temperature.

The average void radius was found to be 1.46 Å and 1.1817 Å for 1:2 ChCl:EG and 1:2 ChCl:urea respectively and listed in **table 3.1**. The small void size in Reline can be attributed to the fact that Ethylene glycol is known to be a relatively weak hydrogen bond donor⁴⁰ while urea is a much stronger hydrogen bond donor which is ascribed to the strong hydrogen bonding in urea based systems. The high viscosity and low conductivity of 1:2 ChCl: urea may be related to the small void size as compared to 1:2 ChCl:EG.

3.2.4 Density

Figure 3.7 show the trend of the change in density in both the solvents as function of silver ion concentration. In both the cases the density increases with increasing the concentration as expected but the effect is more in 1:2 ChCl:urea as compared to 1:2 ChCl:EG.

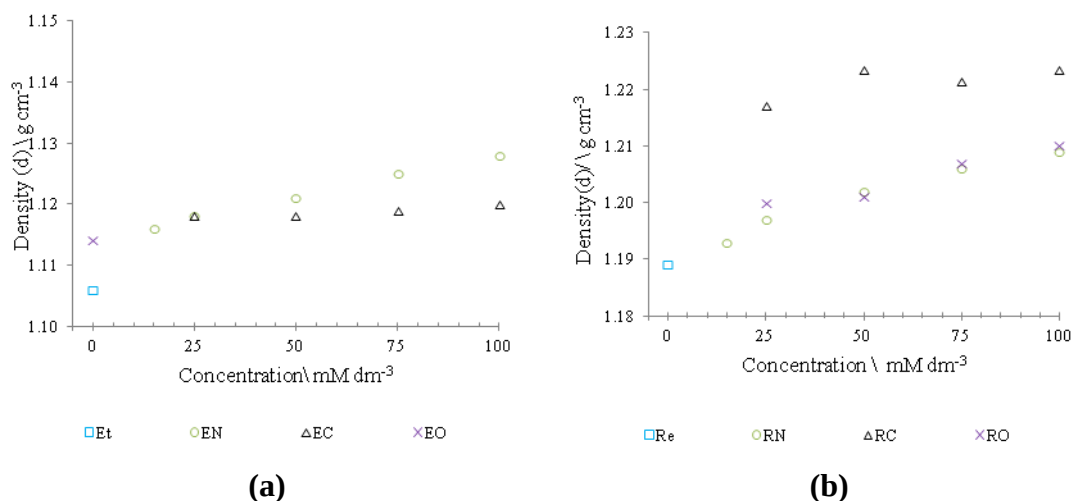


Figure 3.7: The density of (a) 1:2 ChCl:EG and (b) 1:2 ChCl:urea as a function of silver salts and concentration, at 25°C

3.3 Potentiodynamic Study

A cyclic voltammetric study was conducted to define the potential region of the deposition of Ag(I) and to get information about the electrode process kinetics. Cyclic Voltammetry was performed in the potential limits of +0.3 to -0.3 V and with changing scan rates from 0.005, 0.01, 0.02, 0.03, 0.04, 0.05 and 0.1 Vs⁻¹. The potential sweep is initiated at +0.3V and processed in negative direction and reversed (E_{λ}) at -0.3V. A series of cyclic voltammograms are obtained for three silver salts (AgNO₃, AgCl and Ag₂O) for different concentrations (15, 25, 50, 75 and 100 mmol dm⁻³) both in 1:2 ChCl:EG and 1:2 ChCl:urea using a platinum disc working electrode, a platinum flag working electrode and a silver wire quasi reference electrode.

3.3.1 Electrochemical window of Ethaline and Reline

The electrochemical window is the two intersection points between the zero line and the tangents to the reduction and oxidation potential limits, where the current increased strongly and continuously, indicating the decomposition of the ILs. The electrochemical window is determined by cyclic voltammetry at a scan rate of 10 mV s⁻¹ at a platinum disc electrode. **Figure 3.8** exhibits that the electrochemical

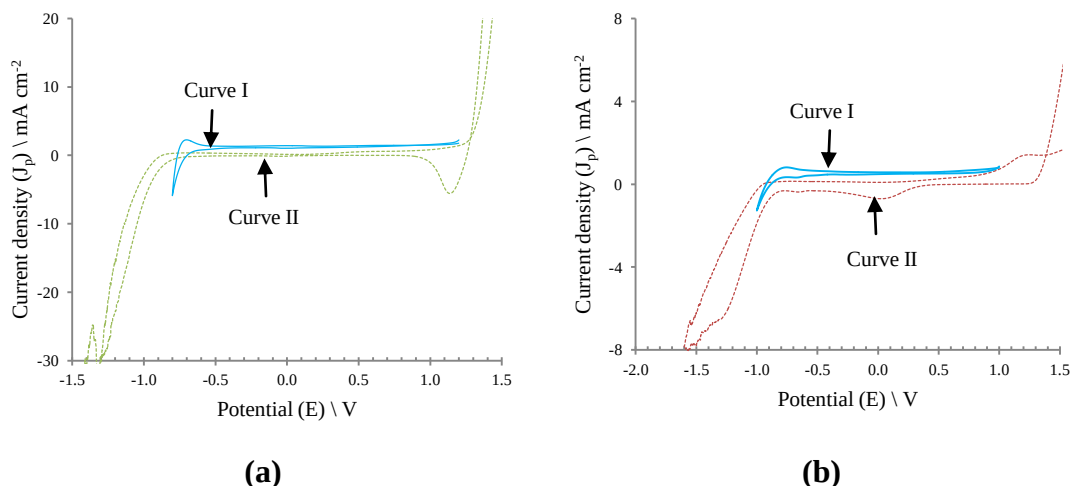


Figure 3.8 : Cyclic voltammograms of the neat DES (a) 1:2 ChCl:EG and (b) 1:2 ChCl: urea , at a scan rate of 10 mV sec^{-1}

window of Ethaline and 1:2 ChCl:urea is about 2 volts extending from +1.3 V to -0.8 V vs. silver wire as quasi reference. The cut off current density arbitrarily used here is the potential at which the current density reached 0.1 mA cm^{-2} (usually the cut off current density is selected between $0.1 - 1 \text{ mA cm}^{-2}$ ^{30, 45} but it is more common to select the cut off current density below 0.1 mA cm^{-2}). The cathodic and anodic limits probably correspond to the reduction of the hydrogen bond donor and oxidation of Cl^- respectively. In 1:2 ChCl:EG zero current is observed throughout the scan up to -0.8 V while in 1:2 ChCl:urea a small wave less than 0.5 mA cm^{-2} at around -0.1 V may be attributed to the presence of H^+ due to the dissociation of water that is surely present in the binary mixture. On the anodic scan in curve I, the presence of the anodic wave at -0.75V is due to the oxidation of the products formed during the cathodic scan.

3.3.2 Cyclic voltammograms

A typical linear sweep voltammogram of silver is shown in **Figure 3.9**. It exhibits a clear redox couple with single reduction wave and a coupled oxidation wave. The broad peak I is associated with silver deposition process (Ag(I) to Ag(0)) while a sharper, more symmetrical peak II is due to dissolution of deposited silver in the forward scan. Beyond the recorded anodic peak , the current almost reaches to zero

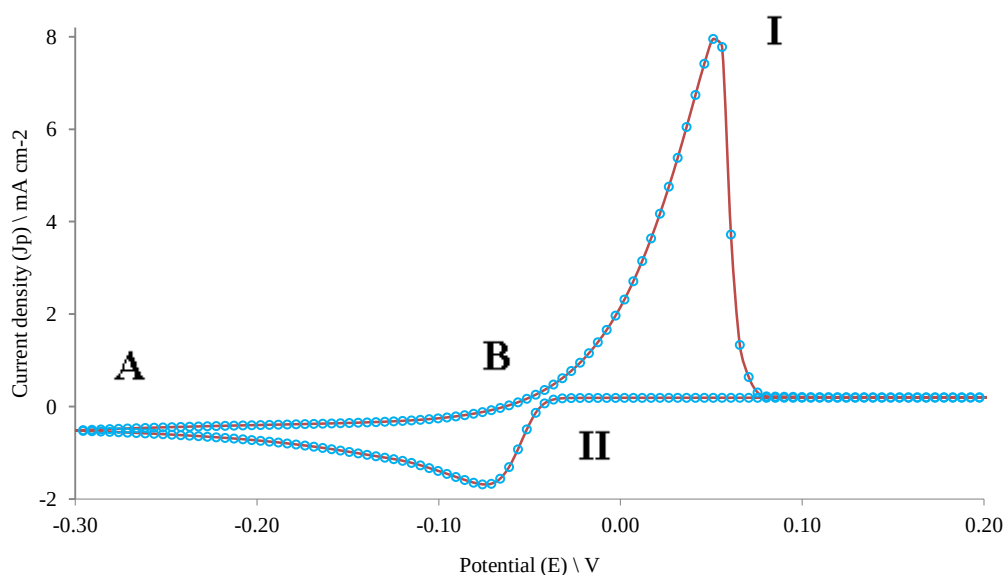


Figure 3.9: Cyclic voltammogram of 1:2 ChCl:EG containing AgNO_3 (50 mmol dm^{-3}), scan rate 10 mV sec^{-1}

indicating the stripping of the deposited silver obtained in the forward scan. In the reduction process, a current plateau A-B is observed indicating the stationary current. The cross over between the cathodic and anodic branches (nucleation loop) indicates that an over potential is required to initiate nucleation and growth of silver bulk deposition¹⁹. These voltammograms are consistent with those expected for silver deposition and stripping reported in aqueous and other ionic liquids^{3, 24, 46, 47}.

A series of cyclic voltammograms for three different silver salts at different scan rates ranging from 5 mV sec^{-1} to 100 mV sec^{-1} at Ag(I) concentration of 100 mmol in 1:2 ChCl:EG and 1:2 ChCl:urea are shown in **Figure 3.10**. Only peak potential and magnitude and not the general shape and the characteristics of the voltammograms are varied in the two solvents. To study the silver deposition process quantitatively, a detailed analysis of the voltammetric peak position and magnitude is conducted.

To gain the information about the kinetics of the electrode process the peak potential and current maxima are correlated with scan rate.

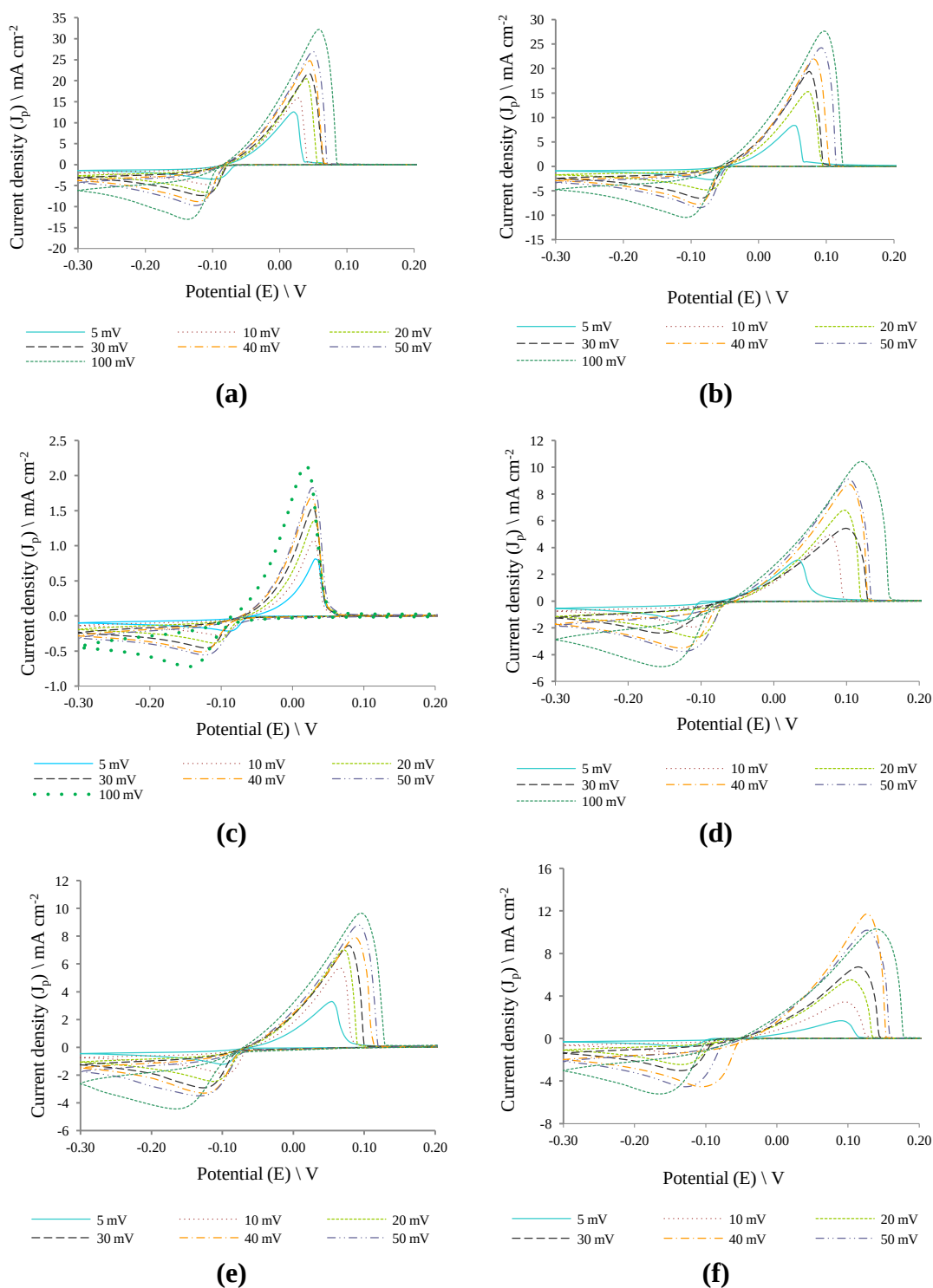


Figure 3.10: Cyclic voltammograms for electrolytes containing 100 mmol dm^{-3} of Ag(I) at different scan rates, (a) 1:2 ChCl:EG + AgNO_3 (b) 1:2 ChCl:EG + AgCl (c) 1:2 ChCl:EG + Ag_2O (d) 1:2 ChCl:urea + AgNO_3 (e) 1:2 ChCl:urea + AgCl (f) 1:2 ChCl:urea + Ag_2O

Figure 3.11(a) shows that the cathodic peak potential is shifted to more negative values with an increase in the scan rate. As the electrolytic current is small the effect of ohmic drop on the peak potential should be negligible. This behaviour is suggestive that the deposition process is limited by charge transfer rate, which occurs together with the mass transport of the electroactive species and the reduction of Ag(I) is electrochemically quasi-reversible. The shift of peak potential is more pronounced in 1:2 ChCl:urea than in 1:2 ChCl:EG.

The reduction and oxidation processes give rise to peak separation (ΔE_p) in the range of 0.12 – 0.19 V for 1:2 ChCl:EG and 0.16 - 0.27 V for 1:2 ChCl:urea (**Figure 3.11(b)**). The spacing between the anodic and cathodic potential peaks increases with increasing scan rate.

Figure 3.11(c) indicates that the peak potential – half peak potential separation [$E_p^{ox} - E_{p/2}^{ox}$] increases with scan rate. At the lowest scan rate, the latter is still considerably larger than the 0.021 V, separation expected for reversible one electron electrode process in which the activity of the deposited metal remains constant^{27, 48}. Taken together, these results suggest this behaviour may be related to some indistinct kinetic limitation of the phase formation process or to quasi reversibility of the Ag(I) / Ag(0) charge transfer reaction.

Figure 3.11(d) shows that the linear dependence of the cathodic peak current and the square root of scan rate with the positive intercept of the current axis indicates that deposition of silver proceed through a nucleation mechanism under diffusion controlled growth⁴⁹. The positive intercept on the current axis can be explained by effect of the sweep rate on nucleation behaviour.⁵⁰ The linear dependence of peak position and height on potential scan rate is the characteristic of an instantaneous nucleation and growth process⁵¹. The steepness of the curves suggest that the silver deposition process in 1:2 ChCl:urea is a slow process.

The diffusion coefficient of silver (D_{Ag^+}) is calculated from the slopes of these curves using the the Randles sevick equation

$$J_p = 2.687 \times 10^5 n^{3/2} \nu^{1/2} D^{1/2} C \quad (3.4)$$

Where constant has units $2.687 \times 10^5 \text{ C mole}^{-1} \text{ V}^{-1/2}$

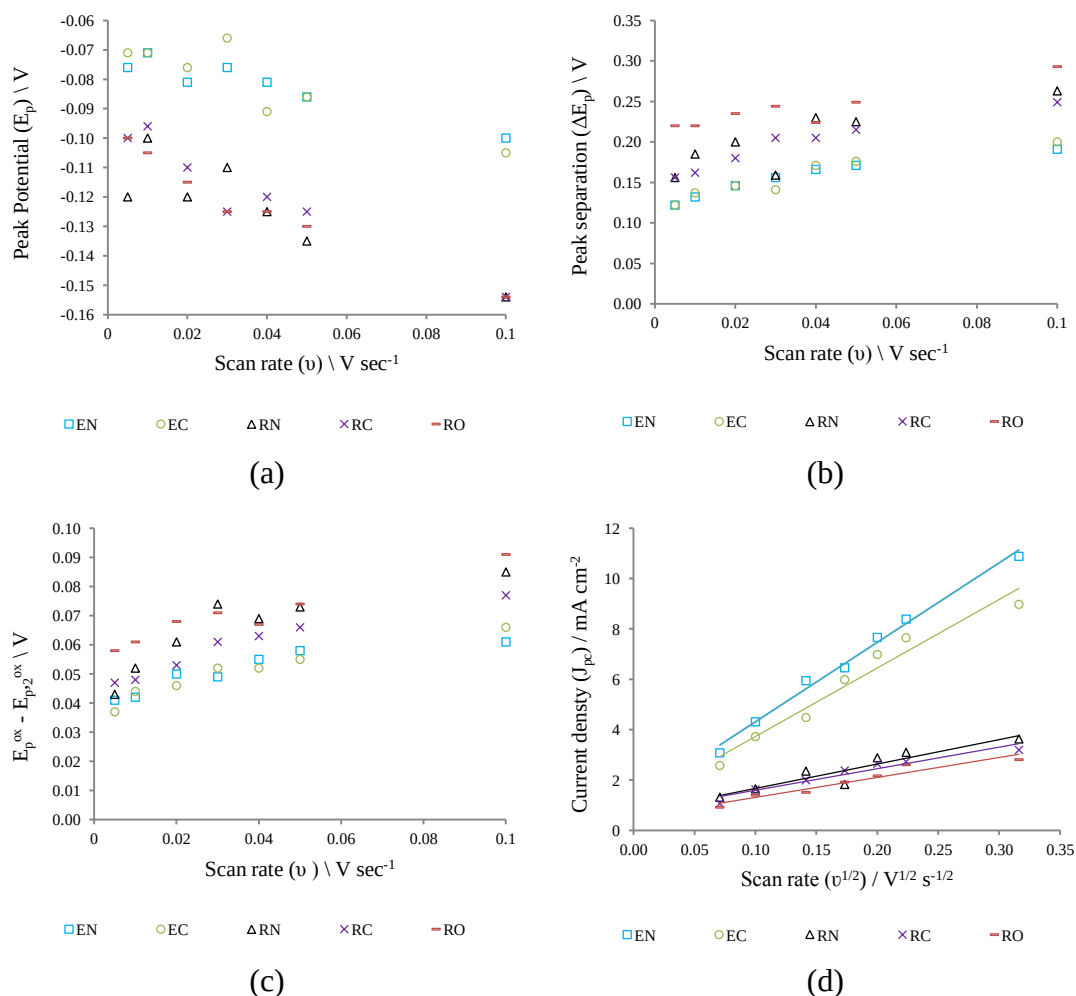


Figure 3.11: Correlation of peak coordinates with the scan rate of silver salts in 1:2 ChCl:EG and 1:2 ChCl:urea containing Ag(I) 100 mmol dm⁻³ (a) peak potential (b) peak separation (c) Anodic peak broadening (d) peak current density vs. square root of scan rate

The values of the diffusion coefficient calculated are tabulated in **table 3.2**. The value for 1:2 ChCl:EG is greater by an order of 10 magnitude than for 1:2 ChCl:urea. The higher values in 1:2 ChCl:EG are ascribed to its lower viscosity than 1:2 ChCl:urea. The values are similar to those found for 1:2 ChCl:urea by Liana Anicai *et al*⁵² and comparable with the diffusion coefficient values for imidazolium based liquids.

3.3.3 Effect of concentration

The current magnitude and voltammetric peak potentials were found to vary with the concentration of Ag(I) in the deposition bath. The peak position of the cathodic peak is shifted towards more positive values. At high concentration, the voltammetric peaks

broadened. The linear relationship between $\log J_p$ and $\log C_{Ag(I)}$ indicates that the reduction process is diffusion controlled as shown in **Figure 3.12(a)**.

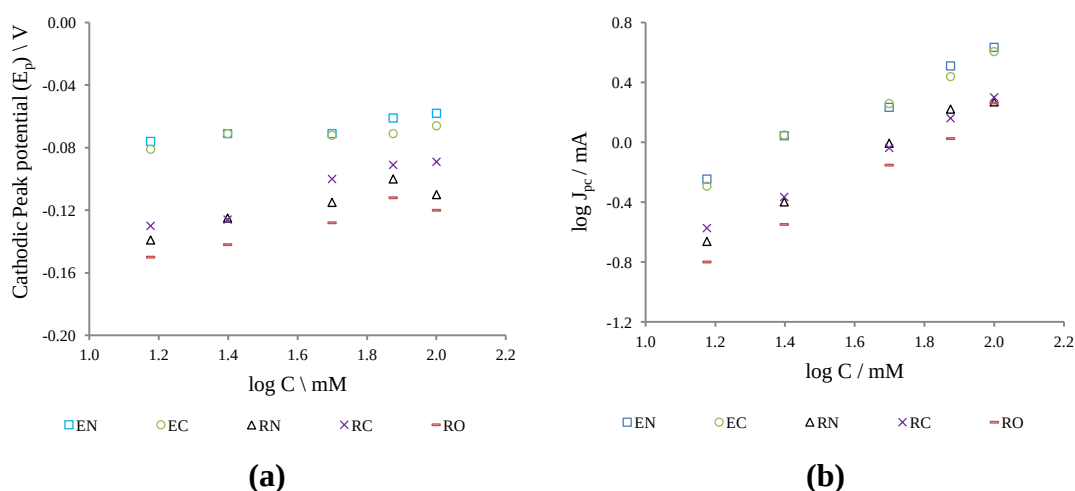


Figure 3.12: Variation of cathodic peak potential and cathodic peak current in (a) 1:2 ChCl:EG and (b) 1:2 ChCl:urea of different silver salts as a function of Ag(I) concentration

Figure 3.12 exhibits the peak reduction potential of a silver deposition measured as a function of concentration of (Ag(I) in both 1:2 ChCl:urea and 1:2 ChCl:EG. The potential E_{red} , shifts to more positive value with increase in concentration and this shift in peak potential seems to be almost uniform with an increase of concentration. The shift in position in 1:2 ChCl:urea is more sharp as compared to 1:2 ChCl:EG. In both the cases the slope is less as predicted by Nernst equation.

$$E_{red} = E^o + \frac{2.303 RT}{n F} \log C_{Ag(I)} \quad (3.5)$$

Where E^o is the formal potential, R is the gas constant in $J \cdot mole^{-1} K^{-1}$ and T is the absolute temperature in K, n is the number of electrons and F is the Faraday constant in $C \cdot mole^{-1}$. This indicates that the Ag(I) deposition process requires an electrocrystallization overpotential, which interestingly also depends on the Ag(I) concentration in the deposition bath, this indicates the different silver deposition mechanism. For high Ag(I) concentration IR_u (Ohmic drop) could have influenced the potential value.

3.3.4 Bulk deposition-stripping efficiency

The efficiency for the deposition and stripping of silver in more than monolayer amounts is investigated by integrating the current corresponding to the reduction and oxidation portions of the sequential cyclic voltammograms shown in

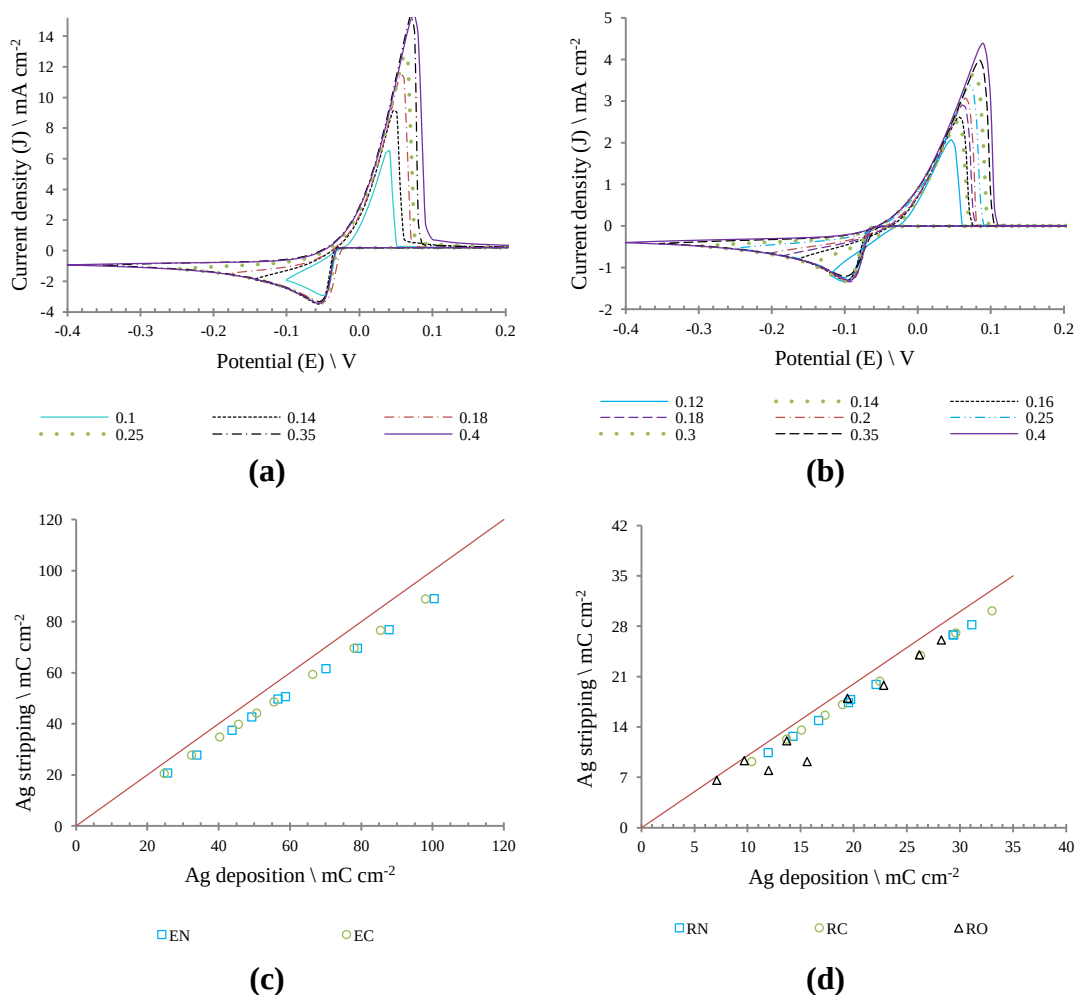


Figure 3.13: *Cyclic voltammograms obtained at different switching potentials in the forward scan for Ag(I) concentration of 100 mmol dm⁻³ at scan rate 10 mV sec⁻¹ in (a) 1:2 ChCl:EG and (b) 1:2 ChCl:urea (c & d) Plot of the charge for silver metal deposition vs. charge for silver metal stripping constructed from the graphs in (a & b) respectively*

Figure 3.13 (a & b). Each of the voltammograms is recorded successively using a more negative switching potential (-0.1 to -0.4 V) during the forward scan. This shows that the cross over potential shifts negatively as the potential reversal become more negative, indicating that as the potential become more negative the deposition reaction is driven into being diffusion controlled⁵³. Moreover the stripping wave

becomes broader and less symmetric as the potential reversal become more negative. In other words, the shape of the stripping wave is related to the amounts of silver that are deposited on the electrode surface during the forward scan, more positive potentials results in less silver deposits and a more symmetric stripping wave.

Figure 3.13 (c & d) show the plot of the charge of silver deposition and silver stripping charge obtained by integrating the cathodic and anodic waves. The solid line in this figure represents a deposition stripping efficiency of 100%, i.e. all of the deposited material is removed during the stripping portion of the cycle. The data shows that the stripping in DES is not 100% and from the slopes of these curves it is found that stripping efficiency vary from 89 to 93%.

3.3.5. Reaction Rate

The standard heterogeneous rate constant for the silver deposition process at the electrode surface can be calculated from the intercept of the plot of log of the peak current density for the reduction of Ag(I) and the difference of the peak and formal potential, E_p and E^o (V) using the Tafel equation⁵⁴

$$\ln J_p = \ln (0.227 n F C_{Ag} K^o) + \frac{\alpha n_a F}{R T} (E_p - E^o) \quad (3.6)$$

Where C_{Ag} is bulk concentration of Ag(I) in mole cm^{-3} , α is the transfer coefficient, n is the number of electrons involved in the reduction process respectively.

The K^o values calculated are tabulated in **table 3.2**. The K^o values are rather smaller than those reported for aqueous solution without complexing agents ($K^o = 2 \times 10^{-2} \text{ cm s}^{-1}$ in KNO_3 solution²⁴ and slightly larger than reduction of Ag(I) in $\text{EMICl} - \text{AlCl}_3$ system and EMIBF_4 ²⁷. The slow kinetics of the reduction of Ag(I) may be explained by the existence of bulky ChCl^+ cation.

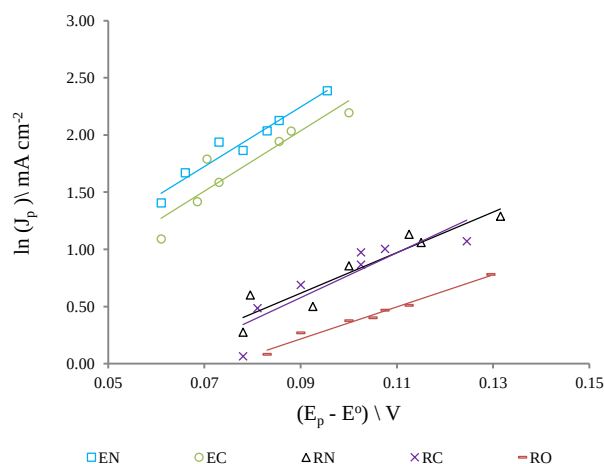


Figure 3.14: *Dependence of the log of the peak current density for Ag(I) / Ag(0) on the difference of the peak and formal potentials in DES containing 100 mmol dm⁻³ for different silver salts*

The Tafel equation is derived considering the variations of the energy of the reactants, transition states and products with the electrode potential. The slope of the curves is used to estimate the transfer coefficient which is found to be 0.7 and 0.4 for 1:2 ChCl:EG and 1:2 ChCl:urea. Transfer coefficient is a measure of the symmetry of the energy barrier for electron transfer⁵⁵.

Table 3.2:	<i>Kinetic parameters for the reduction of Ag(I) in DES and comparison with other system</i>		
System	Diffusion Coefficient (D) $1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$	Heterogeneous Rate constant $1 \times 10^{-4} \text{ cm s}^{-1}$	Transfer coefficient (α)
* 1:2 ChCl:EG + AgNO ₃	1.38	4.14	0.70
* 1:2 ChCl:EG + AgCl	1.03	3.27	0.71
* 1:2 ChCl:EGl + Ag ₂ O	0.23	0.45	0.702
** 1:2 ChCl:urea + AgNO ₃	0.13	1.71	0.48
** 1:2 ChCl:urea + AgCl	0.10	1.39	0.52
*** 1:2 ChCl:urea + Ag ₂ O	0.076	1.32	0.43
Ag(I)/EMIBF ₄ ²⁴	0.6	0.1	0.7
Ag(I)/BMIMPF ₆ ²³	0.01	-	-
Ag(I)/ MeEtimCl ²⁷	1.2	-	-
Ag(I)/DIMCARB ¹²	0.3	-	-
Ag(I)/KNO ₃ ⁵⁶	9.10	200	-
	* **	The likely determination error is $\pm 2 \%$ The likely determination error is $\pm 4 \%$	

3.4 Gravimetric Analysis

The growth behaviour of the silver deposition has been studied by using electrochemical acoustic impedance spectroscopy in gravimetric mode namely Electrochemical Quartz Crystal Microbalance (EQCM). The EQCM is an extremely sensitive technique measuring *in situ* processes at the electrode / solution interface with sub-monolayer resolution and found in a variety of electrochemical applications⁵⁷⁻⁶¹. By this technique the deposited mass of Ag(0) at the electrode has been studied from the variation in resonant frequency (Δf) of the gold coated quartz crystal working as cathode and the response of the quartz crystal's resonance

frequency from its base value (f_o) has been monitored as a function of time during potentiostatic deposition. A full resonance spectrum of the in situ mass loaded crystal at each point in time is acquired and the resonance curves are conventionally presented as an admittance (reciprocal of impedance, Z / Ω), U/ Siemens and frequency plot in **Figure 3.15**.

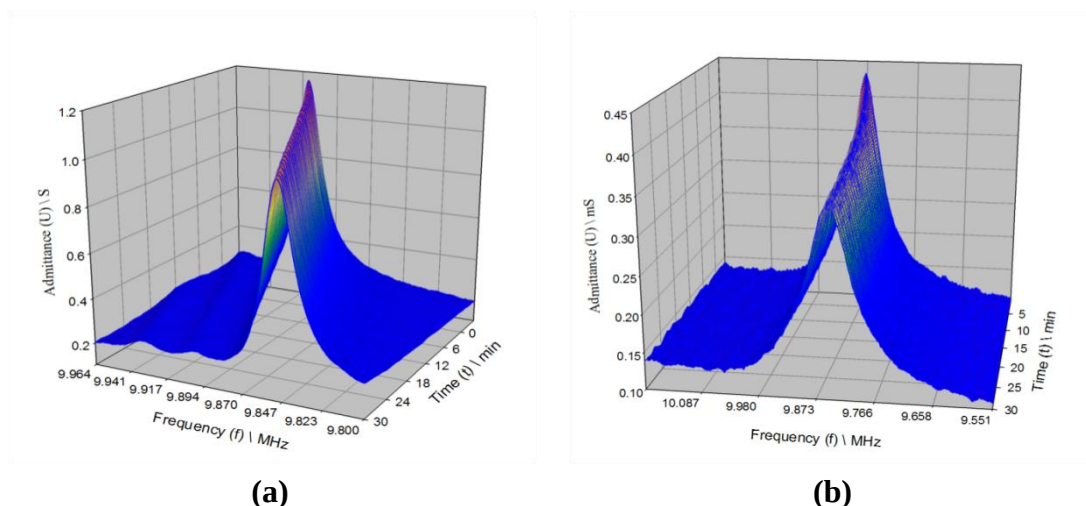


Figure 3.15: *U(f,t) data for the deposition of Ag(I) from (a) 1:2 ChCl:EG and (b) 1:2 ChCl:urea containing 100 mmol dm⁻³ of AgNO₃. Spectra are acquired after every 5 seconds.*

The subsequent curve fitting yields the peak frequency and the real component of the impedance of the crystal circuit, taking the peak frequency of the gold only coated crystal as the reference. The electrical impedance of the crystal circuit is coupled to the mechanical losses at the crystal/ liquid interface which in turn gives the useful quantitative information about surface roughness and density⁶⁰. The change in frequency is related to the additional mass using the Sauerbrey equation⁶²

$$\Delta f_{Hz} = \frac{-2}{\rho v} f_o^2 (\Delta m / g \text{ cm}^{-2}) \quad (3.7)$$

Where ρ is the density of the quartz and v is the wave velocity in the quartz. This expression is only valid if the additional mass is small and rigidly coupled. The rigidity of the film is related to the Q factor of the admittance resonance curve, which is the measure of the broadness of resonance given by⁶⁰

$$Q = \frac{f_o}{\omega} \quad (3.8)$$

Where f_o is the frequency value at the centre of resonance curve and w is the full width of the peak at half height (FWHH). A large shift in Q factor indicates that the surface has become rough and can no longer be assumed as a rigid resonator.

In the present study, the deposition of Ag from three silver salts (AgNO_3 , AgCl and Ag_2O) is studied in 1:2 ChCl:EG and 1:2 ChCl:Urea as a function of Ag(I) concentration using the gold coated quartz crystal as cathode at -500 mV and -600 mV against silver wire as quasi reference electrode and a platinum flag is used as a counter electrode. In this study, a 10 MHz AT-cut polished (flat mirror) finish quartz crystal with a gold film thickness of 900 Å, deposited in a keyhole shape on both sides with central disc active area of 0.211 cm^2 is used.

3.4.1 Frequency trends

Figure 3.16 shows the response of the resonance curves as a function of time. The maximum of these peaks shifted towards lower frequencies and the height of the curve decreases although the shape of these curves remains qualitatively unchanged. This shifting of frequency is found to be the function of the concentration of Ag(I) in

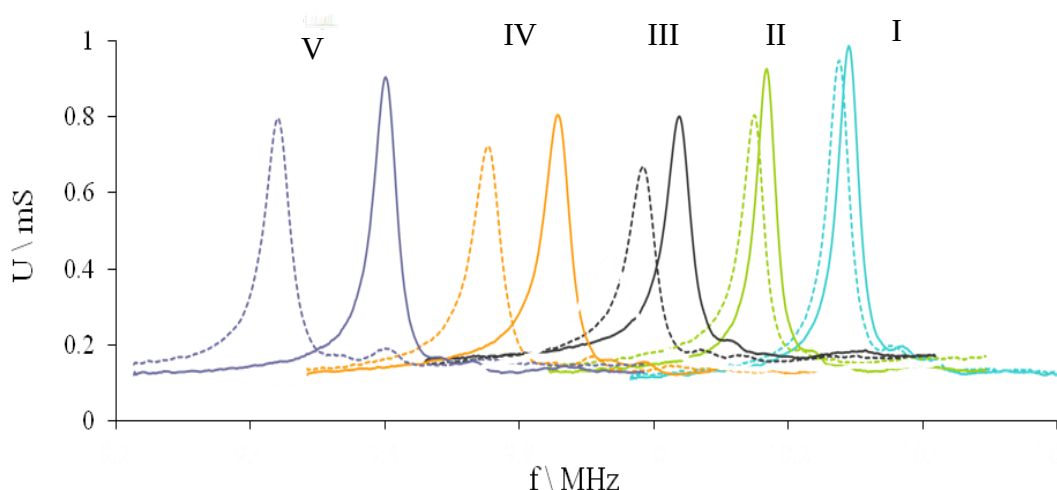


Figure 3.16: *Acoustic impedance spectra of silver deposition in 1:2 ChCl:EG containing AgNO_3 , (I) 15 mmol dm^{-3} (II) 25 mmol dm^{-3} (III) 50 mmol dm^{-3} (IV) 75 mmol dm^{-3} and (V) 100 mmol dm^{-3} . The solid lines are spectra of the dry Au coated polished crystal while the dashed lines show the spectra after the deposition of Ag(I) after 25 mins.*

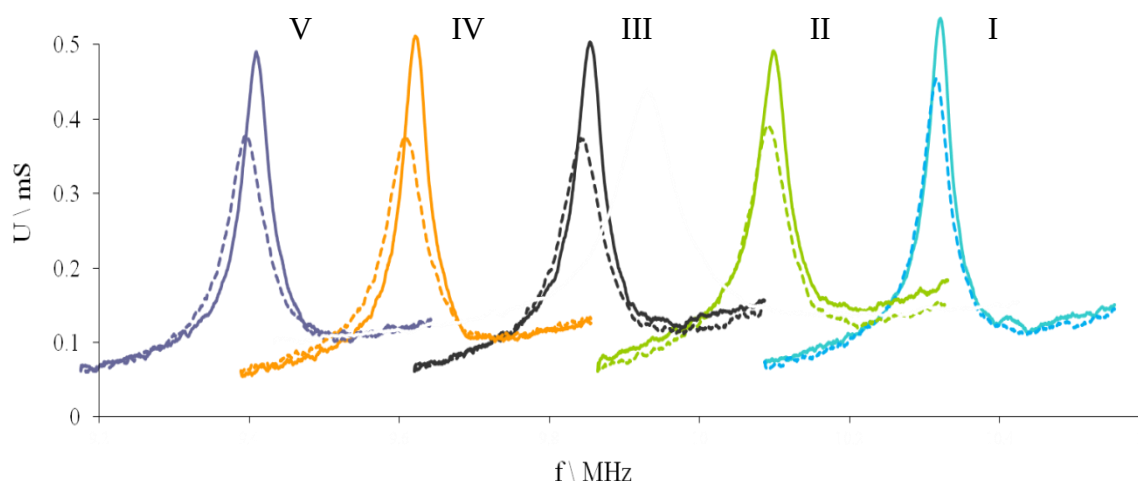


Figure 3.17: Acoustic impedance spectra of silver deposition in 1:2 ChCl: urea containing AgNO_3 , (I) 15 mmol dm^{-3} (II) 25 mmol dm^{-3} (III) 50 mmol dm^{-3} (IV) 75 mmol dm^{-3} and (V) 100 mmol dm^{-3} . The solid lines are spectra of the dry Au coated polished crystal while the dashed lines show the spectra after the deposition of Ag(I) after 25 mins. (I) 15 mmol dm^{-3} (II) 25 mmol dm^{-3} (III) 50 mmol dm^{-3} (IV) 75 mmol dm^{-3} and (V) 100 mmol dm^{-3}

1:2 ChCl:EG and 1:2 ChCl:urea. The change in frequency is between 0.12 and 1.06 % over the concentration range of 15 to 100 mmol dm^{-3} of Ag(I).

In case of 1:2 ChCl:urea, the resonance frequency curves are less high and slightly broader as compared with 1:2 ChCl:EG, this may be due to the fact that the Reline is more viscous by factor of six than 1:2 ChCl:EG and due to some viscoelastic changes. The same frequency trend is observed in 1:2 ChCl:urea but it is of lower magnitude ranging from 0.1 to 0.3 %.

The changes in the shape of the resonance curves are judged by Q factor measurements at the beginning and end of each experiment. The change in broadness of the curve were found to be between 5-6 % in 1:2 ChCl:EG and 10-12% in 1:2 ChCl:urea.

3.4.2 Current Efficiency

The current efficiency of the deposition process can be calculated from the ratio between the apparent molar mass calculated from the EQCM data and the theoretical molar mass of silver. **Figure 3.17** show the plots of the silver mass deposited as a function of charge passed in Ethaline 200 and 1:2 ChCl: urea. These graphs show a linear relationship between the charge and the mass. The slopes of these graphs are

used to calculate the apparent molar mass of silver by multiplying with nF (where n is the number of electrons involved in the process. High current efficiencies with values between 80 – 100% are obtained in both of the solvents. No significant trend of the current efficiencies with the concentration is found. The good linear fit of the data at long time shows that the current efficiency is not a function of time. Similar data were acquired for the urea base liquid Ag deposition. The current efficiency is also insensitive to the salt anions.

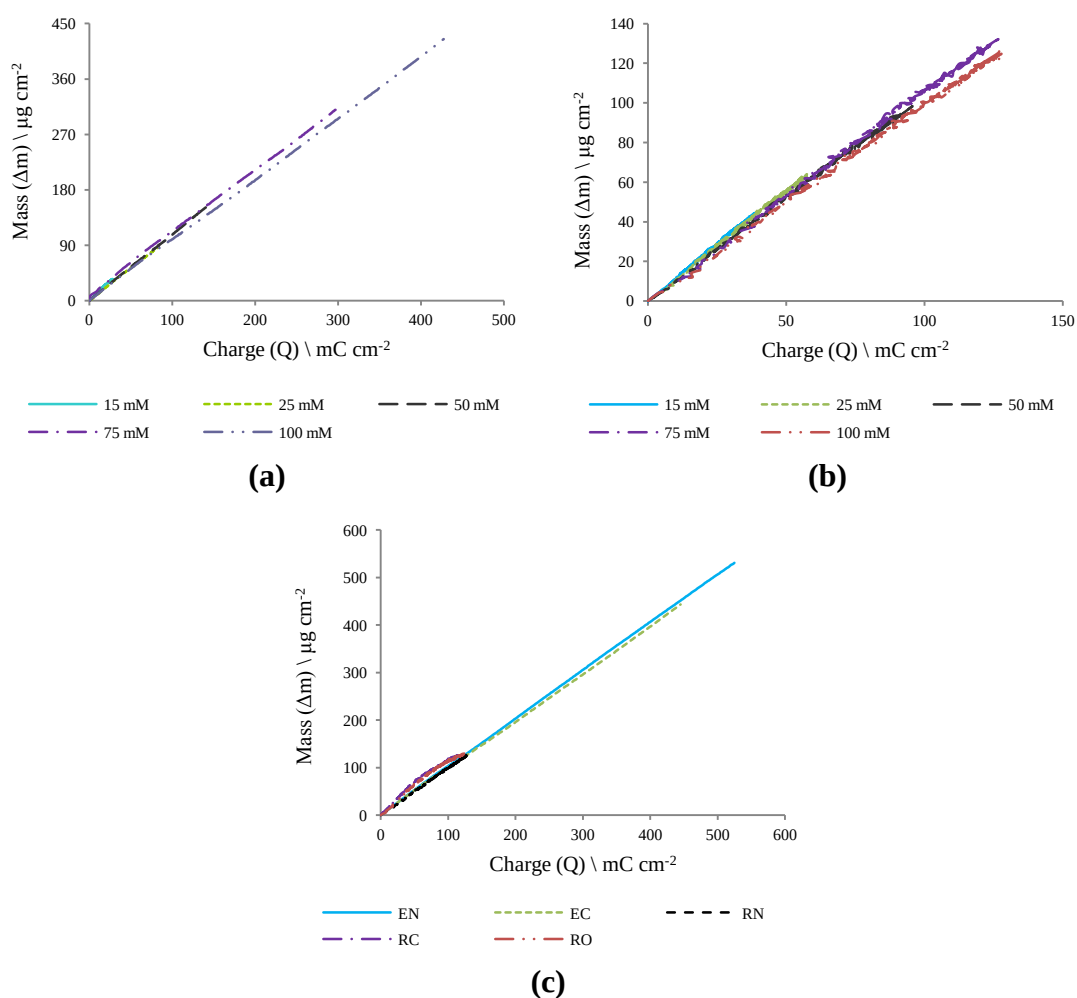


Figure 3.17: Mass of the silver deposited as function of charged passed from (a) 1:2ChCl:ethylene glycol and (b) 1:2 ChCl:urea containing 15-100 mmol dm^{-3} of AgCl (C)the comparison of the mass vs. charge graphs for different silver salts in both the solvents.

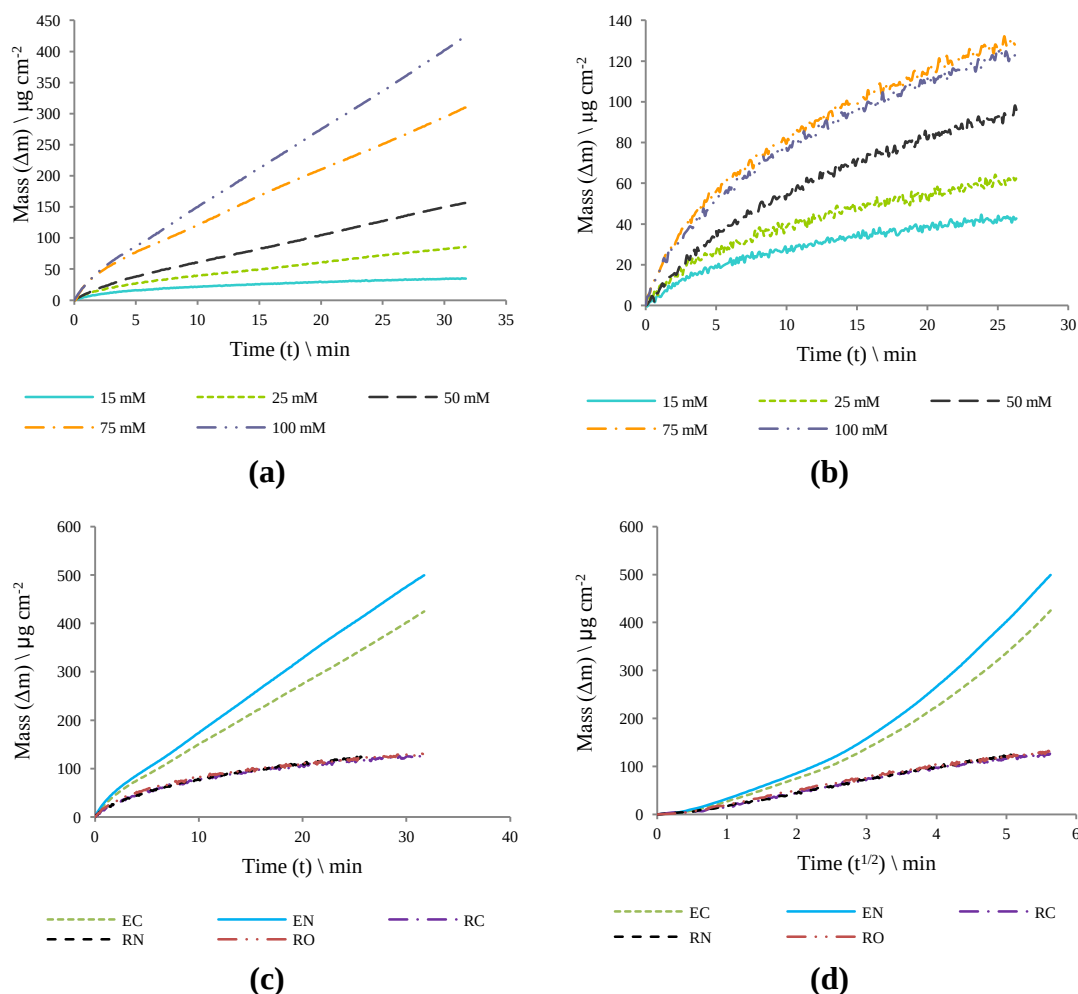


Figure 3.18: Mass of the silver deposited as function of time from (a) 1:2ChCl:ethylene glycol and (b) 1:2 ChCl:urea containing 15-100 mmol dm^{-3} of AgCl (C)the comparison of the mass vs. charge graphs for different silver salts (100 mmol dm^{-3}) in both solvents (d) deposited mass vs. square root of time

3.4.3 Rate of deposition

Figure 3.18 (a,b & c) shows the plot of the deposited mass of silver as a function of time. The examination of these curves suggests two rates of silver deposition. At initial stages, there is a faster rate of deposition while after that silver is deposited linearly at a steady rate for the rest of the time indicating the deposition is under mass transport control. This investigation shows that the nucleation is a rapid process while the bulk growth is a slow process as it is a mass transport controlled phenomena and the deposited mass shows a linear relation with the square root of time (**Figure 3.18 (d)**). The mass and the critical layer thickness of the turn over is

calculated using the density of Ag metal (10.5 g cm^{-3}) and the active area of the crystal (0.23 cm^2) and tabulated in **table 3.3**.

Table 3.3: *Silver deposition from solution containing $100 \text{ mmol dm}^{-3} \text{Ag(I)}$ in EQCM*

System	Current Efficiency	Co-ordinates of turn over in rate in EQCM deposition		
		Time	Deposition mass	Layer Thickness
	%	s	$\mu\text{g cm}^{-2}$	Atomic layers
1:2 ChCl:EG + AgNO_3	90.5	102	47.8	276
1:2 ChCl:EG + AgCl	88.1	120	52.6	303
1:2 ChCl:urea + AgNO_3	88.5	276	48	277
1:2 ChCl:urea + AgCl	91.5	264	50	289
1:2 ChCl:urea + Ag_2O	90.4	282	55	317

3.5 Potentiostatic study

Early stages of the electrocrystallization are extremely crucial as they determine the final features of the macrodeposit such as the smoothness and brightness of the surface. The early stage electrochemical transformations are usually associated with 2D or 3D nucleation processes^{49, 63}, the rate of nucleation and the number of crystallites so formed are strongly dependent on the overpotential. It is therefore important to establish the exact relationship between the overpotential and the kinetics of nucleation, either by direct microscopic observation of the electrode^{2,64} or by indirect procedure of relating the current to the area of electroactive surface and thence the total number of nuclei⁶⁵. The classical electrochemical technique, chronoamperometry is based on current transients measurements and has been extensively used to probe nucleation and growth phenomena⁶⁶. The current transient measurements offer an easy and straight forward method to interpret the electrocrystallization process and to evaluate quantitatively the magnitude and

direction of influence of different parameters like diffusion coefficient, nucleation and growth rates and adsorption kinetics using the different mathematical formalisms proposed for these processes⁶⁷⁻⁷⁰, that are usually not available with any other techniques. The investigations of nucleation and growth mechanism during silver deposition are meaningful for the technological development and fundamental research.

3.5.1 Analysis of the current transients

The chronoamperometric data was obtained on a polycrystalline platinum working electrode by stepping the potential from an initial value (+0.2 V) where no silver deposition takes place to values between -0.04 V and -0.08 V in 1:2 ChCl:EG and 1:2 ChCl:urea respectively for three different silver salts (AgCl, AgNO₃ and Ag₂O) and different Ag(I) concentrations (15, 25, 50, 75 and 100 mmol) in quiescent solutions. A family of current transients for different silver salts (100 mmol) in 1:2 ChCl:EG and 1:2 ChCl:urea is shown in **Figure 3.19**. The current transients are of the same shape with characteristic and well defined current maxima regardless of the applied potential. Each *J-t* curve is divided into and analysed in the following major distinct zones.

- i. The initial rapid surge and exponential decay of the current at the onset of the potential step correspond to the charging of double layer (non Faradaic or capacitance current)^{71, 72}.
- ii. After a short induction time, the rising current (Faradaic current) reflects the increase in electroactive surface either due to the birth and growth of the silver nuclei at the electrode surface and /or the increasing number of nuclei.
- iii. The rising current culminates in a maximum resulting from the coalescence of neighbouring diffusion fields with localized spherical symmetry of the growing crystallites⁷³
- iv. After the current maximum, the Faradaic current fades away slowly and continuously towards zero corresponding to planar diffusion to the whole electrode surface and for a longer time almost merged into a common curve.

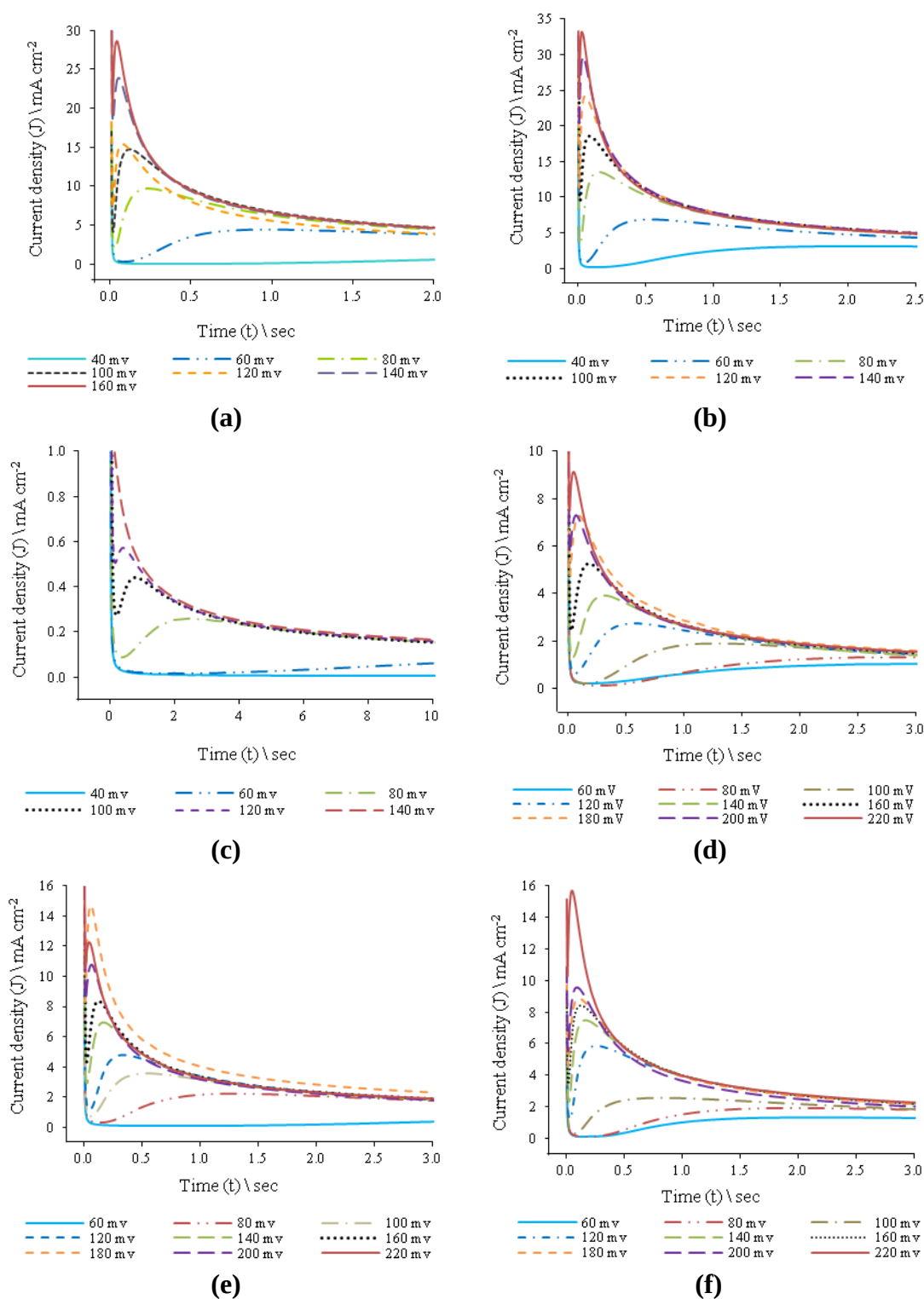


Figure 3.19: A set of chronoamperometric current vs. time data for the reduction of silver deposition of different silver salts (a) $\text{AgNO}_3 + 1:2 \text{ ChCl:EG}$ (b) $\text{AgCl} + 1:2 \text{ ChCl:EG}$ (c) $\text{Ag}_2\text{O} + 1:2 \text{ ChCl:EG}$ (d) $\text{AgNO}_3 + 1:2 \text{ ChCl:urea}$ (e) $\text{AgCl} + 1:2 \text{ ChCl:urea}$ (f) $\text{Ag}_2\text{O} + 1:2 \text{ ChCl:urea}$ for Ag(I) concentration of 100 mmol dm^{-3} while the concentration of Ag(I) in system 'c' is 50 mmol dm^{-3} .

The general shape of the current transients is independent of the applied overpotential while the time required to reach current maximum (t_{max}) is a function of overpotential. The more negative the step potential, the larger and better resolved is the current maxima but shifted towards shorter time.

Figure 3.20 (a & b) shows the effect of concentration on t_{max} as a function of step potential. This shows that the silver deposition in 1:2 ChCl:urea is slow compared to in 1:2 ChCl:EG. Moreover the nucleation process in 1:2 ChCl:EG at low step potentials is sensitive to the concentration while at more negative potential it become insensitive to the Ag(I) concentration while in case of 1:2 ChCl:urea, the nucleation process is a function of concentration at all the step potentials.

Figure 3.20(c & d) exhibit the salt effect on the t_{max} at three over potentials namely 40, 100 and 140 mV in 1:2 ChCl:EG and 100, 160 and 200 mV in 1:2 ChCl:urea. The nucleation process is slightly faster for AgNO₃ than AgCl and Ag₂O in both the solvents.

J_{max} increases linearly with more negative step potential as a function of Ag(I) concentration in both solvents but the corresponding increase in 1:2 ChCl:urea is less than in 1:2 ChCl:EG. The magnitude of J_{max} is slightly higher for AgNO₃ than AgCl and Ag₂O in both the solvents as shown in **Figure 3.21**. This trend is consistent with the data from cyclic voltammetry and EQCM study.

The shapes of the current transients in **Figure 3.19** present a typical response of 3D multiple nucleation with diffusion controlled growth and may be analysed by using the theoretical models proposed by Hills et al^{72, 74} and Scharifker and Monstany⁷⁵. These models describe the kinetics of the early stages of electrolytic phase formation when the diffusion of the depositing species from the bulk solution to the electrode surface is the rate determining step of the process. These models are postulated considering 3D growth of the metallic nuclei and taking into account the columnar diffusion after eventual overlap of diffusion zones^{72, 74, 75} and the development of nucleation exclusion zones

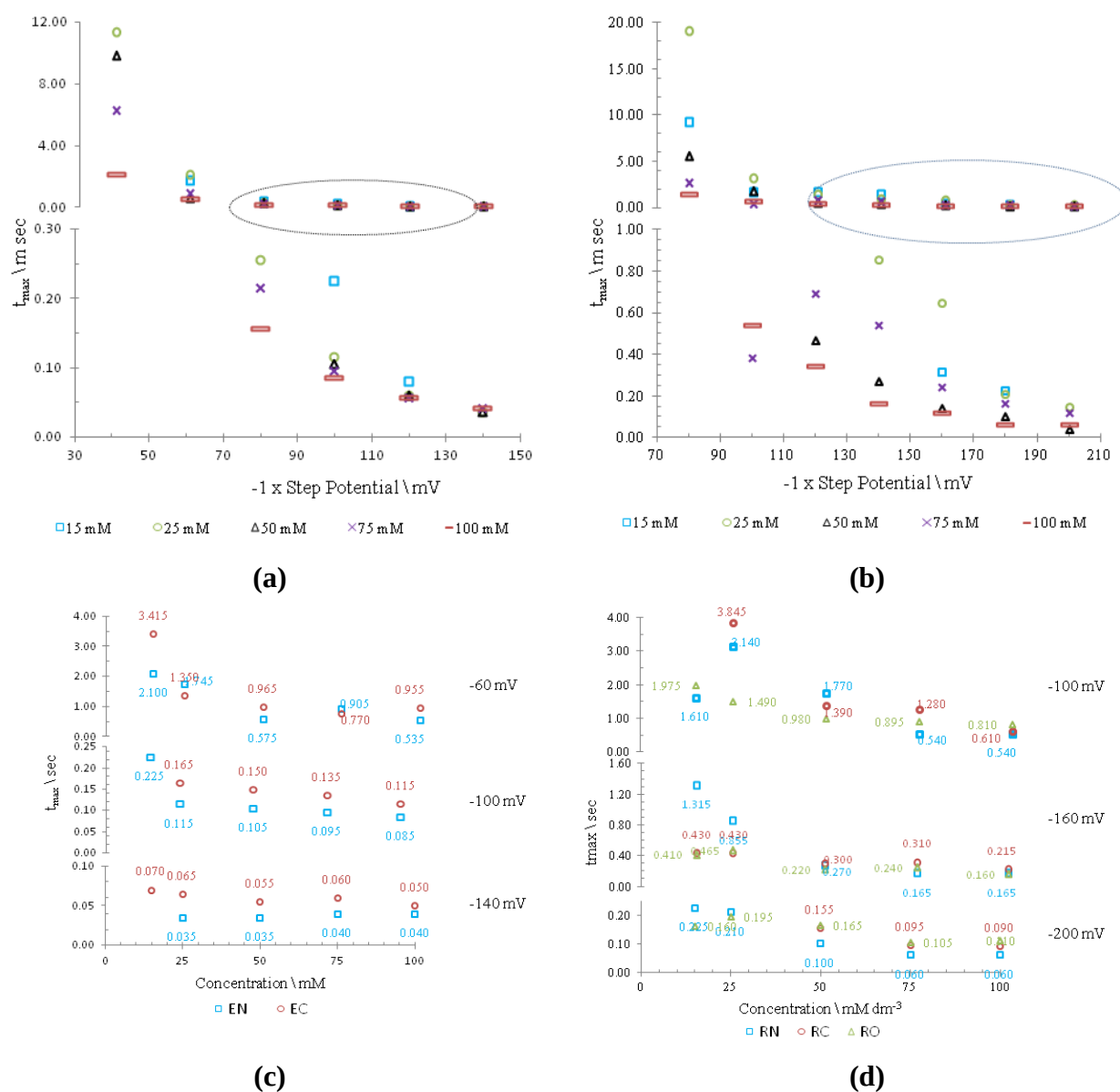


Figure 3.20:

Over potential dependence of the t_{max} of different concentrations of $AgNO_3$ in (a) 1:2 ChCl:EG (b) 1:2 ChCl:urea, lower graphs in both cases show the zoom in of the encircled part

Over potential dependence of the t_{max} of different silver salts (100 mmol dm^{-3}) at step potentials (c) -60 mV, -100 mV, -140 mV in 1:2 ChCl:ethylene glycol (d) -100 mV, -160 mV, -200 mV in 1:2 ChCl:urea

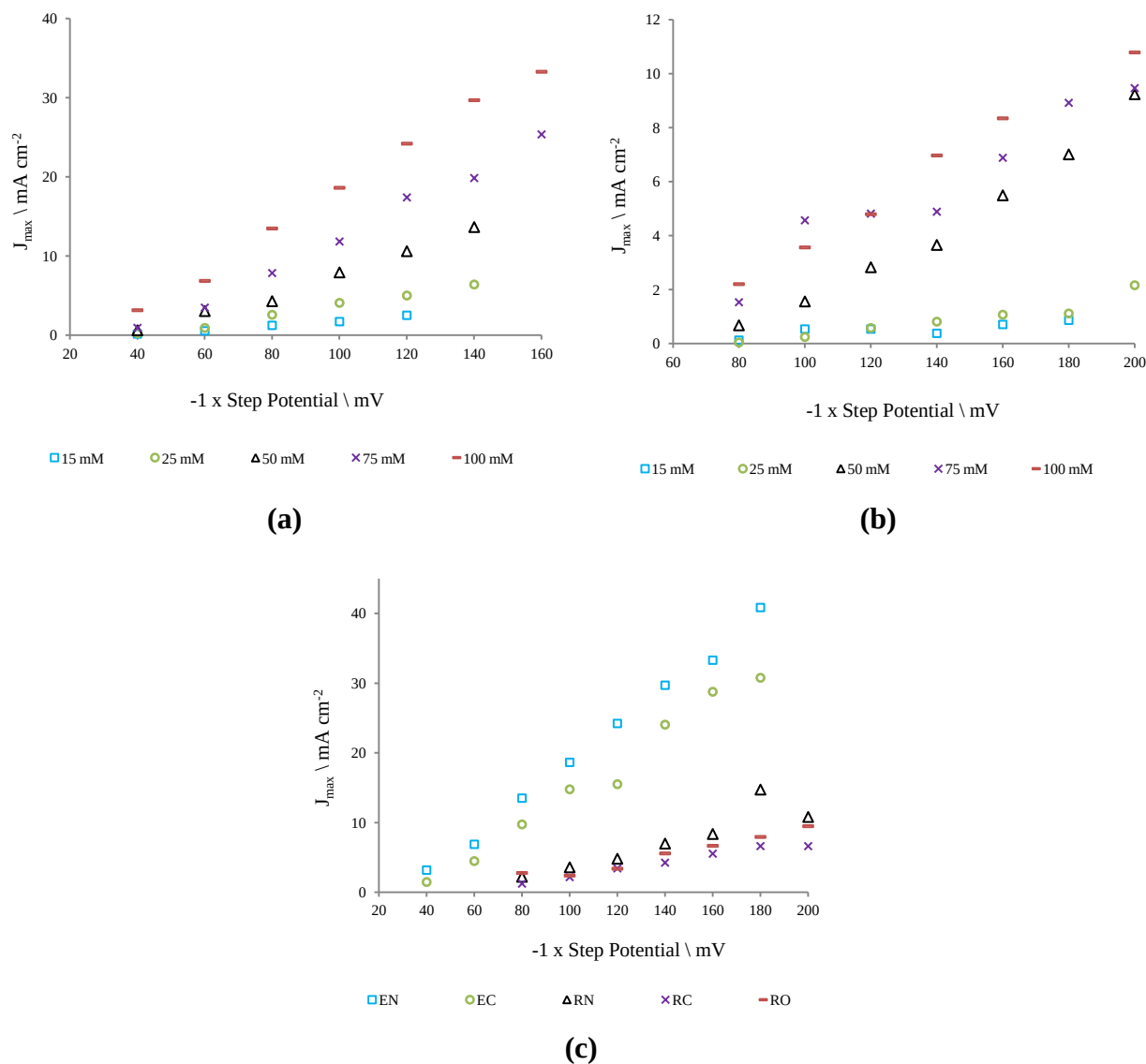


Figure 3.21: J_{max} as a function of step potential for different concentration of AgNO_3 in (a) 1:2 ChCl:EG (b) 1:2 ChCl:urea
 J_{max} dependence on step potential for different silver salts (100 mol dm^{-3}) in both solvents

around the growing nuclei. These models describe the two extreme cases of nucleation: instantaneous and progressive and are given by the following equations^{72, 76}.

$$J(\text{instantaneous}) = \frac{nFD^{1/2}c}{\pi^{1/2}t^{1/2}} [1 - \exp(-N_o\pi kFt)] \quad (3.9)$$

$$k = \left[\frac{8\pi cM}{\rho} \right]^{1/2}$$

$$J(\text{progressive}) = \frac{nFD^{1/2}c}{\pi^{1/2}t^{1/2}} \left[1 - \exp\left(-\frac{AN_o\pi k'Dt^2}{2}\right) \right] \quad (3.10)$$

$$k' = \frac{4}{3} \left[\frac{8\pi cM}{\rho} \right]^{1/2}$$

Where n is the equivalent mole⁻¹, F is the Faraday constant, (Coulomb equivalent⁻¹), D is the diffusion coefficient (cm²s⁻¹), c is the bulk concentration (mol cm⁻³), M is the Molar mass, ρ is the density of the deposited material, t is the time (s), J is the current density (A cm⁻²)

3.5.2 Classification of nucleation process as instantaneous or progressive

As a preliminary step a convenient criterion to distinguish between the two extreme cases of nucleation, equation 3.9 and equation 3.10 can be described in term of the reduced variable j / j_{max} and t / t_{max} after normalizing with time (t_{max}) and current density (j_{max}).

$$\left[\frac{J}{J_{max}} \right]^2 = 1.9542 \left[\frac{t}{t_{max}} \right]^{-1} \left\{ 1 - \exp \left[-1.2564 \left[\frac{t}{t_{max}} \right] \right] \right\}^2 \quad (3.11)$$

$$\left[\frac{J}{J_{max}} \right]^2 = 1.2254 \left[\frac{t}{t_{max}} \right]^{-1} \left\{ 1 - \exp \left[-2.3367 \left[\frac{t}{t_{max}} \right]^2 \right] \right\}^2 \quad (3.12)$$

The theoretical formalisms describe the formation and growth of the nuclei on the substrate surface ($t/t_{max} < 1$) and the physical coalescence of the growing nuclei and/or the overlap of diffusion zones around them ($t/t_m = 1$) and the growth of the initial metal layer ($t/t_m > 1$). The graphical comparison of non dimensional plots, $[j/j_m]^2$ vs. t/t_m of the experimental data with theoretical curves obtained from equations 3.11 and 3.12 is used to predict the dominant case of nucleation kinetics.

The non dimensional plots of the current transient for different silver salts (100 mmol) from 1:2 ChCl:EG and 1:2 ChCl:urea are presented in **Figure 3.22**. The experimental data fits well to the theoretical curve for progressive nucleation for lower values of the overpotential. As the overpotential is shifted to more negative values the non dimensional experimental curve is shifted in the region between progressive and instantaneous nucleation kinetics displaying an intermediate behaviour^{23, 66, 77, 78}. Cao

et al considered this case as instantaneous nucleation with growth controlled by mixed kinetics and diffusion⁷⁹.

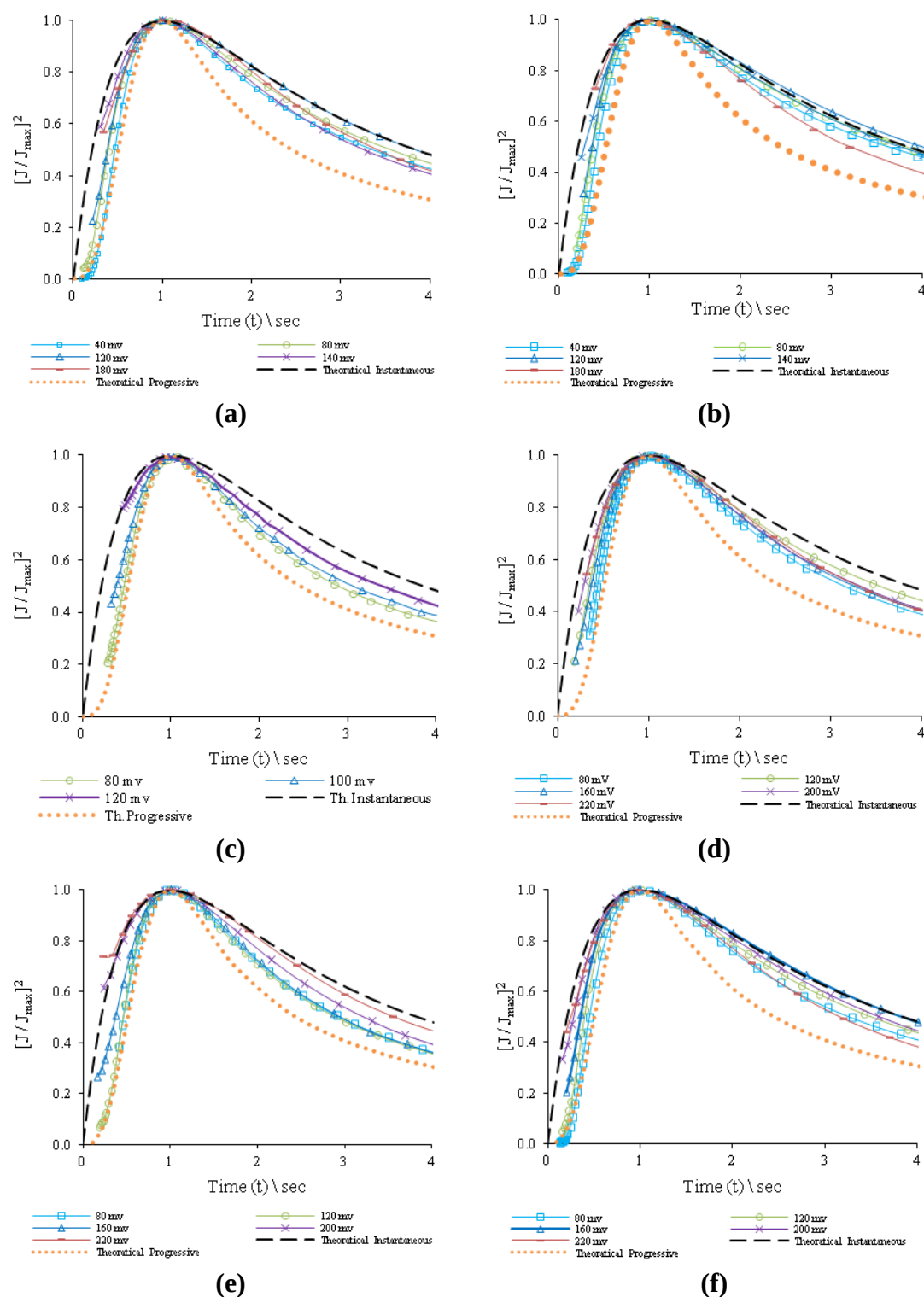


Figure 3.22: *Reduced variable plots for the current transients in Figure 3.19, illuminating the comparison with the theoretical limiting cases i.e. 3D instantaneous and 3D progressive nucleation*

At higher negative overpotential the nucleation kinetics closely follow the instantaneous nucleation kinetics. The nucleation kinetics at the platinum electrode are independent of the solvent system as the same behaviour is observed in both solvent systems, further the nucleation and growth mechanism is not affected by the concentration of Ag(I) in the deposition bath. The falling of the non dimensional experimental curve between two limiting cases suggests the slow nucleation with diffusion controlled growth⁸⁰.

3.5.3 Analysis of the initial rising part

The linear relationship of $j-t^n$ of the rising part of the current transients well before the overlapping of the growing nuclei is also used to distinguish the nucleation and growth mechanism. When $n = 2$ or 3 , the electrocrystallization mechanism can be explained by 3D nucleation limited by the lattice incorporation of adatoms according to the right regular cone model⁸¹ while it can be explained by 3D nucleation according to the diffusion controlled growth when $n = 1/2$ or $3/2$ ⁷² proposed the following current-time relationship.

$$i(t) = \frac{zF\pi (2DC^\infty)^{3/2} NM^{1/2}}{\rho^{1/2}} t^{1/2} \quad (3.13)$$

$$i(t) = \frac{2zF\pi (2DC^\infty)^{3/2} AN_oM^{1/2}}{3\rho^{1/2}} t^{3/2} \quad (3.14)$$

Figure 3.23 shows the $J-t^n$ plots for silver deposition for the initial rising part of the current transients obtained from 1:2 ChCl:EG and 1:2 ChCl:urea. The current shows a linear relationship both with $t^{3/2}$ and $t^{1/2}$. At lower overpotentials the current show a good linear fit with $t^{3/2}$ while at higher negative overpotentials it fits well to $t^{1/2}$ as indicated by the coefficient of correlation. This behaviour is the same as predicted by the non dimensional plot of the current transients.

For a quantitative description of the Ag deposition process and evaluation of the several kinetic parameters such as nuclear number density (N_o), rate of nucleation (A) and diffusion coefficient (D) the following equations are used.

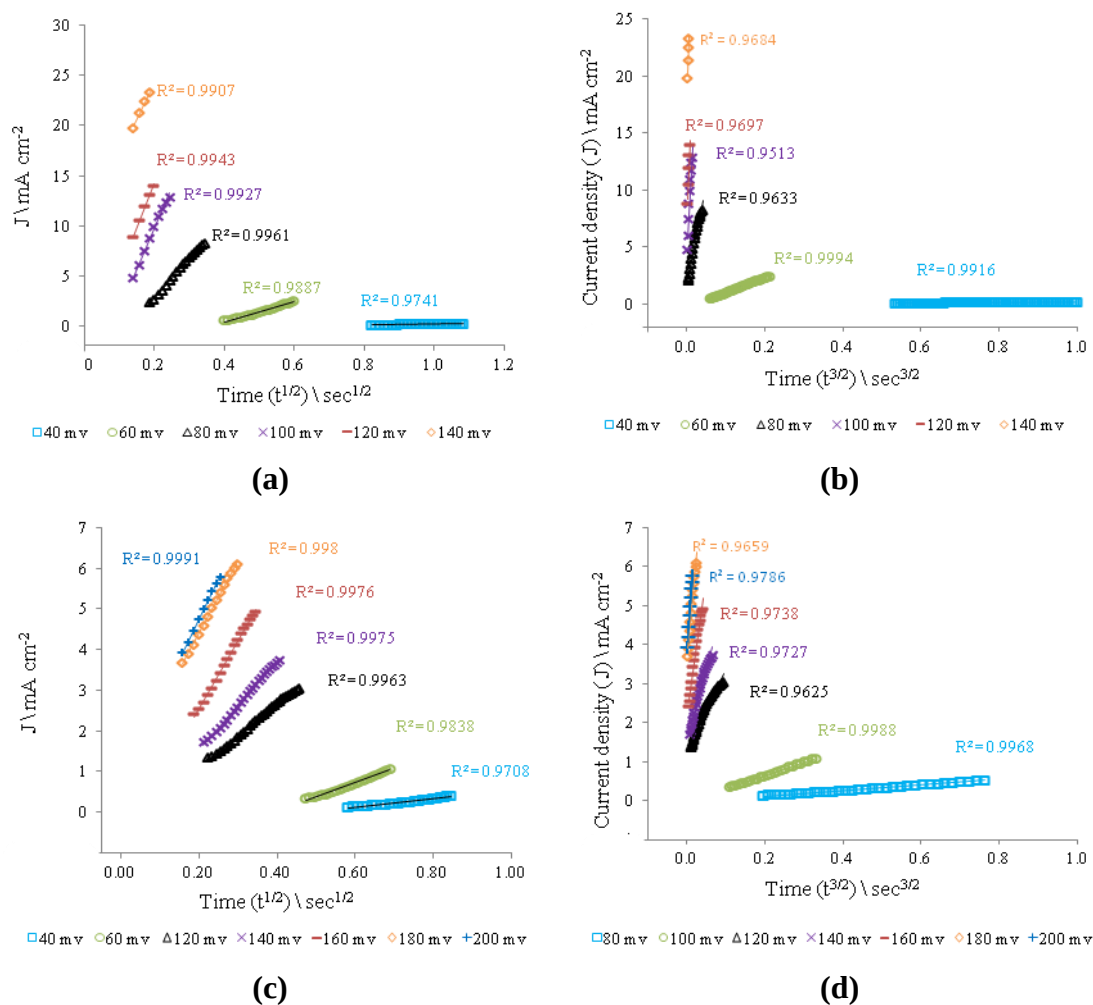


Figure 3.23: J vs. t^n plot for the rising part of the current transients for AgCl (100 mmol dm^{-3}) (a & c) $n=1/2$ and (b & d) $n=3/2$ in 1:2 ChCl:EG(a & b) and 1:2 ChCl:urea (c&d)

The current maximum occurs at a time

$$t_m = \left(\frac{4.6733}{AN_o \pi KD} \right)^{1/2} \quad (3.15)$$

With a maximum current density

$$J_m = 0.4615 z F D^{3/4} C (AN_o K)^{1/4} \quad (3.16)$$

The product $j_m^2 t_m$ yields

$$J_m^2 t_m = 0.2598 (z F C_{Ag(I)})^2 D_{Ag(I)} \quad (3.17)$$

$$N_s = \left(\frac{AN_o}{2KD} \right)^{1/2} \quad (3.18)$$

Treatment of the potentiostatic transients requires that the product $J_m^2 t_m$ should be independent of the nucleation and growth rates and its value should not vary significantly with potential so as to render the surface concentration of Ag(I) effectively zero.

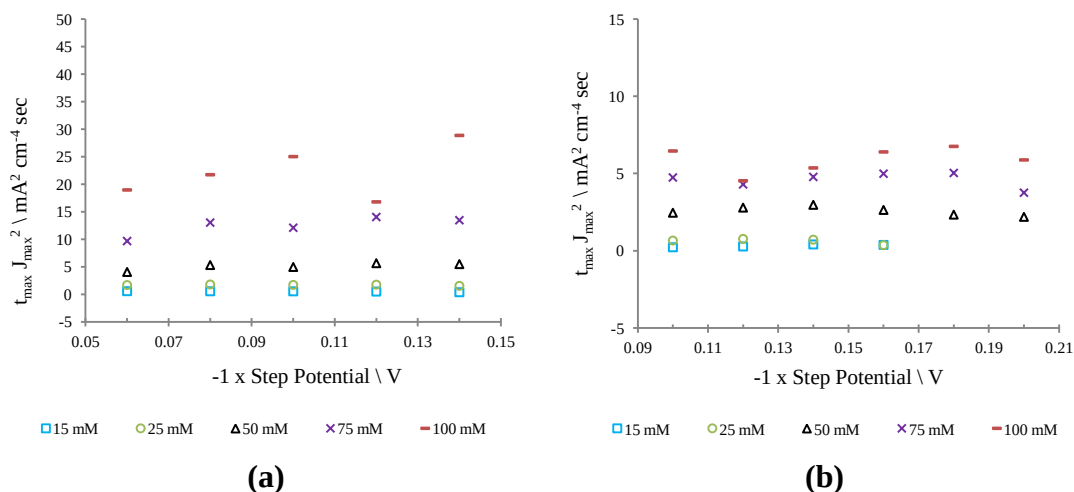


Figure 3.24: $J_m^2 t_m$ plot for silver deposition from (a) 1:2 ChCl:EG and (b) 1:2 ChCl:urea containing AgCl 100 mM dm^{-3}

Figure 3.24 shows the $j_m^2 t_m$ vs. overpotential of AgCl in Ethaline and Reline for different concentrations and it fits well the conditions to be used for estimation of the value of N_o , A and D using equations 3.17, 3.18 and 3.19.

3.5.4 Diffusion coefficient

Diffusion coefficient values are calculated by analysing the part of the current transients after j_{max} on the basis of the Cottrell equation.

$$I(t) = \frac{nFD^{1/2}C}{\pi^{1/2}t^{1/2}} \quad (3.19)$$

The decaying portion of the current transients shows a linear relationship with $J-t^{-1/2}$ and from the slope of these curves the diffusion coefficient can be calculated. The diffusion coefficient values thus obtained and averaged and the mean value for the different concentration of Ag(I) is tabulated along with the values calculated from cyclic voltammetry and the equations proposed by Hills and comparison is made

with diffusion coefficient values reported for other systems^{23, 24, 82} in **table 3.4**. The D values are smaller than obtained in KNO_3 aqueous solution that which be ascribed to the large difference in viscosity. At very high negative values of the step potential relative to F_p^{red} , then well known diffusion controlled $t^{-1/2}$ Cottrellian decay⁶⁴ is detected and no current maximum is observed

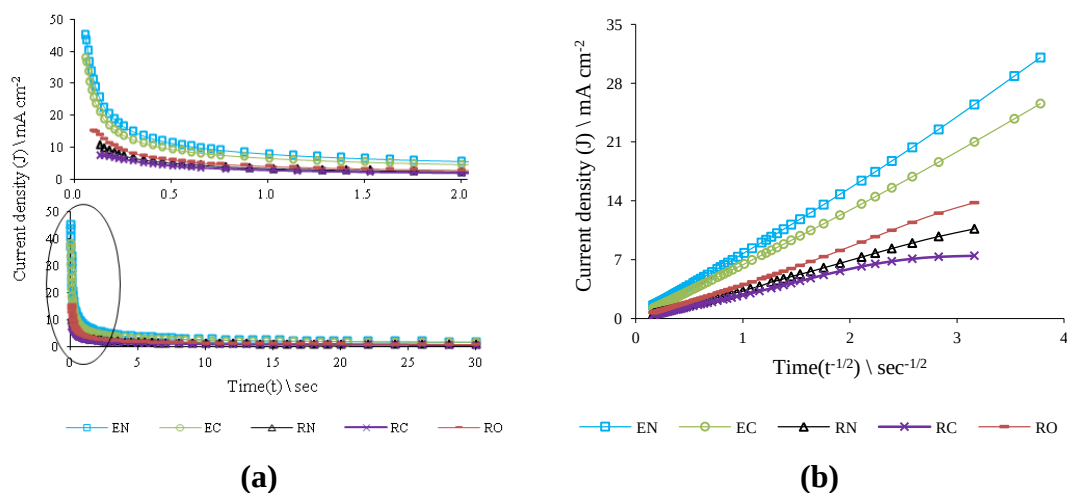


Figure 3.25: (b) J vs. $t^{-1/2}$ plots of the decaying portions of the current transients for different silver salts (100 mmol dm^{-3}) obtained in 1:2 ChCl:EG and 1:2 ChCl:urea (a) decaying portion after j_{max} of the current transients

Table 3.4: Comparison of the diffusion coefficient in DES and comparison with other system Calculated by different methods

	Cyclic voltammetry	Cottrell Equation (Equation 3.19)	$D_{\text{Ag(I)}}$ (Equation 3.16)
System	$D_{\text{Ag(I)}}$ $10^6 \text{ cm}^2 \text{ sec}^{-1}$	$D_{\text{Ag(I)}}$ $10^6 \text{ cm}^2 \text{ sec}^{-1}$	$D_{\text{Ag(I)}}$ $10^6 \text{ cm}^2 \text{ sec}^{-1}$
* 1:2 ChCl:EG + AgNO_3	1.38	2.00	1.80
* 1:2 ChCl:EG + AgCl	1.03	1.44	1.35
** 1:2 ChCl:urea + AgNO_3	0.129	0.49	0.42
** 1:2 ChCl:urea + AgCl	0.10	0.28	0.13
** 1:2 ChCl:urea + Ag_2O	0.076	0.12	0.099

Table 3.4: *Comparison of the diffusion coefficient in DES and comparison with other system Calculated by different methods*

	Cyclic voltammetry	Cottrell Equation (Equation 3.19)	$D_{\text{Ag(I)}}$ (Equation 3.16)
System	$D_{\text{Ag(I)}}$ $10^6 \text{ cm}^2 \text{ sec}^{-1}$	$D_{\text{Ag(I)}}$ $10^6 \text{ cm}^2 \text{ sec}^{-1}$	$D_{\text{Ag(I)}}$ $10^6 \text{ cm}^2 \text{ sec}^{-1}$
Ag(I)/EMIBF ₄ ²⁴	0.6	0.99	-
Ag(I)/BMIMPF ₆ ²³	0.01	0.03	-
Ag(I)/KNO ₃ ⁵⁶	9.10	26	-
	*	The likely determination error is $\pm 2\%$	
	**	The likely determination error is $\pm 4\%$	

3.5.5 Non-linear best fit

The kinetic information of the Ag electrocrystallization in these two solvent systems can not be explained well by the non linear graphs using Hills et al and Scharifker and Monstany models and the analysis of the initial rising part of the current transients. Therefore in order to determine the different nucleation parameters such as N_o , A , the entire experimental evidence (J - t plots) is used and the methodology of non linear fitting of the theoretically calculated current transients is used^{71, 83-85}. This methodology is discussed in detail in the next chapter.

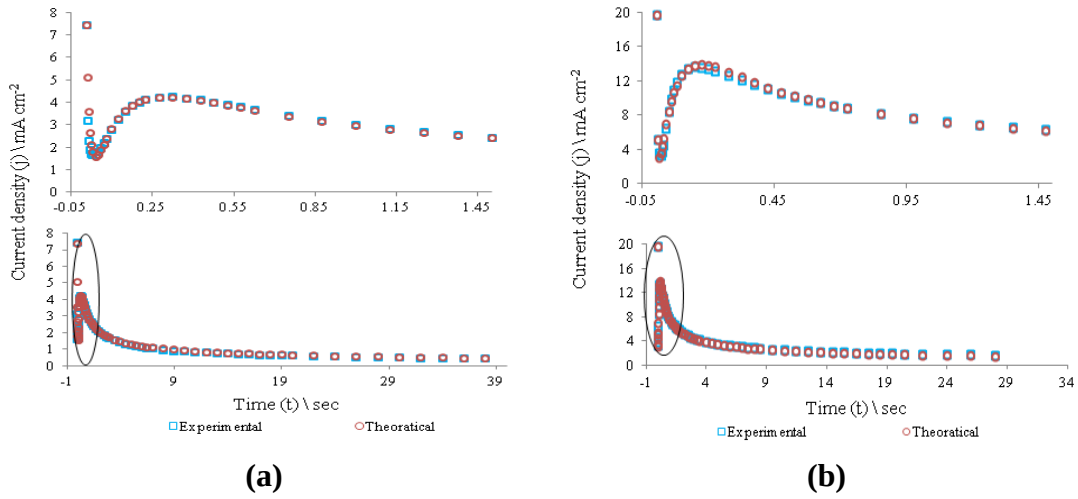


Figure 3.26: Comparison of the current density transients recorded at step potential (a) -80 mV in 1:2 ChCl:EG (b) -140 mV in 1:2 ChCl:urea and the theoretical transients obtained by non-linear best fit

3.5.6 Variation of the number densities of active sites

The dependence of the number of active sites for nucleation of silver with overpotential is shown in **Figure 3.27**. This shows that an exponential relationship between N_o and the overpotential exists.

3.5.7 Size and mechanism of formation of the critical nucleus

The largest cluster for which the probability for attachment of one is less than one half is defined as critical. The attachment of a new atom converts this cluster into a stable one, for which the probability for attachment of the next atom is already higher than one half and henceforth able to grow spontaneously. The number of atoms necessary to form the critical nucleus (n_k) is estimated using the Atomistic theory⁸⁶⁻⁸⁸.

$$A = k_1 \exp \left[-\frac{\omega_k}{kT} \right] \exp \left[\frac{\alpha z e_o \eta}{KT} \right] \quad (3.20)$$

Where k_1 is the pre-exponential factor, e_o is the elementary electric charge, α is the cathodic transfer coefficient, η is the overpotential, W_k is the reversible work for the formation of a critical nucleus consisting of n_k atoms, z is the number of electron involved in the process, k is the Boltzmann's constant and T is the temperature in Kelvin.

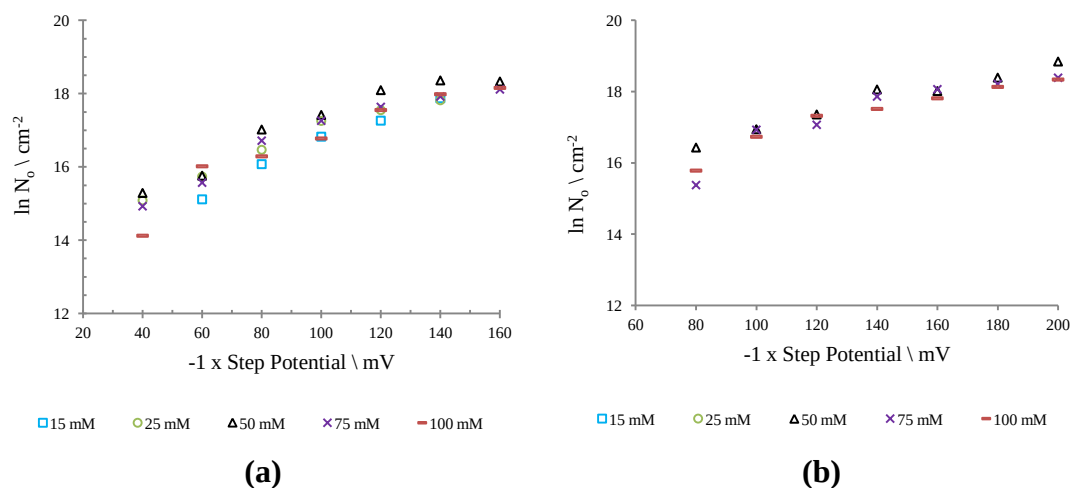


Figure 3.27: Over potential dependence of the nuclear number density of AgCl (100 mmol dm^{-3}) in (a) 1:2 ChCl:EG and (b) 1:2 ChCl:urea.

Regardless of the nucleation model and for the case when excess Gibbs energy of nucleus formation is overpotential independent n_k , A and η are related through

$$n_k = \frac{KT}{ze_o} \left[\frac{d \ln A}{d\eta} \right] - \alpha \quad (3.21)$$

From the slopes of $\ln A$ vs η plots and using the α values calculated from cyclic voltammetry, the number of atoms that form the critical nucleus is estimated. The n_k values were found to vary for different Ag(I) concentrations. Therefore the transformation of the single adsorbed atoms into atomically stable clusters either by combination of adsorbed atoms or by reduction of silver ions onto adsorbed atoms, constitutes in this case the critical step of the nucleation process. The value of n_k obtained is similar to those obtained by others using other method range between 0 and 1 atom^{89, 90}

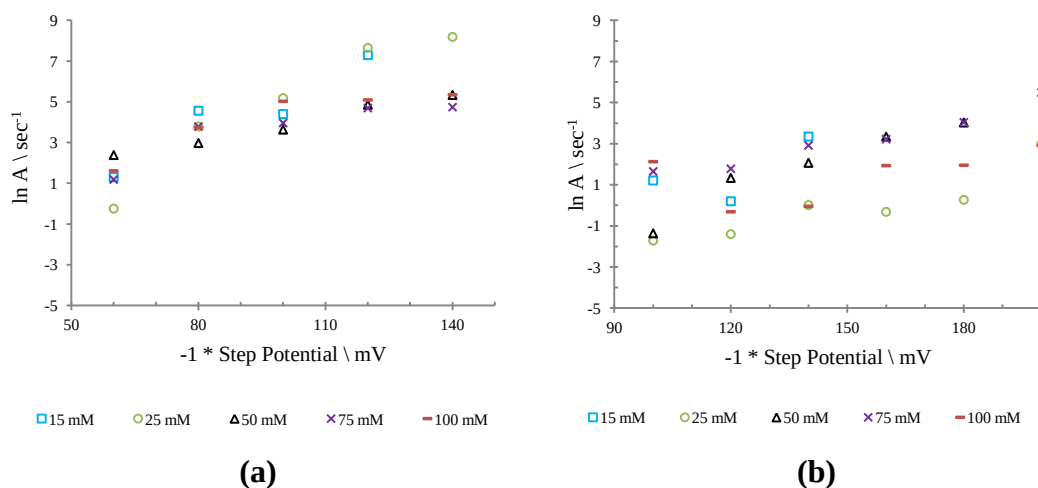


Figure 3.28: Over potential dependence of the rate of nucleation of AgCl (100 mmol dm⁻³) in (a) 1:2 ChCl:EG and (b) 1:2 ChCl:urea.

3.6 Bulk Silver deposition and Surface characterization

Silver was electrodeposited on the platinum substrate potentiostatically from 1:2 ChCl:EG at -0.5 V for 30 minutes at 40 °C and from 1:2 ChCl:urea at -0.6 V for one hour at 50 °C respectively. After deposition the substrate is thoroughly washed with deionized water followed by acetone and ethanol to completely remove the residual liquids. The potentiostatic reduction of Ag(I) yields a silver white electrodeposit. The topography of the deposited silver layers is characterized by atomic force microscopy and scanning electron microscopy coupled with EDX to explore the surface morphologies and composition.

Figure 3.29 show the micrographs for the silver deposit from 1:2 ChCl:EG containing 100 mmol dm⁻³ AgNO₃ and AgCl. The micrographs reveal that the silver deposits consist of randomly sized silver grains and some large agglomerated crystallites formed from fine crystallites of nanometre size. They vary from spherical to elliptical in shape. The deposit obtained from AgCl contained some nodular structures on the large silver grains, thus making the facet grains lose their regular geometries. The silver surface appears porous with nanometre voids around the Ag grains.

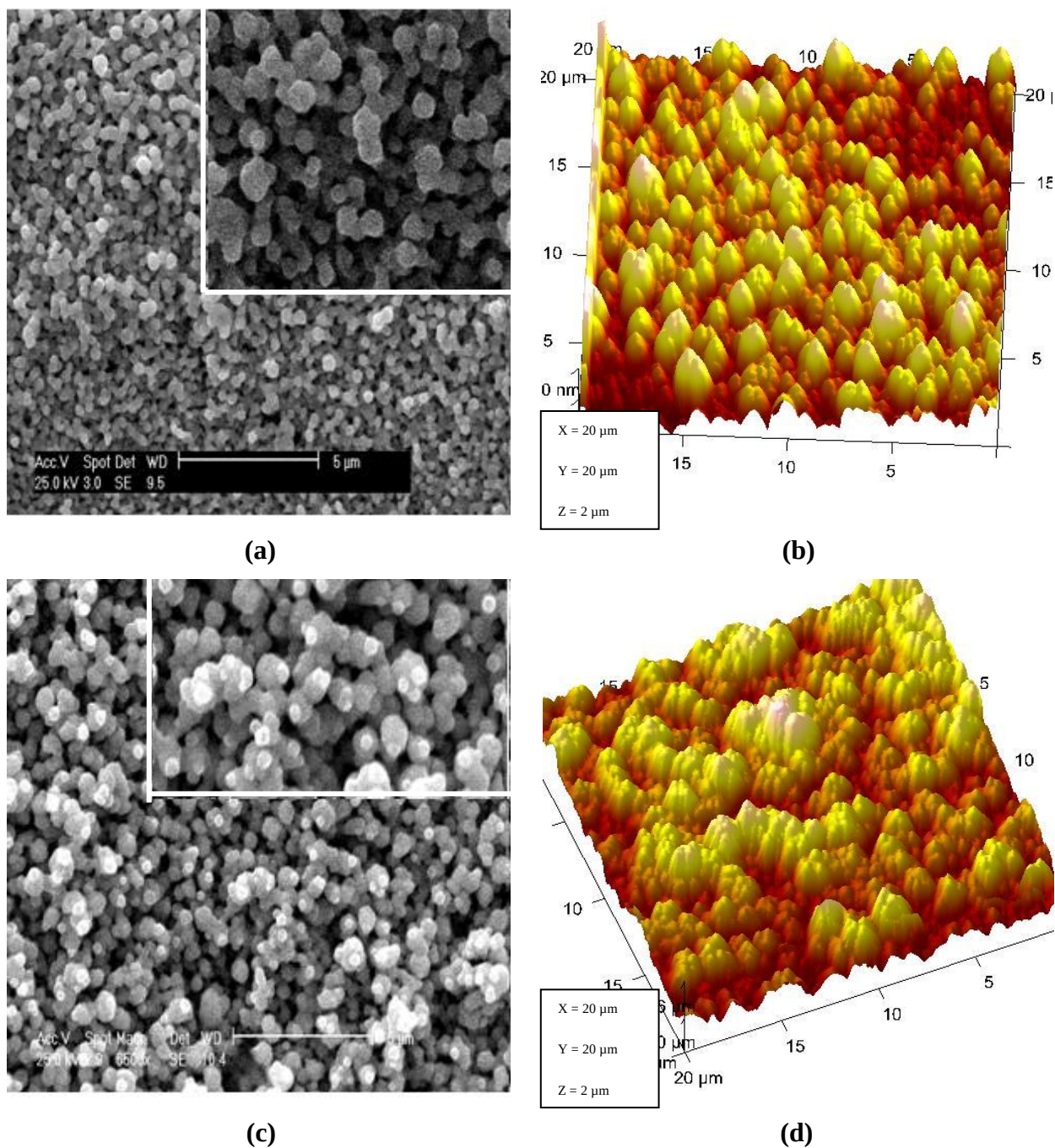


Figure 3.29: SEM and AFM images for the silver deposit from 1:2 ChCl:EG containing 100 mol dm⁻³ Ag(I) (a & b) AgNO₃ and (c & d) AgCl. Right upper corner shows the image at higher magnifications

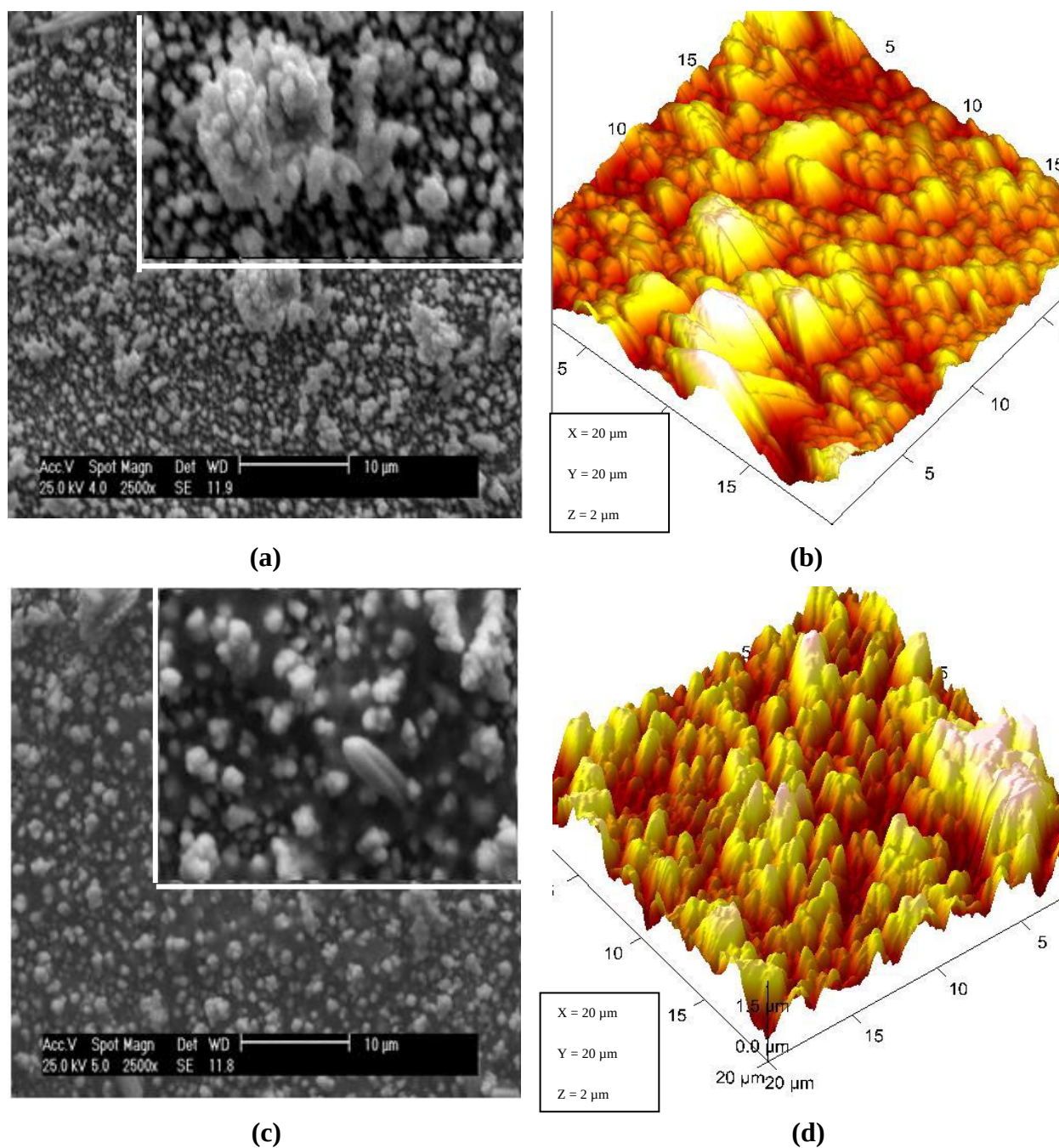


Figure 3.30: SEM and AFM images for the silver deposit from 1:2 ChCl:urea containing 100 mmol dm⁻³ Ag(I) (a & b) AgNO₃ and (c & d) AgCl. Right upper corner shows the image at higher magnifications

Figure 3.30 exhibits the SEM images of the silver deposit from AgNO₃ (100 mmol dm⁻³) and AgCl (100 mmol dm⁻³) in 1:2 ChCl:urea. In both the cases the deposit is granular and the silver grain size is smaller than the similar deposit from 1:2 ChCl:EG. In case of AgNO₃, multiply twinned grains clusters have appeared. The

silver films are more dense than the films from 1:2 ChCl:EG. Low density structures are obtained from Ag_2O in 1:2 ChCl:urea as shown in **Figure 3.31**.

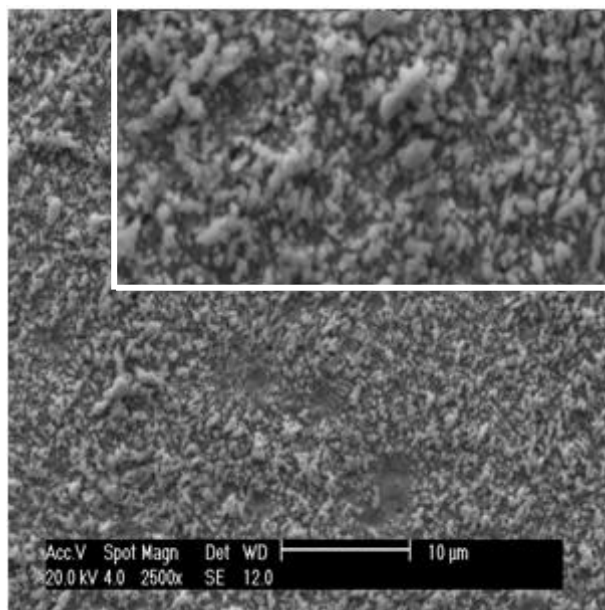


Figure 3.31: SEM micrograph of silver film from 1:2 ChCl:urea containing $100 \text{ mmol dm}^{-3} \text{Ag}_2\text{O}$. Right upper corner shows the image at higher magnifications

The AFM images reveals a rough but fairly dense silver film corresponding to an island (Volmer-Webber growth) model⁹¹. EDX analysis shows a pure silver (90-94%) deposit.

The granular morphology of the Ag layer is similar to that reported by other groups from other ionic liquids^{60, 92, 93} but completely different from the dendritic or filiform morphology obtained from⁹⁴ aqueous electrolytes^{95, 96}.

3.7 Conclusion

The electrochemical reduction of Ag(I) to Ag(0) has been studied on platinum electrodes using the techniques of cyclic voltammetry, electrochemical quartz crystal microbalance and chronoamperometry in the deep eutectic solvents 1:2 ChCl:EG and 1:2 ChCl:urea. The physical properties of the solutions are correlated to the

electrodeposited silver layers as a function of Ag(I) concentration and the counter ion effect of the silver salts.

The silver electrodeposition was successfully carried out in these solvents. The higher viscosity of 1:2 ChCl:urea is attributed to the strength of the hydrogen bond donor and subsequently to the small average void radius. The electrochemical window for both the solvents is found to be 2 V extending from +1.2 V to -0.8 V. The cyclic voltammograms exhibit a redox wave associated with deposition / stripping of silver with a nucleation loop. The over potential for silver deposition in 1:2 ChCl:urea is slightly higher than 1:2 ChCl:EG.

The EQCM study reveals that the current efficiency in both the solvents is almost the same and ranges from 85 – 100 % and the rate of silver deposition is slower in the 1:2 ChCl:urea as compared to 1:2 ChCl:EG.

A qualitative evaluation of the nucleation and growth mechanism and quantitative estimation of the kinetic parameters of the silver electrocrystallization process was carried out using existing theoretical formalisms. The electrochemical deposition of silver is characteristic of multiple 3D nucleation with mass transport controlled hemispherical growth. The nucleation mechanism is found to be step potential dependent varying from progressive to instantaneous from low to more negative step potential. A detailed analysis of the maximum coordinates of the current transients and non-linear best fit of the whole experimental current transients is used to calculate the kinetic parameters like nuclear number density, rate of nucleation and diffusion coefficient and critical nuclear size.

The surface topographical characterization of the silver deposits on the platinum reveals the top layers of silver are loosely packed with granular characteristics having a grain size in the nanometre region. The morphology of these deposits seems to be effected slightly by the counter ion of the salts and the type of DES.

This electrochemical study reveals that the silver reduction process in 1:2 ChCl:urea is slow compared with 1:2 ChCl:EG which can be attributed to its higher viscosity but these studies suggest that both 1:2 ChCl:EG and 1:2 ChCl:urea are capable of acting as an alternative electroplating bath for silver deposition without using toxic reagents.

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Chapter 4 : The Effect of Additives on Silver Electrodeposition from DES

4.1 Introduction

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4.1 Introduction

In chapter 3, the deposition of silver in deep eutectic solvents has been studied qualitatively and quantitatively to probe the kinetics of the nucleation and growth mechanism. The effect of the concentration of silver salt and the salt type has been investigated using electrochemical techniques (cyclic voltammetry, chronoamperometry), acoustic impedance spectroscopy and the surface morphology using microscopic techniques. In this chapter the effect of different additives on the kinetics of silver reduction and the morphology of the silver deposit are presented.

Adding organic compounds to an electroplating bath is one of the most effective and most frequently used methods to improve the quality of the deposits, control the surface morphology and improve the throwing power of the baths¹. A wide range of additives such as levellers, surfactants and brighteners are generally added to improve the efficiency and characteristics of the deposition process. Much of the work on the mechanisms of action of additives in electrodeposition has concentrated on their ability to modify the nucleation²⁻⁵. However, additives also affect the rates of the other steps in the electrodeposition process and there are various ways in which additives may affect the rate of deposition of metals^{6, 7} which include:

- ☐ blocking the surface,
- ☐ changes in the Helmholtz layer
- ☐ complex formation including induced adsorption and ion bridging,
- ☐ ion pairing,
- ☐ changes in interfacial tension and film formation on electrode surface
- ☐ hydrogen evolution effects,
- ☐ hydrogen absorption,
- ☐ anomalous codeposition,
- ☐ effects on intermediates.

Surfactants are organic materials added to aqueous electrolytes to alter electrodeposition characteristics. Surfactants change interfacial tension⁸ hence help in cleaning the surface by removing blocking species like hydrogen. Surfactants, such as long chain sulfonates, quaternary ammonium salts or alcohols are adsorbed on the substrate surface and at concentration well below the critical micelle concentration⁹⁻¹³

they form hydrophobic films on the electrode surface and change the electrode surface characteristics and properties.¹⁴ This hydrophobic film has a much lower interfacial tension hence wets the hydrophobic dirt in the interface and thus aids in its removal from the surface. If these films are charged they promote the reduction of the electroactive species on the surface but at the same time the low interfacial tension allows some non polar compounds to wet the surface. The hydrophobic and hydrophilic bonding between these molecules may result in organized multilayers with an increase in surfactant concentration. Therefore one will pass alternately from a hydrophobic surface to a hydrophilic surface and back to a hydrophobic surface. This accounts for the periodic rises and falls in the rate of reaction with gradual increase in concentration e.g electro-oxidation reactions and catalytic processes on the metal surfaces.^{15, 16}

It is reasonable to assume that similar effects may occur in electrodeposition processes. This coating of the electrode by hydrophobic films excludes water from the surface. It is indeed a modified electrode as the ion pass through this hydrophobic layer, the water molecules are stripped off, making the metal ion easier to reduce. As a result the reduction peak shifts to more positive potentials but for the steady state electrolysis the film may act as resistor and thus inhibit the reduction process.

It has been shown that surfactants such as cetyltrimethylammonium bromide (CTAB) act as effective levelling agents whilst also improving the current efficiency¹⁷. More recent investigations by Gomes *et al.* have determined that changing the charge of the surfactant head group has an effect on the electrodeposition mechanism. It was found that cationic surfactants such as CTAB reduce the crystallinity and grain size of Zn, whereas anionic surfactants such as sodiumdodecylsulphate (SDS) increase grain size and crystallinity^{18, 19}. It is probable that these surfactants are specifically adsorbed at the electrode surface as described above and act to alter the structure of the electrochemical double layer.

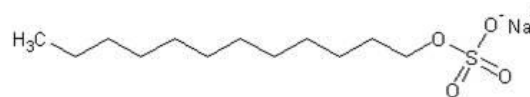
As the interest in the use of ionic liquids as electrodeposition media continues to grow, it is important to investigate how additives function in ionic liquids. However, to date no systematic studies of the effect of brighteners or surfactants in ionic liquids have appeared in the literature²⁰. The majority of studies which have touched upon this crucial area are often limited to the addition of organic solvents as diluents, to

reduce the melting points and viscosities of the ionic liquids. The addition of large volumes of diluents, often of between 20- 50 weight % of the ionic liquid, raises the question of whether these liquids can still be truly classed as ionic liquids, or are more accurately described as co-solvents. Sun *et al.* have used polypropylene carbonate as a co-solvent in the electrodeposition of Zn^{21} and Zn-Co^{22} from the acidic ZnCl_2 -1-ethyl-3-methylimidazolium chloride ionic liquid. In both studies the addition of propylene carbonate acted to reduce the melting point of the fluid, allowing electrodeposition to be carried out at lower temperatures^{21, 22}. Hussey *et al.* showed that the quality of Al electrodeposited from acidic AlCl_3 : 1-ethyl-3-methyl imidazolium chloride was improved by the addition of 20 wt. % benzene²³. In an analogous study of Ag/ Al alloys in the same melt it was found that benzene inhibited the nucleation of Ag. The addition of benzene to chlorozincate liquids was also found to inhibit the nucleation of Zn.²⁴ These studies highlight the complex nature of additive behaviour in ionic liquids and that a large amount of research is still required to develop a full understanding of their function. It is likely that a suitable additive and concentration will be specific to each metal/ alloy and ionic liquid system²⁰.

Results and Discussion

In this chapter the effect of additives on the electrode interface and the kinetics of silver nucleation and growth is investigated in 1:2 ChCl:EG and 1:2 ChCl:urea. For this purpose the following surfactants and brighteners are selected. Their effect is studied for silver deposition from three silver salts AgCl , AgNO_3 and Ag_2O in both 1:2 ChCl:EG and 1:2 ChCl:urea. Three concentrations of the additive ranging from 2-10% of electroactive species are used. The investigation in all the systems is conducted on the same lines as in chapter 3. The effect of the additives in all the systems is found to be similar and the results of a study of silver deposition from solutions containing AgNO_3 are presented here.

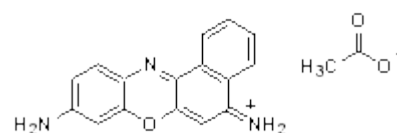
Sodium dodecyl sulphate (SDS)



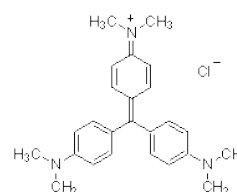
Cetyl trimethylammonium bromide (CTAB)



Cresyl fast violet (9-amino-5-imino-5H-benzo (a) phenoxazine acetate salt) (CFV)



Crystal violet (Hexamethyl-para-rosaniline chloride) (CV)



4.2 Physical Properties

The physical properties of 1:2 ChCl:EG and 1:2 ChCl:Urea containing AgNO_3 50 mmol dm^{-3} such as viscosity, conductivity, density and surface tension are measured as a function of additive concentration at room temperature. The viscosity and electrical conductivity of these systems have been explained in terms of the hole theory proposed for the high temperature molten salts.

4.2.1 Viscosity and Conductivity

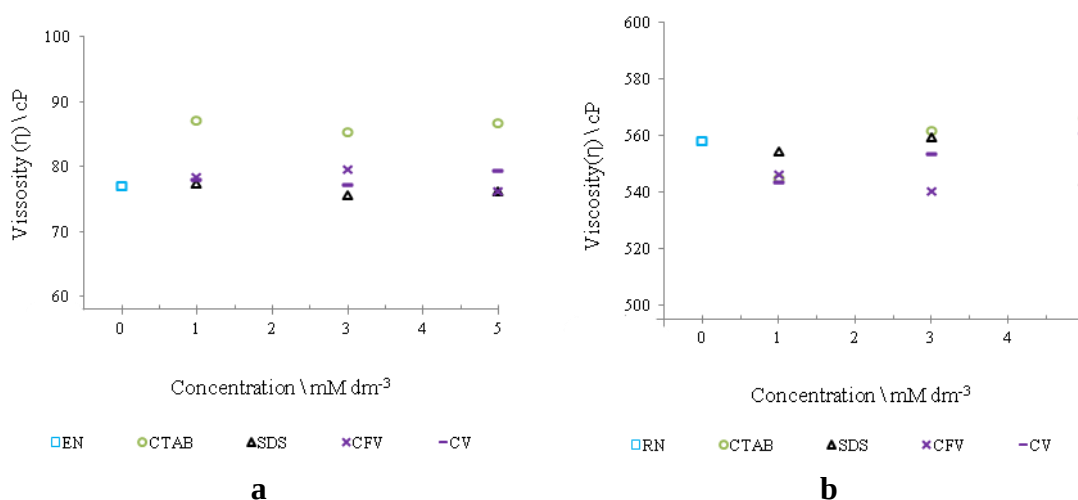


Figure 4.1: The viscosity of (a) 1:2 ChCl:EG and (b) 1:2 ChCl:urea containing AgNO_3 50 mmol dm^{-3} as a function of the concentration of different additives, at 25°C

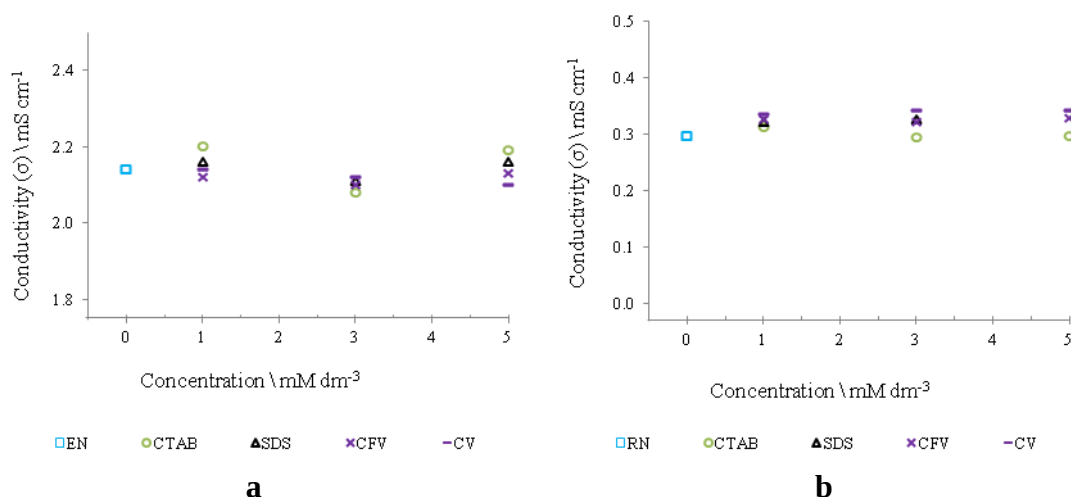


Figure 4.2: The conductivity of (a) 1:2 ChCl:EG and (b) 1:2 ChCl:urea containing AgNO_3 50 mmol dm^{-3} as a function of concentration of different additives, at 25°C

Figures 4.1 shows the viscosity of 1:2 ChCl:EG and 1:2 ChCl:urea with different additives as a function of additive concentration. The viscosity of 1:2 ChCl:EG is 77 cP while that of 1:2 ChCl:urea is 620 cP at 25°C . In both cases the addition of additives has no effect on the viscosity. Barron has shown that brighteners had a large effect upon the viscosity of the 1:2 ChCl:urea system but the additive concentrations were 1 to 2 orders of magnitude larger than those studied here²⁵.

The conductivity of 1:2 ChCl:EG and 1:2 ChCl:urea containing AgNO_3 (50 mmol dm^{-3}) were determined with the addition of additives ranging from 1 to 5 mmol dm^{-3} at 25°C and plotted as a function of additive concentration in **Figure 4.2**. The conductivity of 1:2 ChCl:EG is found to be 2 mS cm^{-1} at 25°C while the conductivity of 1:2 ChCl:urea is found to be 0.3 mS cm^{-1} . In an analogous manner to the viscosity, the different additives show no effect on the conductivity.

4.2.2. Surface tension and density

The surface tension of 1:2 ChCl:EG is found to be 56 mNm^{-1} and the surface tension of 1:2 ChCl:urea is found to be 82 mNm^{-1} at 25°C and is shown in **Figure 4.3 (a&b)**. The surfactants show a marked effect on the surface tension while dyes have no effect on the surface tension in 1:2 ChCl:EG. In 1:2 ChCl:urea SDS decrease the surface tension of the solution by a factor of 2 while CTAB has no effect on surface tension. Dyes slightly decrease the surface tension of the solution.

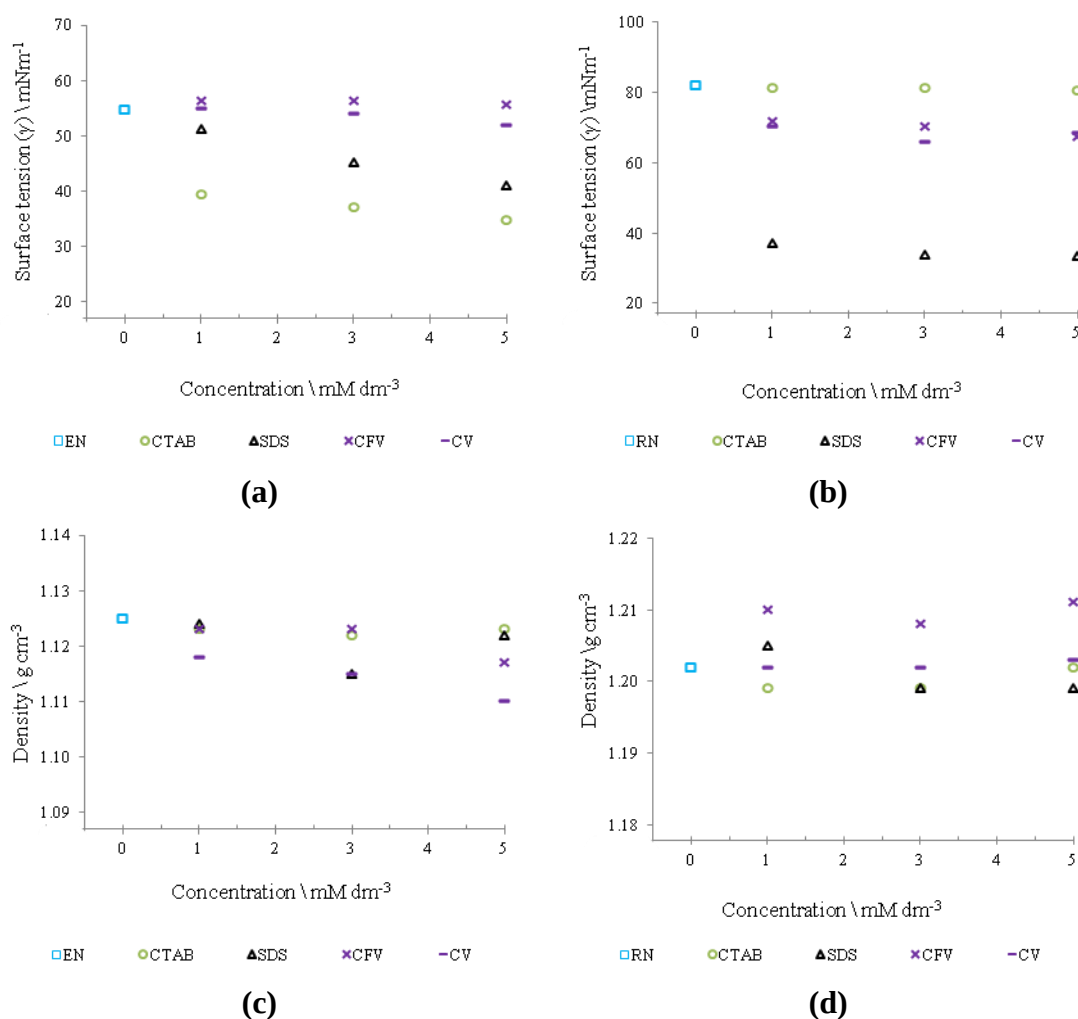


Figure 4.3: The surface tension (a) and density (c) of 1:2 ChCl:EG and Surface tension (c) and density (d) 1:2 ChCl:urea containing Ag(I) as a function of additive concentration, at 25°C

Figure 4.3 (c & d) show that the density of the solution is slightly effected by the addition of additives in both 1:2 ChCl:urea and 1:2 ChCl:EG.

4.3 Cyclic Voltammetry

The effect of additives on the electrochemical behaviour of silver deposition in deep eutectic solvents was studied using cyclic voltammetry. A potentiodynamic study was performed in the potential region +0.3 to -0.3V at different scan rates 0.005, 0.01, 0.02, 0.03, 0.04, 0.05 and 0.1 Vs⁻¹. In all cases the direction of the potential scan was from the anodic region (+0.3V) to the cathodic region and the potential was reversed at -0.3V and swept to the starting potential. A series of cyclic voltammograms were obtained to study the effect of the additives (surfactants (CTAB , SDS) and dyes

(CFV, CV)) on the deposition of silver from deep eutectic solvents 1:2 ChCl:EG and 1:2 ChCl:urea. The concentration of the electroactive species 'Ag(I)' in the solution was 50 mmol dm^{-3} while three concentration of additive (2%, 6% and 10% of silver concentration) were used. The voltammograms were obtained using the standard three electrode system consisting of a platinum disc working electrode, a platinum flag working electrode and a silver wire quasi-reference electrode.

4.3.1 Cyclic voltammograms

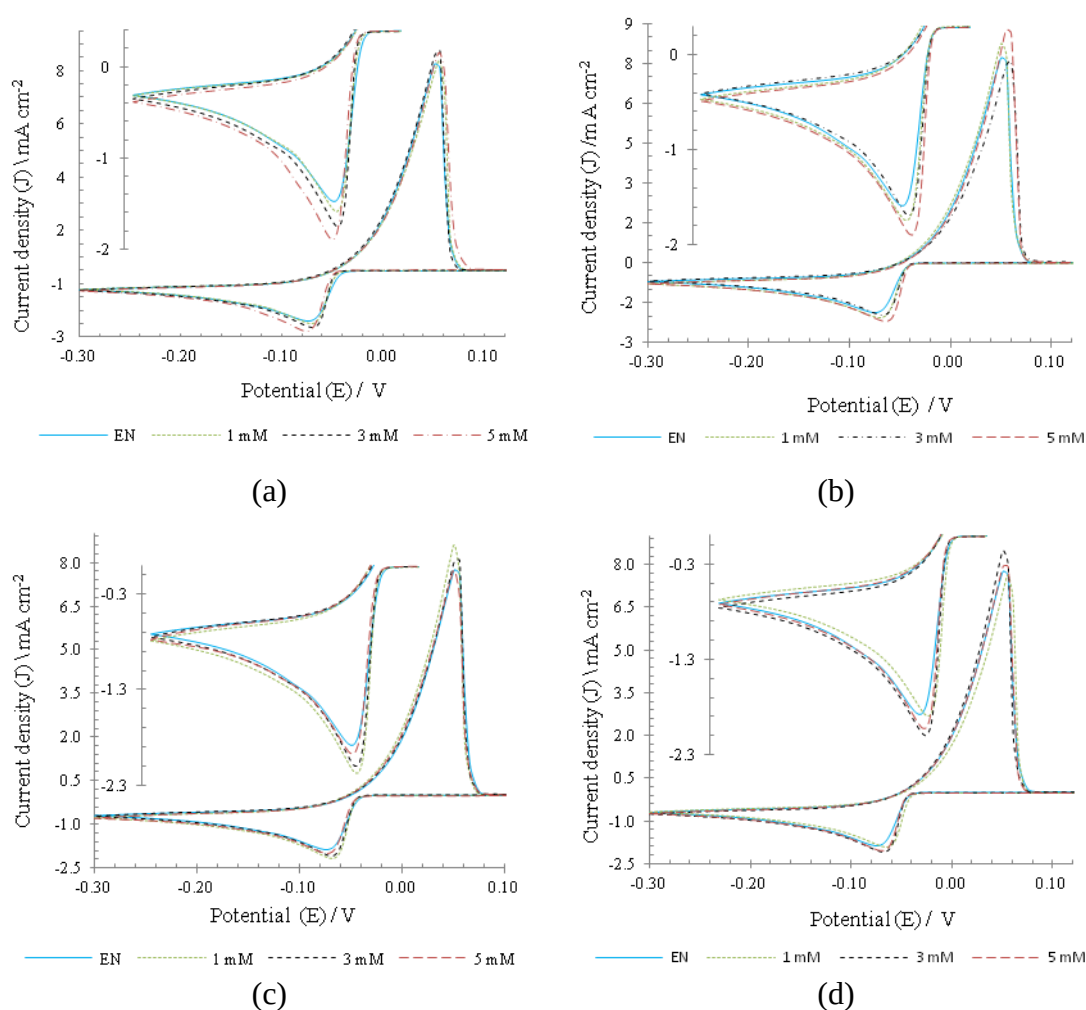


Figure 4.4: Cyclic voltammogram of 1:2 ChCl:EG containing AgNO_3 (50 mmol dm^{-3}), scan rate 10 mV sec^{-1} (a) CTAB (b) SDS (c) CFV and (d) CV

A series of cyclic voltammograms obtained at a scan rate of 10 mV s^{-1} for silver deposition with different additive concentrations in 1:2 ChCl:EG are shown in **Figure 4.4**. The voltammograms are characteristic of silver deposition with single cathodic and anodic peaks. The cathodic peak is broader and represents the reduction of silver

while the anodic peak is sharp and more symmetrical. These voltammograms are consistent with those obtained from other system for silver deposition and stripping²⁶⁻²⁹.

The above experiments were repeated for the 1:2 ChCl:urea system and these are shown in **Figure 4.5**. While the voltammograms maintain the same general shape and characteristics, the magnitude and position of the peaks is affected to different extents in 1:2 ChCl:EG and 1:2 ChCl:urea.

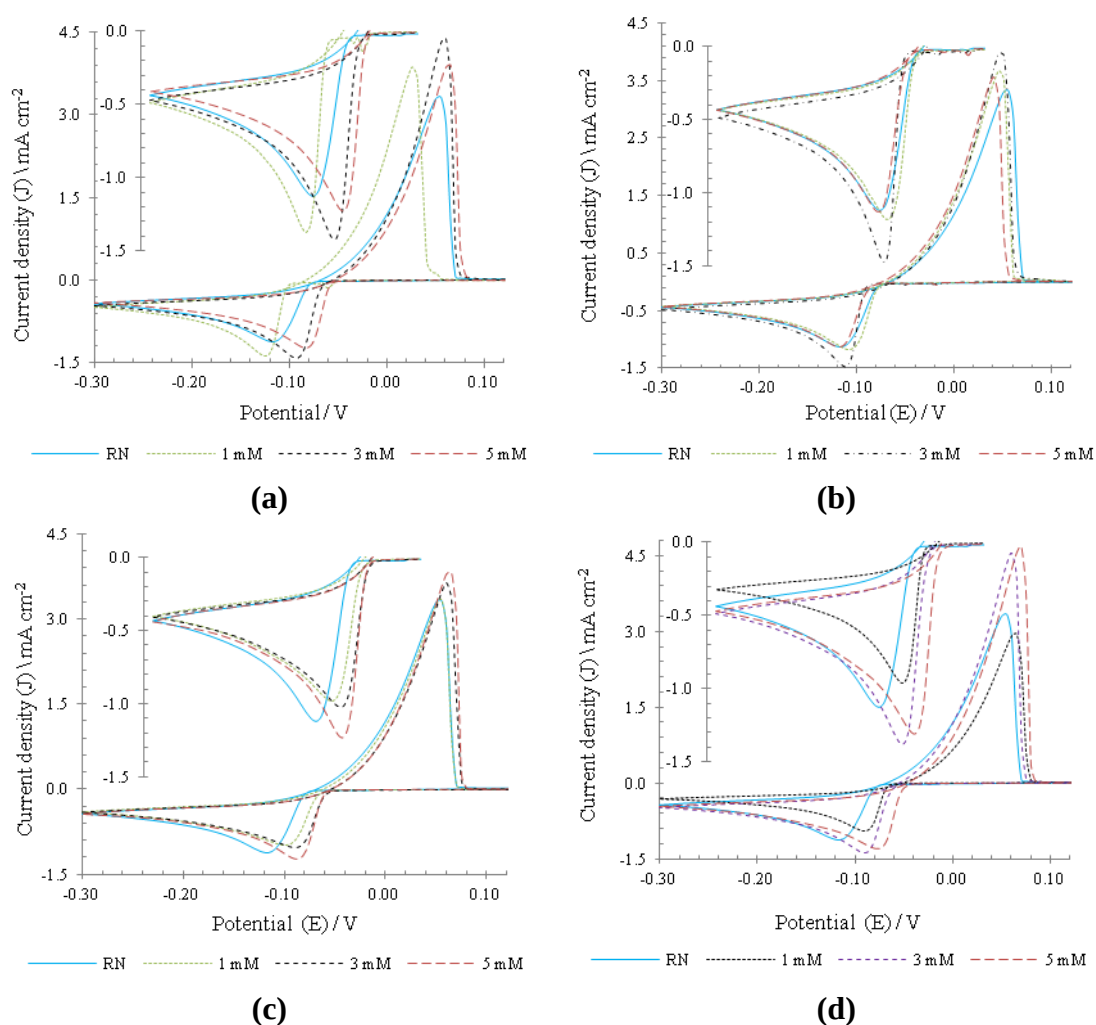


Figure 4.5: Cyclic voltammograms containing 50 mmol dm^{-3} of Ag(I) at different scan rate of 10 mV sec^{-1} in 1:2 ChCl:urea (a) CTAB (b) SDS (c) CFV (d) CV

4.3.2 Peak characterization

To study the silver deposition process quantitatively, a detailed analysis of the voltammetric peak position and magnitude was conducted and the correlation of the peak potential and current maxima with the scan rate yielded information about the kinetics of the electrode process. The additives had minimal effect on the peak positions in 1:2 ChCl:EG (**Figure 4.6(a)**) while in 1:2 ChCl:urea the peak position shifts to more positive values for most additives indicating an increase in the ease of reduction of silver with addition of additives and this was also found to be a function of concentration. The cathodic peak potential is dependent on the scan rate and shifts to more negative values with an increase in the scan rate.

As the electrolytic current is small the effect of ohmic drop on the peak potential should be negligible. At higher scan rates the shifting of peak potential to more negative values is greater than for the solution without additives in 1:2 ChCl:EG and 1:2 ChCl:urea. This behaviour suggests that the bulky nature of the additives may slightly hinder the transportation of the Ag(I) to the electrode surface.

Figure 4.6(b) exhibits the variation of the peak separation (ΔE_p) with the scan rate and it falls in the range of 0.12 – 0.19 V for 1:2 ChCl:EG and 0.16 - 0.27 V for 1:2 ChCl:urea. The addition of additives has no effect on the peak separation in 1:2 ChCl:EG while in 1:2 ChCl:urea the separation is slightly shifted to lower values indicating the shift to a more reversible process.

Figure 4.6(c) indicates that the peak potential – half peak potential separation $[(E_p^{ox} - E_p^{ox})/2]$ increases with scan rate. The anodic peak broadening is less in the 1:2 ChCl:urea with solutions containing additives while the additives have no effect on the broadening of the peak in 1:2 ChCl:EG. At the lowest scan rate, the latter is still considerably larger than the 0.021 V separation expected for a reversible one electron transfer process in which the activity of the deposited metal remains constant^{30, 31}.

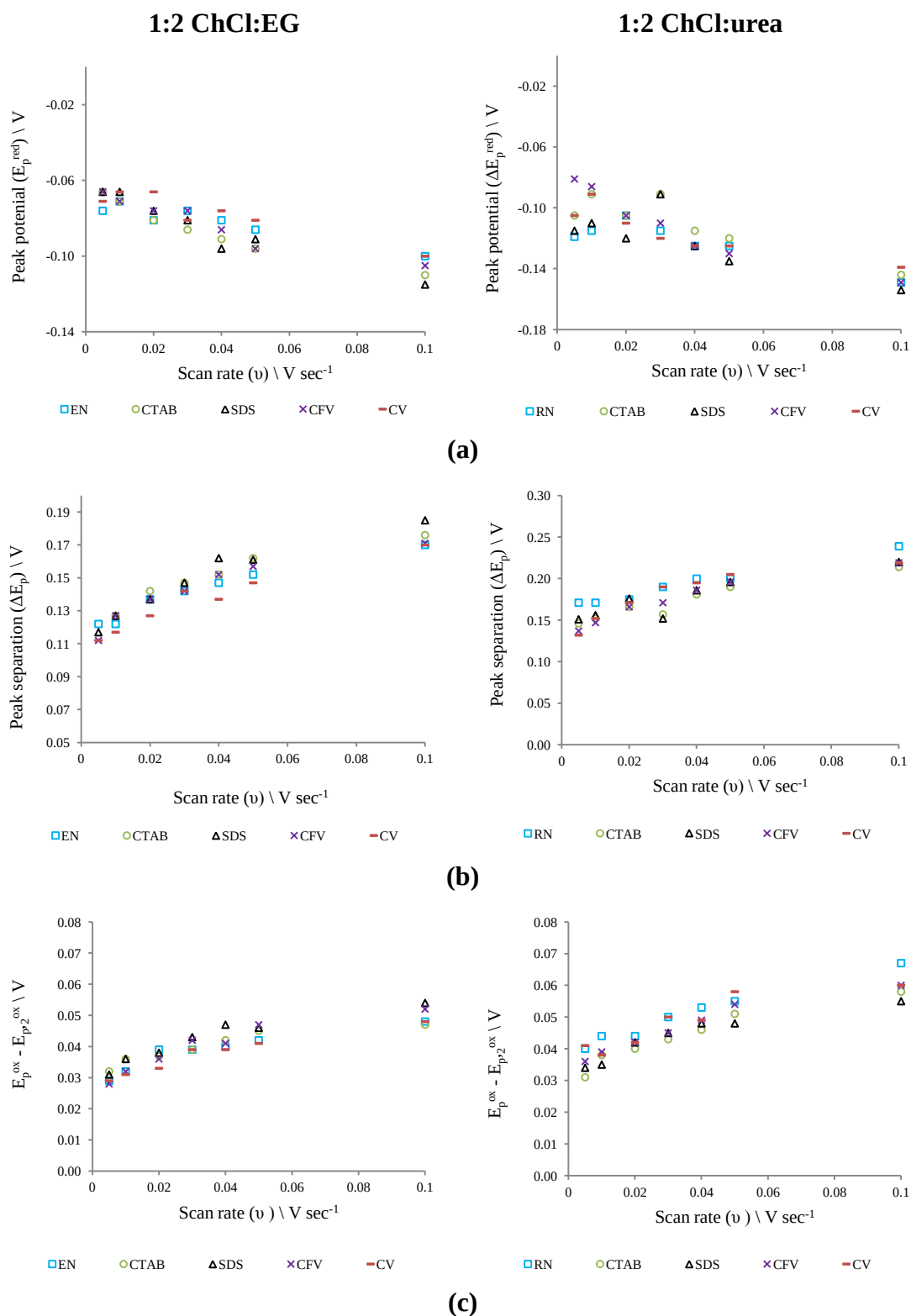


Figure 4.6: Correlation of peak coordinates with the scan rate of silver deposition with various additives (5 mmol dm^{-3}) in solution in 1:2 ChCl:EG(left) and 1:2 ChCl:urea (right) containing Ag(I) 50 mmol dm^{-3} (a) cathodic peak potential (b) peak separation (c) Anodic peak broadening

The above results suggest the reduction of silver may be related to some indistinct kinetic limitation of the phase formation process or to quasi-reversibility of the Ag(I) / Ag(0) charge transfer reaction. The addition of additives has some effect on the electrode surface kinetics in 1:2 ChCl:urea but they show no effect in 1:2 ChCl:EG.

Figure 4.7(a) shows the effect of the concentration on peak heights for silver deposition. The additives slightly increase the peak currents in 1:2 ChCl:EG and it is found to be a function of the concentration. In 1:2 ChCl:urea the surfactants increase the peak current while the dyes shift slightly to lower values. In both cases the behaviour is insensitive to the additive concentration.

Figure 4.7(b) shows that the plot of the cathodic peak heights vs. the square root of the scan rate follows the behaviour predicted by the Randles-Sveik **equation 4.1** suggesting the that the deposition of silver proceeds through a nucleation mechanism under diffusion controlled growth³².

$$J_p = 2.687 \times 10^5 n^{3/2} \nu^{1/2} D^{1/2} C \quad (4.1)$$

The positive intercept on the current axis may be attributed to change in nucleation behaviour with the sweep rate³³. The steepness of the curves in both the solvents is different indicating a slower rate of deposition in 1:2 ChCl:urea and hence lower diffusion co-efficient values due to its high viscosity as compared to 1:2 ChCl:EG.

The diffusion coefficient of silver (D_{Ag^+}) was calculated from the slopes of these curves using the Randles-Sevick equation

where constant has units i.e. $2.687 \times 10^5 \text{ C mole}^{-1} \text{ V}^{-1/2}$

The values of the diffusion coefficient calculated are tabulated in **Table 4.1**. The additives have almost no effect on the diffusion coefficient in both solvents and D values for 1:2 ChCl:EG are greater by a factor of 10 compared to those in 1:2 ChCl:urea. The higher values in 1:2 ChCl:EG is ascribed to its lower viscosity compared to 1:2 ChCl:urea.

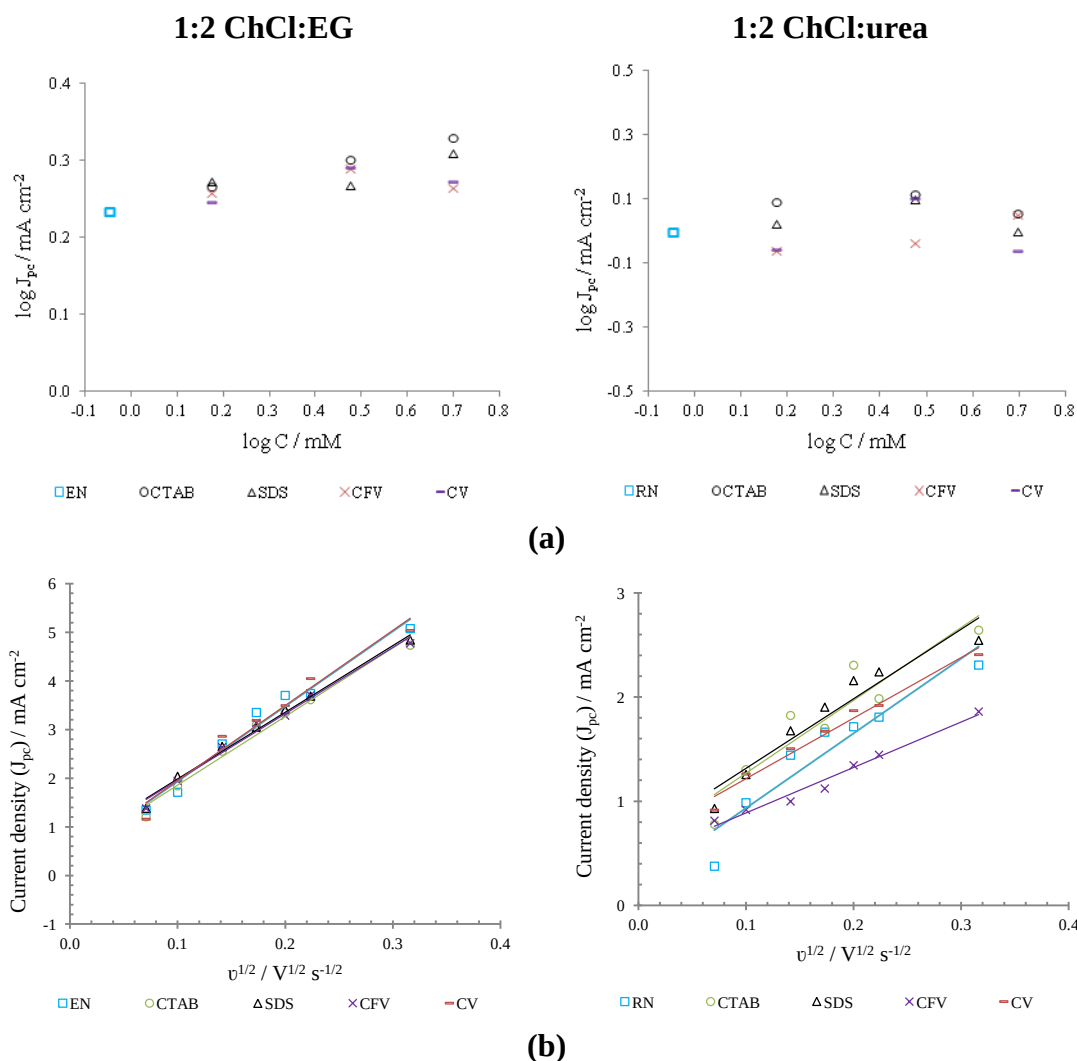


Figure 4.7: Correlation of peak magnitude with the scan rate of silver deposition with and without additives in 1:2 ChCl:EG (left) and 1:2 ChCl:urea (right) containing Ag(I) 50 mmol dm^{-3} (a) peak height vs. concentration of additives (b) peak current density vs. square root of scan rate

4.3.3 Bulk deposition-stripping efficiency

Figure 4.8 show the ratio of the anodic and cathodic charges, Q_a / Q_c from the integrated peak areas under the voltammograms and this is plotted against the scan rate. The solid line in this figure represents a ratio of 1 i.e. deposition stripping efficiency of 100%. The data shows that the stripping in DES is not 100% and varies from 85 to 93%, showing the quasi reversible behaviour of silver deposition and stripping in DES and that additive have no effect on the efficiency.

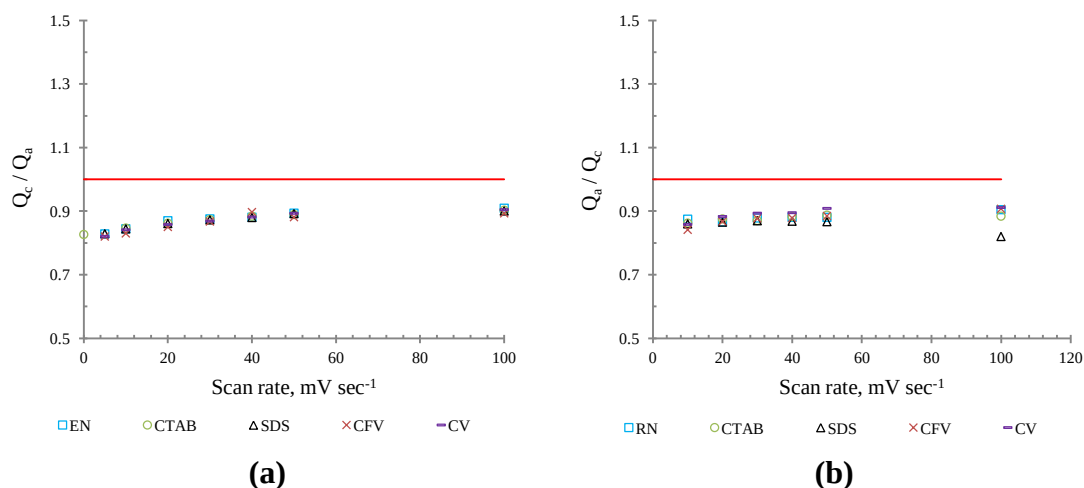


Figure 4.8: The ratio of anodic charge to cathodic charge vs. scan rate for silver deposition and stripping at scan rate, 10 mV sec^{-1} for Ag(I) 50 mmol dm^{-3} with additives in (a) 1:2 ChCl:EG (b) 1:2 ChCl:urea

4.3.4. Reaction Rate

Variation in energy of the reactants, transition states and products with the electrode potential are correlated by the Tafel equation²⁹

$$\ln J_p = \ln (0.227 n F C_{Ag} K^o) + \frac{\alpha n_a F}{R T} (E_p - E^o) \quad (4.2)$$

Where C_{Ag} is bulk concentration of Ag(I) in mole cm^{-3} , α is the transfer coefficient, n is the number of electrons involved in the reduction process respectively.

$\ln J$ shows a linear dependence on the difference of the peak and formal potentials, E_p and E^o (V) suggesting that the electrode kinetics of silver deposition can be explained by using the Butler-Volmer equation. The intercept and slope of these curves are used to calculate the standard heterogeneous rate constant (k^o) and the transfer co-efficient (α) and the values are reported in **table 4.1**. The slight increase in K^o values in DES with the addition of additives suggest that there is no specific adsorption of these additives on the electrode surface and they have no inhibiting effect of the silver deposition process.

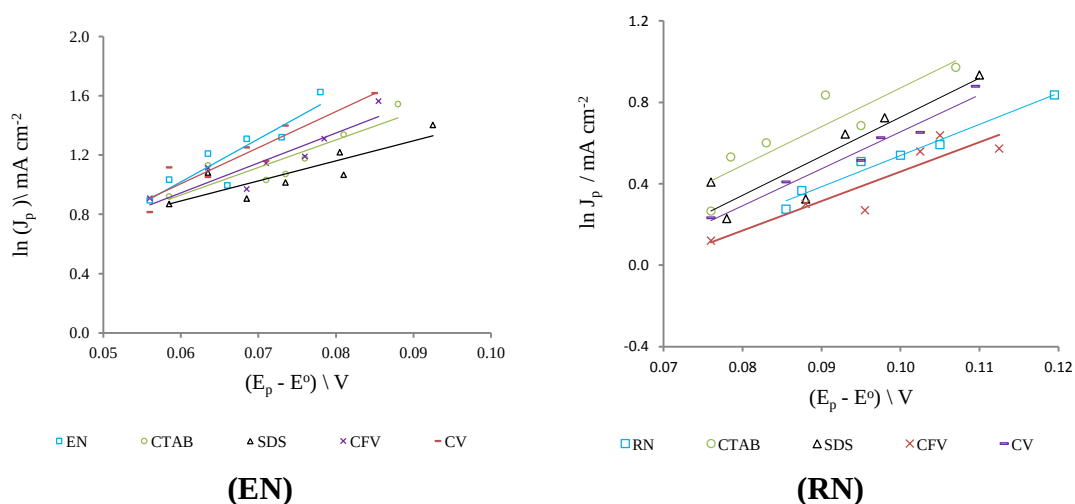


Figure 4.9: Dependence of the log of the peak current density for $\text{Ag(I)} / \text{Ag(0)}$ on the difference of the peak and formal potentials in DES containing AgNO_3 50 mmol dm^{-3} for different additives (5 mmol dm^{-3})

Table 4.1: Kinetic parameters for the reduction of Ag(I) in DES with additives in solution

System		Diffusion Coefficient (D)	Heterogeneous Rate constant (k^0)	Transfer coefficient (α)
		$\times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$	$\times 10^{-4} \text{ cm s}^{-1}$	
* 1:2 ChCl:EG	AgNO_3 (50 mmol dm^{-3})	1.32	4.44	0.7
	CTAB (5 mmol dm^{-3})	1.21	6.56	0.6
	SDS (5 mmol dm^{-3})	1.04	6.36	0.6
	CFV (5 mmol dm^{-3})	1.27	4.43	0.7
	CV (5 mmol dm^{-3})	1.03	5.81	0.6
** 1:2 ChCl:urea	AgNO_3 (50 mmol dm^{-3})	0.29	1.24	0.4
	CTAB (5 mmol dm^{-3})	0.26	2.78	0.5
	SDS (5 mmol dm^{-3})	0.37	2.76	0.5
	CFV (5 mmol dm^{-3})	0.11	1.77	0.4
	CV (5 mmol dm^{-3})	0.22	1.22	0.5
* The likely determination error is $\pm 2 \%$				
** The likely determination error is $\pm 4 \%$				

4.4 Gravimetric Analysis

The electrochemical Quartz Crystal Microbalance (EQCM) is an electrogravimetric analysis technique which measures the mass change on the surface of a quartz crystal through the change in the resonating frequency of the quartz crystal. It is a very sensitive technique with sub monolayer resolution and finds a variety of electrochemical applications³⁶⁻⁴⁰. The change in the resonating frequency of the quartz crystal (Δf) of the quartz crystal from its fundamental value (f_o) is related to the change in mass using the the Sauerbrey equation⁴¹

$$\Delta f_{Hz} = \frac{-2}{\rho v} f_o^2 (\Delta m/g\ cm^{-2}) \quad (4.3)$$

In the present study, the effect of the additives on the deposition of Ag from $AgNO_3$ (100 mmol dm^{-3}) was studied in 1:2 ChCl:EG and 1:2 ChCl:urea as a function of additive concentration (2, 6 and 10 mol % of the Ag(I) concentration) using the gold coated quartz crystal as cathode at -500 mV and -600 mV vs. silver wire as the quasi reference electrode and a platinum flag as a counter electrode. In this study, a 10 MHz AT-cut polished (flat mirror) finish quartz crystal with a gold film thickness of 900 Å, deposited in a keyhole shape on both sides with central disc active area of 0.211 cm^2 is used.

4.4.1 Frequency trends

Figure 4.9 and **4.10** shows the change in the frequency of the quartz crystal as a function of time. The peak position and the height of these curves changed with time while the shape of these curves remains qualitatively unchanged. This shifting of frequency is found to be 1.06 ± 0.05 % and is insensitive to the addition of additives in 1:2 ChCl:EG indicating no effect on the deposited mass of silver on the quartz crystal.

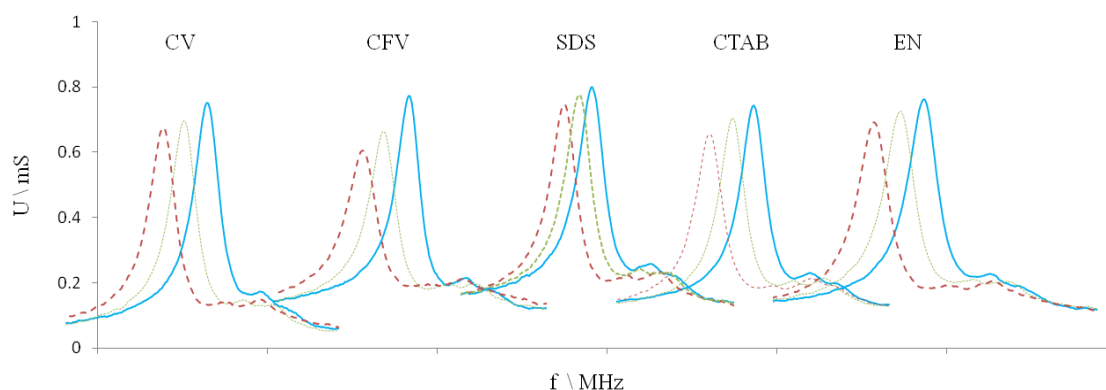


Figure 4.9: *Acoustic impedance spectra of silver deposition in 1:2 ChCl:EG containing $\text{AgNO}_3 100 \text{ mmol dm}^{-3}$ and additives 10% of Ag(I). The solid blue lines are the spectra of the dry Au coated polished crystal while the dashed lines show the spectra after the deposition of Ag(I) for 20 mins. The dotted line show the deposition after 10 mins.*

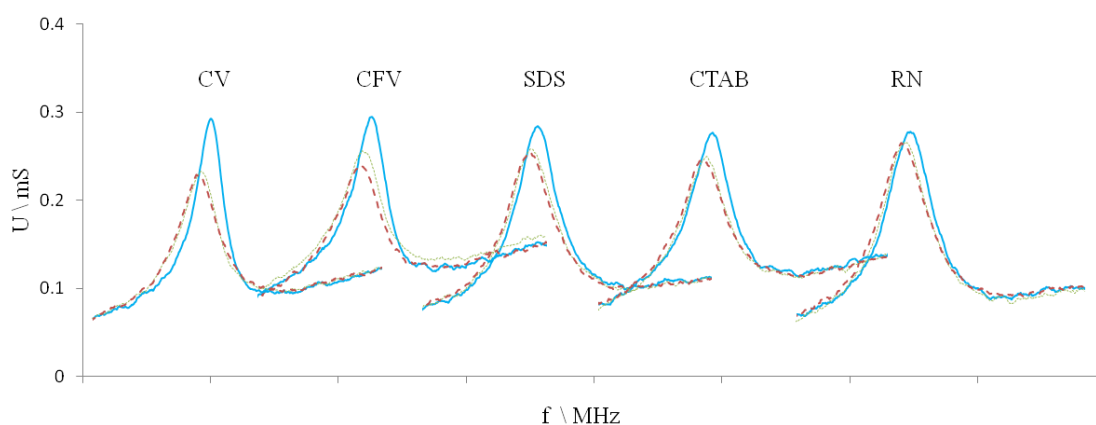


Figure 4.10: *Acoustic impedance spectra of silver deposition in 1:2 ChCl:urea containing $\text{AgNO}_3 100 \text{ mmol dm}^{-3}$ and additives 10% of Ag(I). The solid blue lines is spectra of the dry Au coated polished crystal while the maroon lines show the spectra after the deposition of Ag(I) after 20 mins.*

In case of 1:2 ChCl:urea, the addition of the additives slightly shifts the resonance frequency more when compared to the solution without additives and the change in frequency varies from 0.2 to 0.4 %. The broader curves may result from the high viscosity and be due to some viscoelastic changes.

The Q factor is used to measure the changes in the shape of the resonance curves and is the ratio of the frequency (f_0) at the centre of resonance curve and w the full width of the peak at half height (FWHH). The Q factor is calculated using the equation³⁹

$$Q = \frac{f_0}{\omega} \quad (4.4)$$

The change in broadness of the curve is estimated by comparing the Q factor values at the beginning and end of each experiment. The change in broadness of the curve was found to be between 5-6 % in 1:2 ChCl:EG and 10-12% in 1:2 ChCl:urea.

4.4.2 Current Efficiency

The current efficiency of the deposition process of silver in 1:2 ChCl:EG and 1:2 ChCl:urea in the presence of additives is calculated from the relation of the deposited mass to the charge passed. **Figures 4.11** show the plots of the silver mass deposited as a function of charge passed. The apparent molar mass of silver is calculated by multiplying nF (where n the number of electrons involved in the process) with the slope of the charge – mass curve.

High current efficiencies with values between 80 – 100% are obtained in both of the solvents. No significant trend of the current efficiencies with the addition of additives was found. The good linear fit of the data at long time shows that the current efficiency is not a function of time. Similar data were acquired for the urea based liquid.

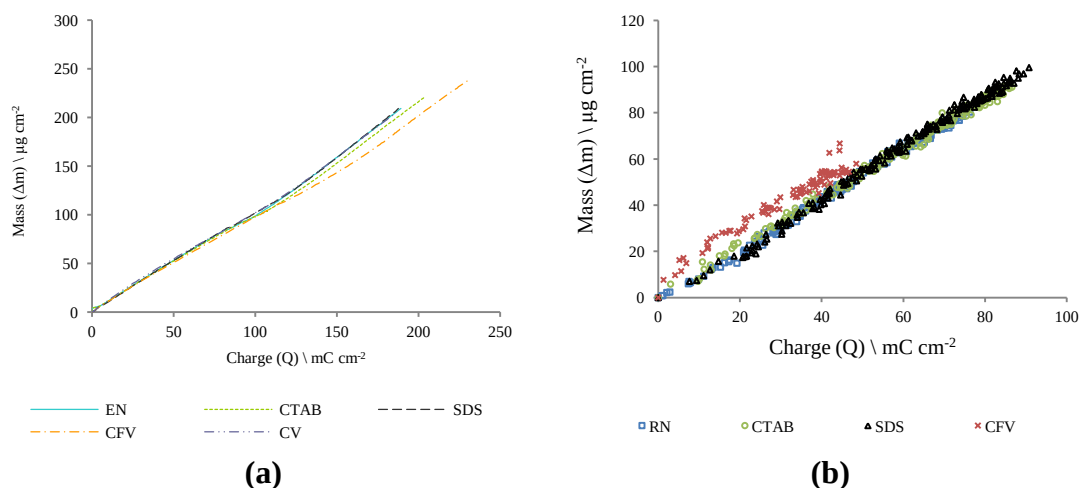


Figure 4.11: Comparison of mass of silver deposited as function of charge passed from solution containing AgNO_3 with and without additives in (a) 1:2ChCl:ethylene glycol and (b) 1:2 ChCl:urea

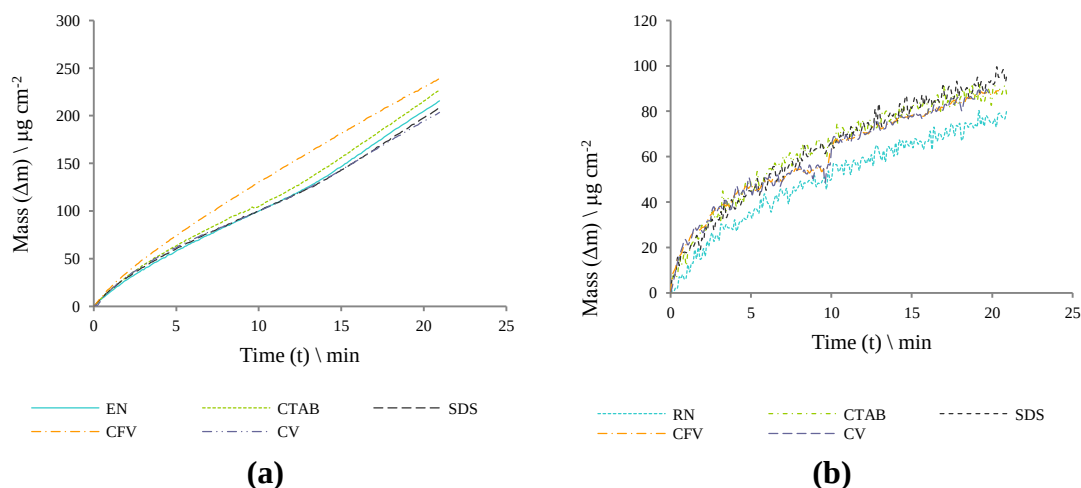


Figure 4.12: Comparison of mass of the silver deposited as function of time of deposition from solution containing AgNO_3 with and without additives in (a) 1:2ChCl:ethylene glycol and (b) 1:2 ChCl:urea

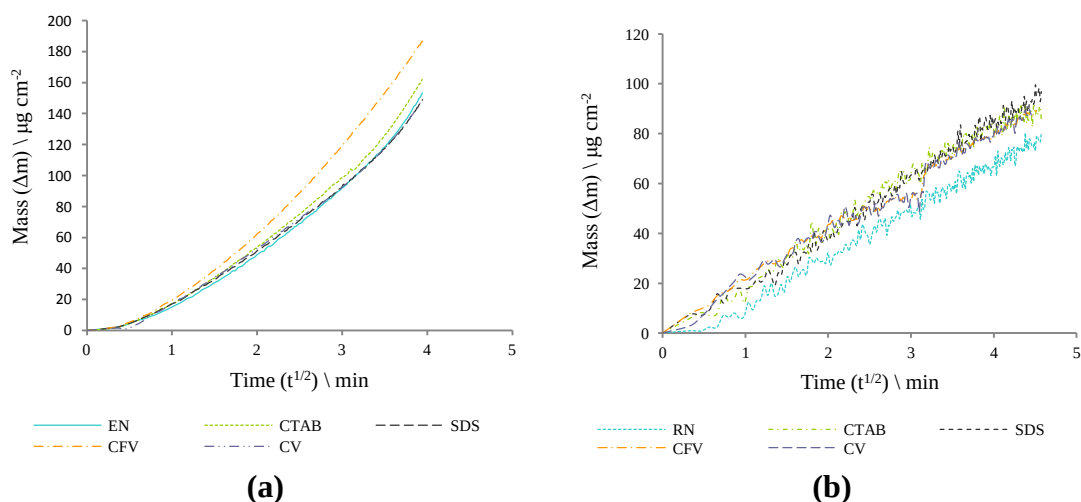


Figure 4.13: Comparison of mass of the silver deposited as function of square root of time of deposition from solution containing AgNO_3 with and without additives in (a) 1:2ChCl:ethylene glycol and (b) 1:2 ChCl:urea

4.4.3 Rate of deposition

Figure 4.12 shows plots of the deposited mass of silver as a function of time from solutions containing $100 \text{ mmol dm}^{-3} \text{ AgNO}_3$ and the selected additives in concentration 10% of the electroactive species. The examination of these curves reveals two rates of silver deposition. At short time the rates of silver deposition is fast and a change in rate is observed after completion of nucleation suggesting the deposition is under diffusion control as shown in **Figure 4.13**. In 1:2 ChCl:EG the

addition of additives does not significantly affect the silver mass deposited while in 1:2 ChCl:urea a slight increase in the mass of deposited silver is observed. The mass and the critical layer thickness of the turn over is calculated using the density of Ag metal (10.5 g cm^{-3}) and the active area of the crystal (0.23 cm^2) and tabulated in **table 4.2**

Table 4.2: *Effect of additives on Silver deposition from solution containing $100 \text{ mmol dm}^{-3} \text{Ag(I)}$ in EQCM*

System		Current Efficiency	Co-ordinates of turn over in rate in EQCM deposition		
			Time	Deposition mass	Layer Thickness
		%	s	$\mu\text{g cm}^{-2}$	Atomic layers
1:2 ChCl:EG)	AgNO_3 (100 mmol dm^{-3})	95.43	1.6	23	133
	CTAB (10 mmol dm^{-3})	94.3	1.7	25	144
	SDS (10 mmol dm^{-3})	96.36	1.7	24	139
	CFV (10 mmol dm^{-3})	92.15	1.6	28	162
	CV (10 mmol dm^{-3})	91.75	1.6	32	173
1:2 ChCl:urea + AgNO_3 (50 mmol dm^{-3})	AgNO_3 (100 mmol dm^{-3})	97.89	3.6	28	162
	CTAB (10 mmol dm^{-3})	95.62	3.8	40	231
	SDS (10 mmol dm^{-3})	94.57	3.4	38	219
	CFV (10 mmol dm^{-3})	91.5	3.4	51	294
	CV (10 mmol dm^{-3})	91.45	3.4	62	358
*		The likely determination error is $\pm 2 \%$			
**		The likely determination error is $\pm 4 \%$			

4.5 Chronoamperometric study

Chronoamperometry is a classical electrochemical technique that offers the quantitative evaluation of the influence of different parameters like diffusion coefficient, nucleation and growth rates and adsorption on the kinetics of the electrocrystallization through different theoretical models⁴²⁻⁴⁵. The morphological features of the macrodeposit like the smoothness and brightness are determined by the crystallite density and the nucleation process that may be classified as either 2D or

3D.^{32, 46} The nuclear number density is directly related to the nucleation overpotential and hence dictates the topographical morphology and the film thickness. Chronoamperometric measurements are based on the response of the current to the applied potential and have been extensively used to probe nucleation and growth phenomena⁴⁷. The effect of different additive on the early stages of nucleation and growth of silver is probed using current transient measurements.

4.5.1 Analysis of the current transients

The chronoamperometric data was obtained on a polycrystalline platinum working electrode by stepping the potential from an initial value (+0.2 V) where no silver deposition takes place to values between -0.04 V and -0.16 V and -0.08 V and -0.220 V in 1:2 ChCl:EG and 1:2 ChCl:urea respectively for deposition of silver from solutions containing 50 mmol dm⁻³ Ag(I). The concentration of the additives varies from 2 to 10 % of the silver concentration. The silver salt used was AgNO₃. A family of current transients obtained in 1:2 ChCl:EG and 1:2 ChCl:urea is shown in **Figures 4.14** and **4.15**.

The shape of the current transients is the same and not a function of the step potential. It is similar to that of the theoretical models derived to describe the growth of a system under diffusion control. The current transients have well defined current maxima which is sensitive to the applied potential. The initial exponential decay of the current at the onset of the potential step corresponds to the capacitive current.^{48, 49} After a short induction time, the rising current either due to the birth and growth of the silver nuclei at the electrode surface and /or the increasing number of nuclei culminates in a maximum reflecting the coalescence of neighbouring diffusion fields with localized spherical symmetry of the growing crystallites.⁵⁰ After the current maximum, the current fades away slowly and continuously according to the Cottrell relation corresponding to planar diffusion to the whole electrode surface and merges into a common curve at longer time.

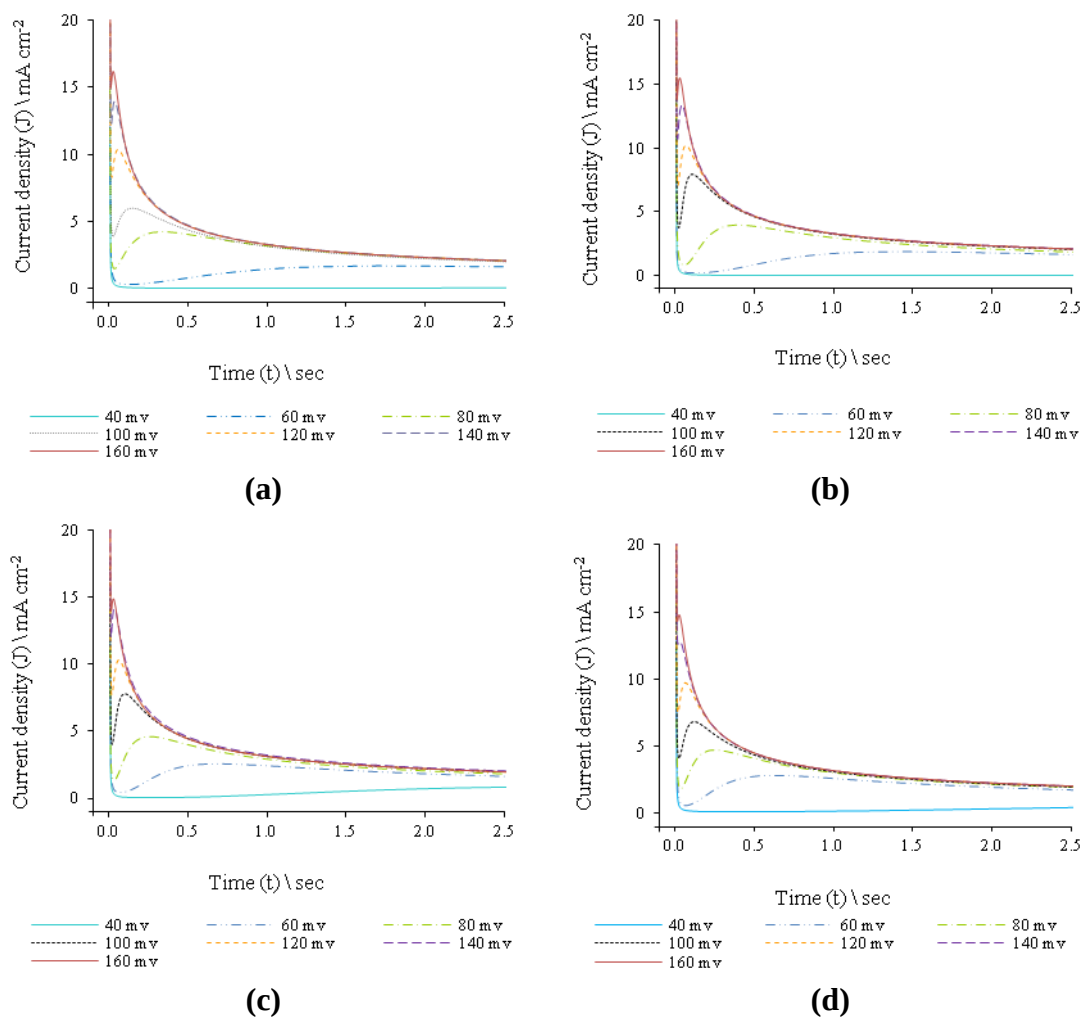


Figure 4.14: A set of chronoamperometric current vs. time data for the reduction of silver from 1:2 ChCl:EG for Ag(I) concentration of 50 mmol dm^{-3} with different additives (10% of Ag(I) concentration) (a) $\text{AgNO}_3 + \text{CTAB}$ (b) $\text{AgNO}_3 + \text{SDS}$ (c) $\text{AgNO}_3 + \text{CFV}$ (d) $\text{AgNO}_3 + \text{CV}$

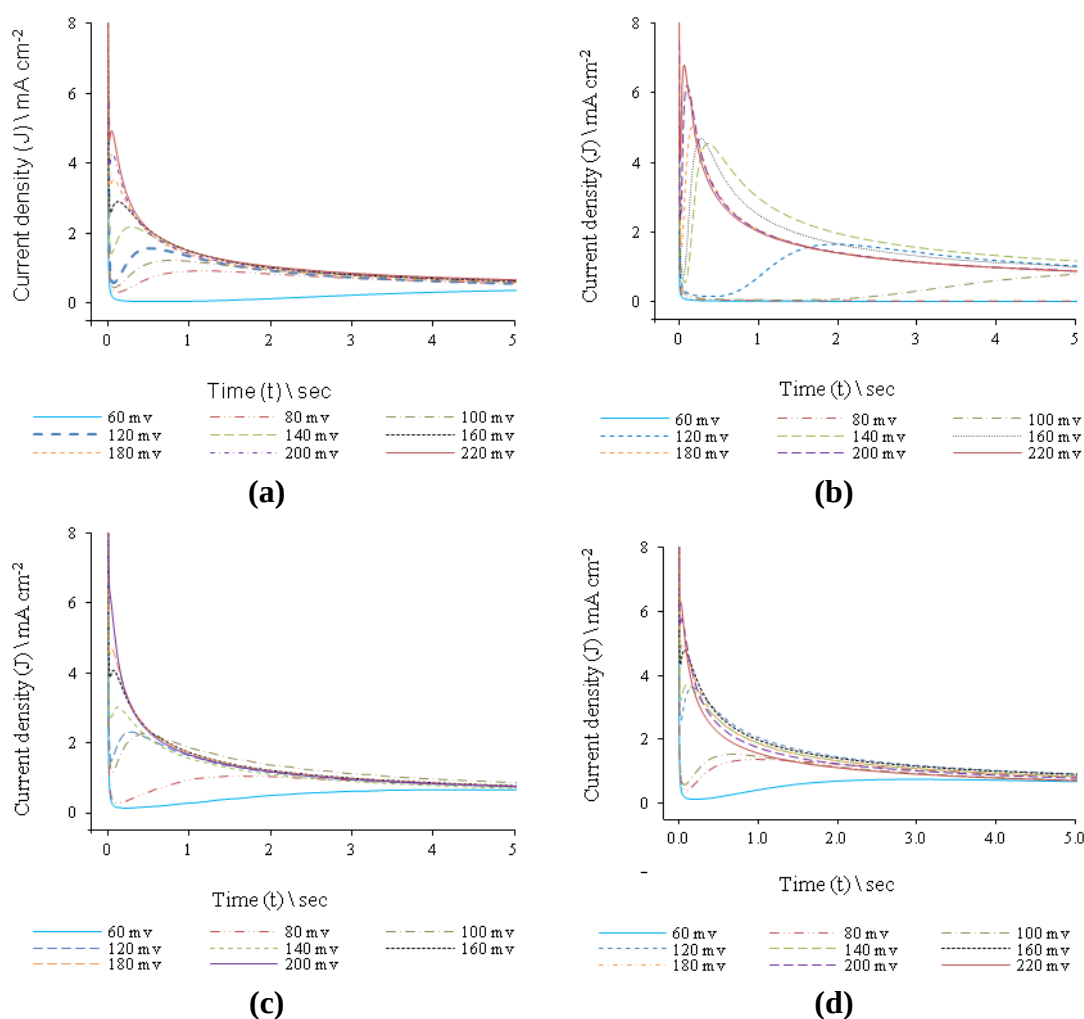


Figure 4.15: Set of $j - t$ curves for the reduction of silver from 1:2 ChCl:urea for Ag(I) concentration of 50 mmol dm^{-3} with different additives (10% of Ag(I) concentration) (a) $\text{AgNO}_3 + \text{CTAB}$ (b) $\text{AgNO}_3 + \text{SDS}$ (c) $\text{AgNO}_3 + \text{CFV}$ (d) $\text{AgNO}_3 + \text{CV}$

All the current transients are similar to those which have been obtained for different silver salts in 1:2 ChCl:EG and 1:2 ChCl:urea without additives as shown in **chapter 3** and analysed using the theoretical models proposed by Hills et al.^{49, 51} and Scharifker and Monstany⁵². These models describe the kinetics of the early stages of new phase formation through 3D multiple nucleation with mass transport growth. The two extreme cases of nucleation can be described by the following equations^{49, 53}.

$$J(\text{instantaneous}) = \frac{nFD^{1/2}c}{\pi^{1/2}t^{1/2}} [1 - \exp(-N_o\pi kFt)] \quad (4.5)$$

$$k = \left[\frac{8\pi cM}{\rho} \right]^{1/2}$$

$$J(\text{progressive}) = \frac{nFD^{1/2}c}{\pi^{1/2}t^{1/2}} \left[1 - \exp\left(-\frac{AN_o\pi k'Dt^2}{2}\right) \right] \quad (4.6)$$

$$k' = \frac{4}{3} \left[\frac{8\pi cM}{\rho} \right]^{1/2}$$

Where n is the equivalent mole⁻¹, F is the Faraday constant, (Coulomb equivalent⁻¹), D is the diffusion coefficient (cm²s⁻¹), c is the bulk concentration (mol cm⁻³), M is the Molar mass, ρ is the density of the deposited material, t is the time (s), J is the current density (A cm⁻²)

The major assumptions made while formulating these models is that the columnar diffusion occurs after eventual overlap of spherical diffusion zones^{49, 51, 52} around the growing nuclei and the development of nucleation exclusion zones.

4.5.2 Maxima co-ordinates of the current transients

In general the shape of the current transients is independent of the applied overpotential. The maximum coordinates of the current transients are a function of the overpotential and, at more negative step potentials, larger and better resolved current maxima are obtained but these are shifted towards shorter times.

Figure 4.16 (a and b) show a comparison of the effect of different additives on t_{max} as a function of step potential on silver deposition in 1:2 ChCl:EG and 1:2 ChCl:urea. This shows that additives have no effect on the t_{max} in 1:2 ChCl:EG but they cause t_{max} to move to slightly smaller values in 1:2 ChCl:urea.

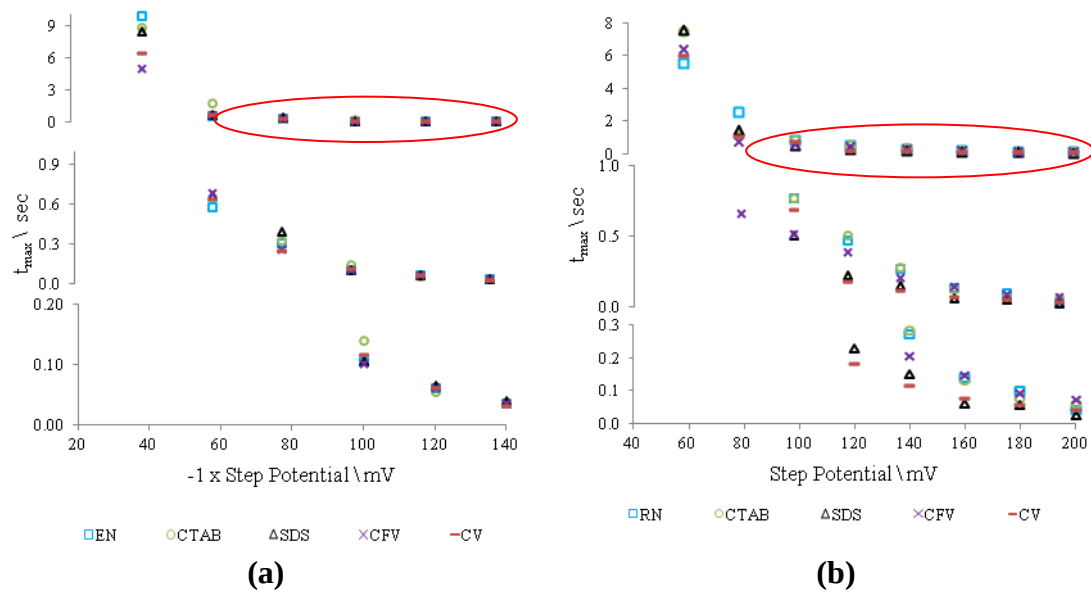


Figure 4.16: Overpotential dependence of the t_{max} of silver deposition from $AgNO_3$ with addition of additives in (a) 1:2 ChCl:EG (b) 1:2 ChCl:urea, lower graphs in both cases show a zoom in of the encircled part

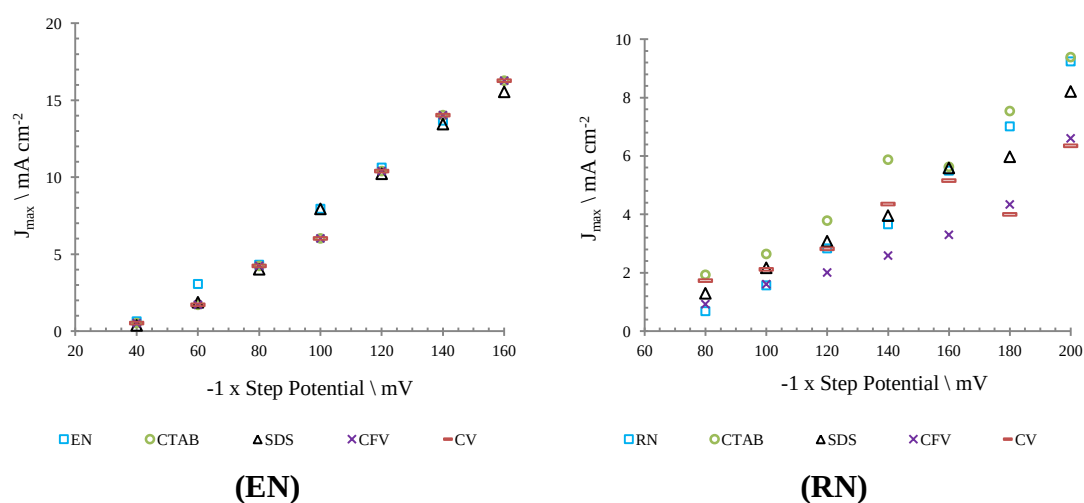


Figure 4.17: J_{max} as a function of step potential of silver reduction with addition of additives for $AgNO_3$ in (a) 1:2 ChCl:EG (b) 1:2 ChCl:urea

J_{max} increases linearly with more cathodic step potential in both solvents as shown in **Figure 4.17**. The J_{max} values are insensitive to the addition of additives in 1:2 ChCl:EG while in 1:2 ChCl:urea the surfactants show no effect on the J_{max} values

while the dyes slightly shift the J_{max} values to lower values at higher negative over potentials.

4.5.3 Qualitative characterization of nucleation mechanism

As a first step to determine qualitatively the dominant nucleation behaviour of the silver deposition from 1:2 ChCl:EG and 1:2 ChCl:urea in the presence of additives a graphical comparison is made with the two extreme possibilities of nucleation i.e instantaneous and progressive nucleation by plotting **equation 4.7 and 4.8**.

$$\left[\frac{J}{J_{max}}\right]^2 = 1.9542 \left[\frac{t}{t_{max}}\right]^{-1} \left\{1 - \exp\left[-1.2564 \left[\frac{t}{t_{max}}\right]\right]\right\}^2 \quad (4.7)$$

$$\left[\frac{J}{J_{max}}\right]^2 = 1.2254 \left[\frac{t}{t_{max}}\right]^{-1} \left\{1 - \exp\left[-2.3367 \left[\frac{t}{t_{max}}\right]^2\right]\right\}^2 \quad (4.8)$$

The above equations are obtained by normalizing the time and current density with the t_{max} and J_{max} co-ordinates of the current transient maxima. **Figures 4.18 and 4.19** show a graphical comparison of non dimensional plots, $[J/J_m]^2$ vs. t/t_m with theoretical curves for the current transients presented in **Figure 4.14 and 4.15**. An investigation of these plots shows a dependence of the nucleation process on the over potential in both 1:2 ChCl:EG and 1:2 ChCl:urea. The nucleation mechanism changes from progressive at low over potential to instantaneous behaviour at more cathodic over potentials. The falling of the non dimensional experimental curve after t_{max} between two limiting cases suggest the slow nucleation with diffusion controlled growth⁵⁴. This type of behaviour is consistent with the observations made in **chapter 3** for silver deposition without additives suggesting that the additives have no effect on the nucleation behaviour.

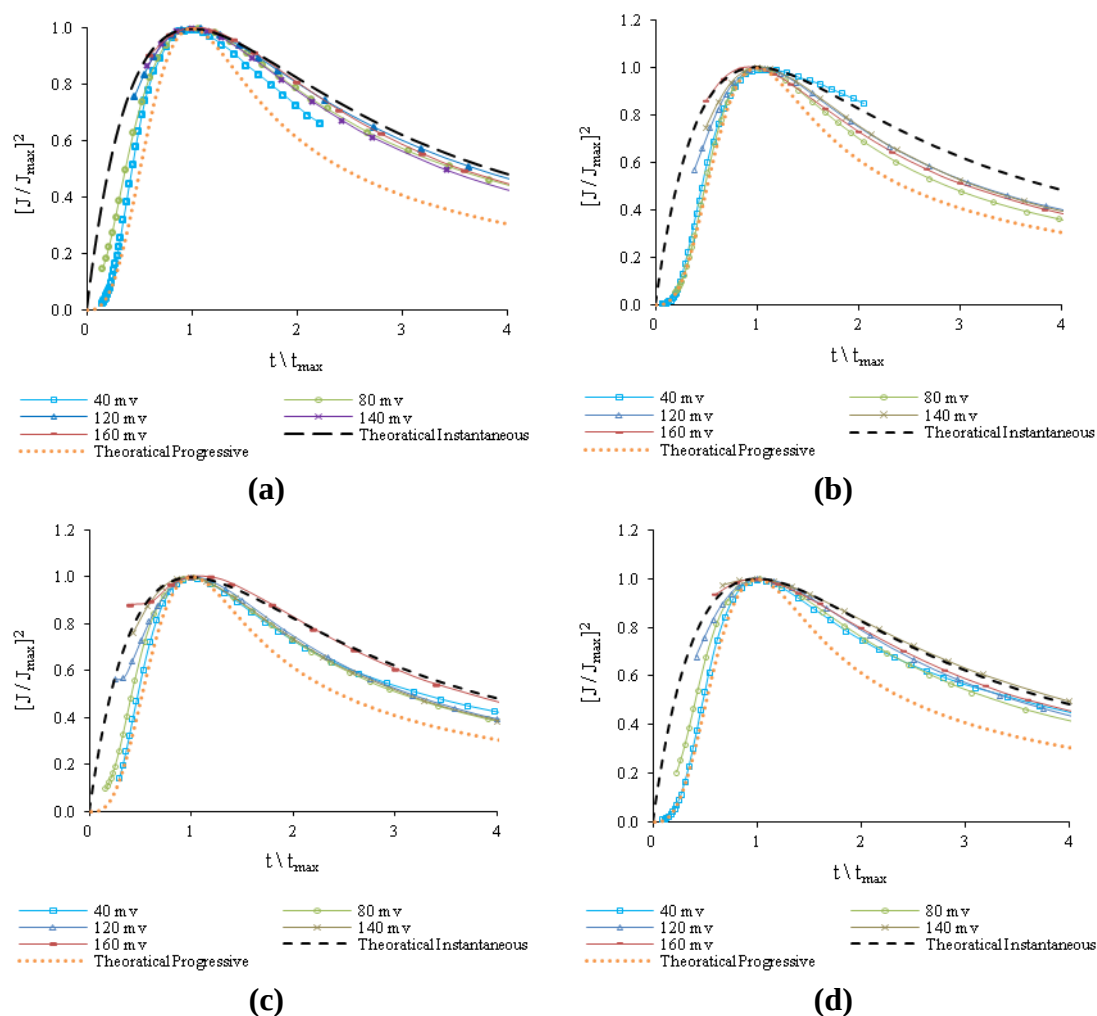


Figure 4.18: *Reduced variable plots for the current transients in Figure 4.14, illuminating the comparison with the theoretical limiting cases i.e. 3D instantaneous and 3D progressive nucleation for silver deposition from 1:2 ChCl:EG (Ag(I) 50 mmol dm⁻³) (a) CTAB (b) SDS (c) CFV (d) CV*

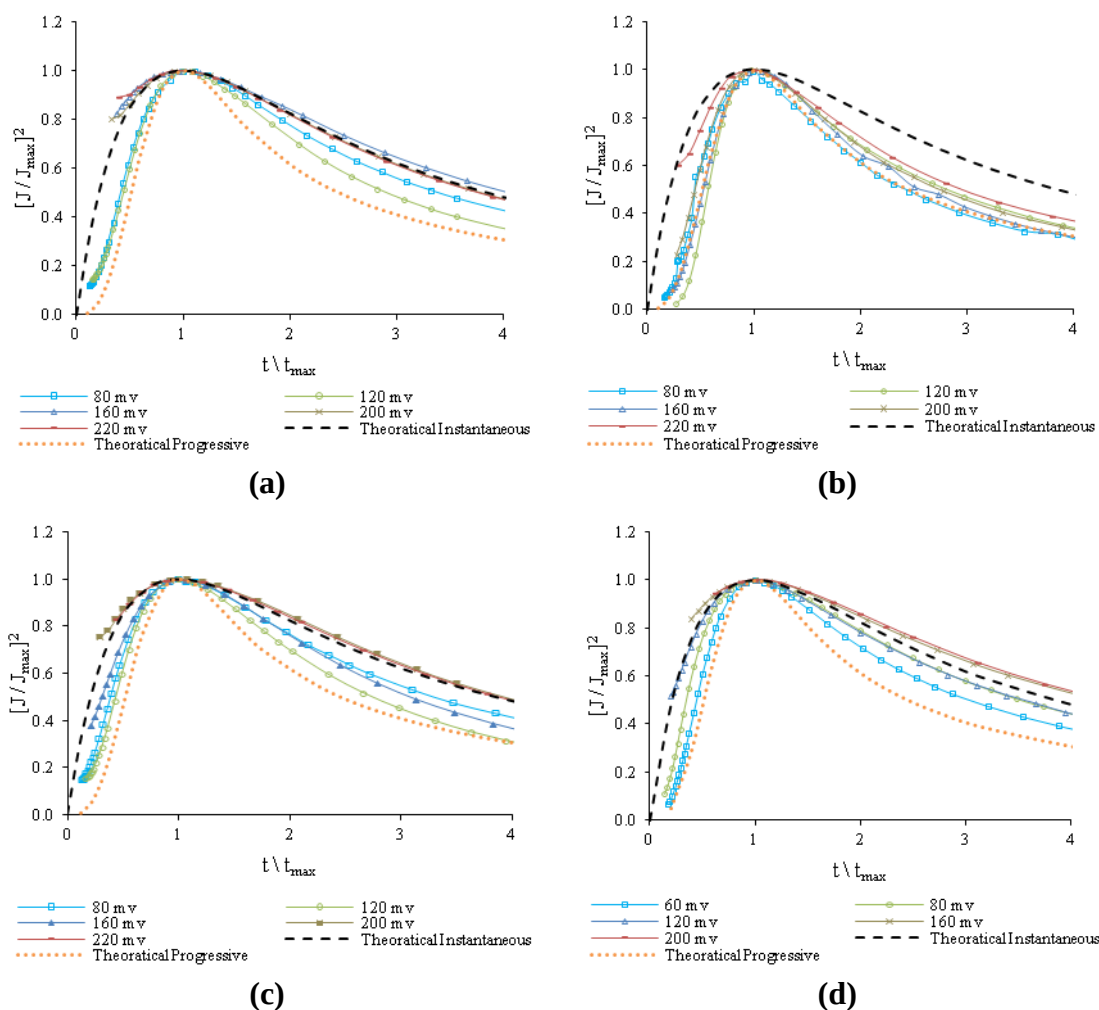


Figure 4.19: Non dimensional graphical comparison plots for the current transients in Figure 4.15, with the theoretical limiting cases i.e. 3D instantaneous and 3D progressive nucleation for silver deposition from 1:2 ChCl:urea (Ag(I) 50 mmol dm^{-3}) (a) CTAB (b) SDS (c) CFV (d) CV

4.5.4 Diffusion coefficient

The Faradaic current after $j_{\max}$ of the current transients decays slowly corresponding to mass transport to the electroactive surface and shows a linear relationship with $Jt^{-1/2}$ according to the Cottrell equation

$$I(t) = \frac{nFD^{1/2}C}{\pi^{1/2}t^{1/2}} \quad (4.9)$$

At very high negative values of the step potential relative to E_p^{red} , the well known diffusion controlled $t^{-1/2}$ Cottrellian decay⁵⁵ is detected and no current maximum is

observed. **Equation 4.9** is used to calculate the diffusion co-efficient from the slopes of the $J-t^{-1/2}$ curves for silver deposition with addition of the surfactants and dyes in the solution as additives. These are compared in table 4.3 and comparison is also made with values calculated from cyclic voltammetry.

Diffusion co-efficient values are calculated from the product of the maximum coordinates of the chronoamperometric transients by using the **equation 4.10**

$$J_m^2 t_m = 0.2598 (zFC_{Ag(I)})^2 D_{Ag(I)} \quad (4.10)$$

Table 4.3: Comparison of the diffusion coefficient in DES calculated with different methods

		Cyclic voltammetry	Cottrell Equation (Equation 4.9)	$D_{Ag(I)}$ (Equation 4.10)	Non linear simulation	
					Scharifkar model	Luc Heermann
					$D_{Ag(I)}$	$D_{Ag(I)}$
System		$D_{Ag(I)}$ $10^6 \text{ cm}^2 \text{ sec}^{-1}$	$D_{Ag(I)}$ $10^6 \text{ cm}^2 \text{ sec}^{-1}$	$D_{Ag(I)}$ $10^6 \text{ cm}^2 \text{ sec}^{-1}$	$D_{Ag(I)}$ $10^6 \text{ cm}^2 \text{ sec}^{-1}$	$D_{Ag(I)}$ $10^6 \text{ cm}^2 \text{ sec}^{-1}$
1:2 ChCl:EG)	AgNO ₃ (50 mmol dm ⁻³)	1.32	1.3	1.53	1.3	1.20
	CTAB (5mmol dm ⁻³)	1.21	1.14	1.46	1.14	1.30
	SDS (5 mmol dm ⁻³)	1.04	1.03	1.50	1.04	1.16
	CFV (5 mmol dm ⁻³)	1.27	1.09	1.46	1.09	1.12
	CV (5 mmol dm ⁻³)	1.03	1.05	1.29	1.05	1.13
1:2 ChCl:urea	AgNO ₃ (50 mmol dm ⁻³)	0.29	0.73	0.91	0.74	0.67
	CTAB (5 mmol dm ⁻³)	0.26	0.26	0.3	0.27	0.27
	SDS (5 mmol dm ⁻³)	0.37	0.56	0.63	0.57	0.56
	CFV (5 mmol dm ⁻³)	0.11	0.24	0.21	0.23	0.42
	CV (5 mmol dm ⁻³)	0.22	0.44	0.43	0.44	0.41
*		The likely determination error is $\pm 2 \%$				
**		The likely determination error is $\pm 4 \%$				

4.5.5 Non-linear best fit

Kinetic information on Ag electrocrystallization in these two solvent systems cannot be explained well by the non linear graphs constructed using the Hill et al model and the analysis of the initial rising part of the current transients. Therefore in order to determine the different nucleation parameters such as N_o , A , the entire experimental evidence (J - t plots) is used and the methodology of non linear fitting of the theoretically calculated current transients is used.⁵⁶⁻⁵⁹ The total current (j) is calculated by considering the contribution of the double layer charging current (J_{DL}) and the nucleation process according to the equation²⁶

$$J = J_{DL} + J_{3D \text{ nucleation}} \quad (4.11)$$

The contribution due to the double layer charging can be quantitatively calculated using the approach proposed by Kolb and coworkers⁴⁸. The estimation is based on a Langmuir type adsorption-desorption equilibrium and is quantified using,

$$J_{DL} = k_1 \exp(-k_2 t) \quad (4.12)$$

For the contribution due to the nucleation process two models proposed to describe the nucleation mechanism under diffusion control system are used separately and a comparison of the results is made to check the validity of the method. In one procedure the model proposed by Scharifker and Mostany⁶⁰ is used and hence **equation 4.11** takes the form

$$J_{theoretical} = k_1 \exp(-k_2 t) + zFDc(\pi Dt)^{-1/2} [1 - \exp(-\pi k N_o Dt \Theta)] \quad (4.13)$$

where

$$k = \left(\frac{8\pi Mc}{\rho} \right)^{1/2} \text{ and } \Theta = 1 - \frac{[1 - \exp(-At)]}{At}$$

An alternative method is that proposed by Luc Heerman and Tarallo⁶¹ to calculate the nucleation response to the theoretical transient and **equation 4.11** becomes

$$J_{theoretical} = k_1 \exp(-k_2 t) + zFc \left(\frac{D}{\pi} \right)^{1/2} \left(\frac{\phi}{\Theta t^{1/2}} \right) [1 - \exp(-\pi k N_o Dt \Theta)] \quad (4.14)$$

where $\phi = 1 - \frac{\exp(-At)}{At^{1/2}} \int_0^{(At)^{1/2}} \exp \lambda^2 d\lambda$ and is called Dawson's integral. The value of Dawson's integral can be approximated by a rational function⁶²

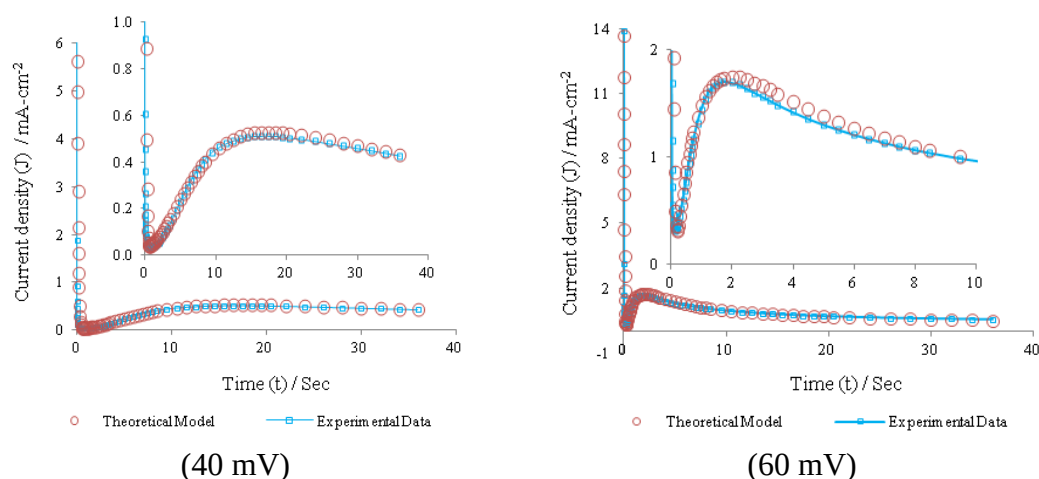
$$F(x) \equiv e^{-x^2} \int_0^x e^{\lambda^2} d\lambda \cong \frac{0.051314213 + 0.47910725x}{1 - 1.2068142x + 1.185724x^2} \quad (4.15)$$

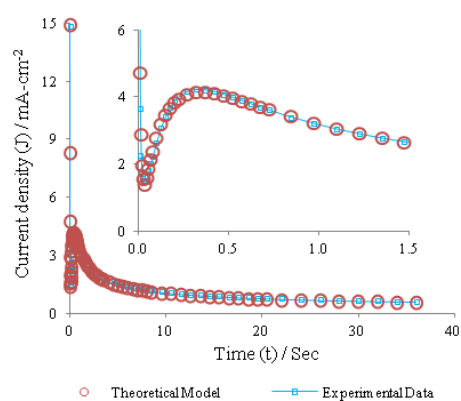
and the product $\frac{\phi}{\theta t^{1/2}}$ in **equation 4.14** becomes⁶³

$$\frac{\phi}{\theta t^{1/2}} = \frac{0.520893AAt^{1/2} - 1.206814A^{3/2}t + 1.185724A^2t^{3/2} - 0.051314A^{1/2}}{[At - 1 + \exp(-At)](1 - 1.206814A^{1/2}t^{1/2} + 1.185724At)} \quad (4.16)$$

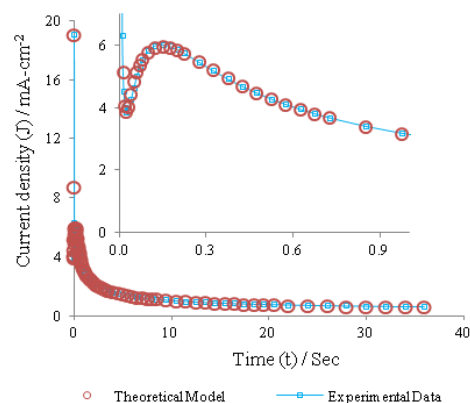
This reduces the equation to a relatively simple mathematical form.

Figures 4.20 and 4.21 shows the fitting of the experimental current transients obtained for deposition of silver from solution containing 50 mmol dm⁻³ AgNO₃ and 5 mmol dm⁻³ CTAB as additives in 1:2 ChCl:EG and 1:2 ChCl:urea respectively. The fitting of current transients at step potential (-40 mV to -160 mV) for 1:2 ChCl:EG and step potential (-80 mV to 220 mV) for 1:2 ChCl:urea containing Ag(I) and CTAB 50 and 5mmol dm⁻³ respectively is done by a 'non-linear best fitting' method using **equations 4.13 and 4.14** by varying the parameters k_1 and k_2 for charging the double layer and A , N_o and D for the nucleation contribution. The simulation of data is conducted by a macro written in Microsoft Excel using Visual Basic.

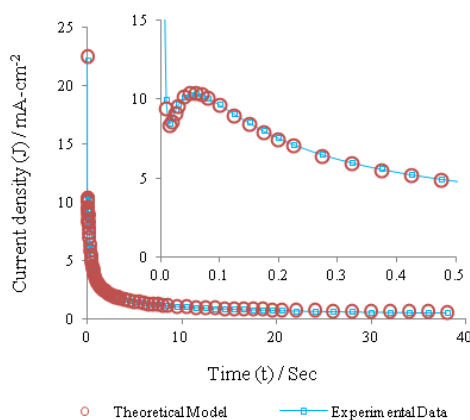




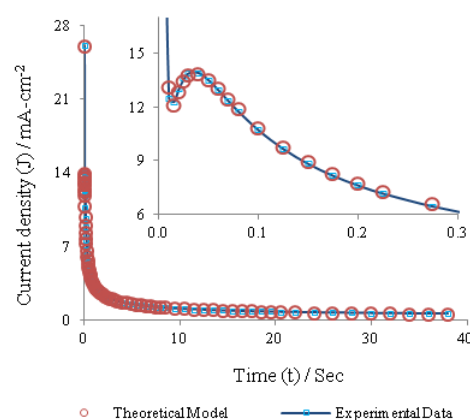
(80 mV)



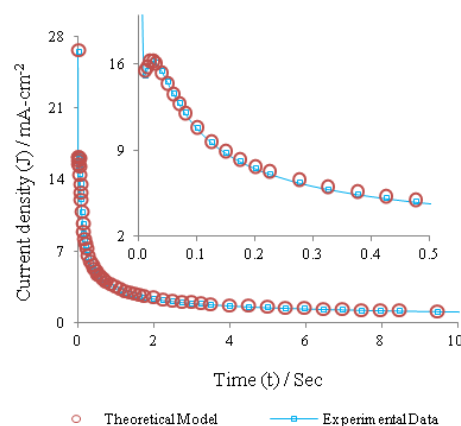
(100 mV)



(120 mV)

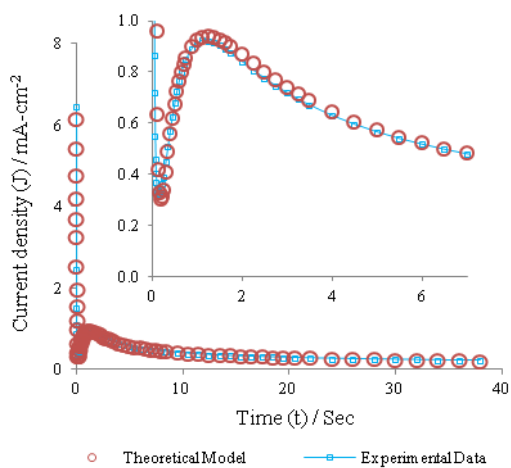


(140 mV)

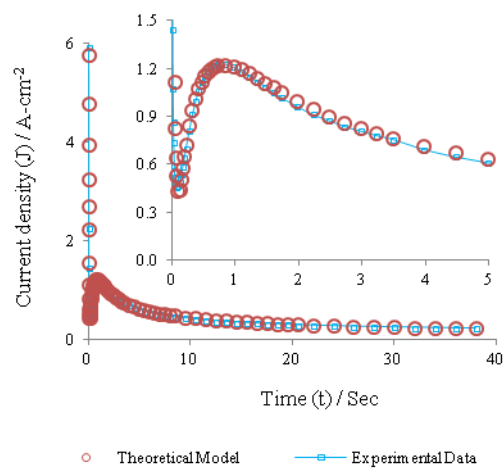


(160 mV)

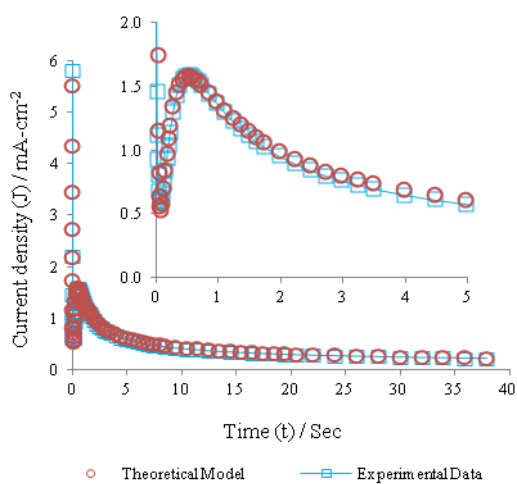
Figure 4.20: The non-linear best fitting using equation 4.14 of the current density transients recorded at different step in 1:2 ChCl:EG containing Ag(I) and CTAB 50 and 5 mmol dm⁻³ respectively



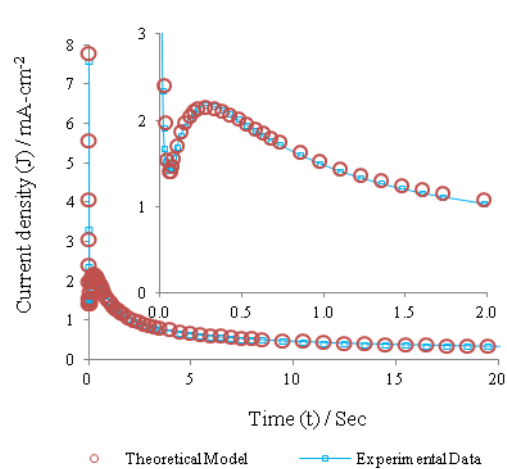
(80 mV)



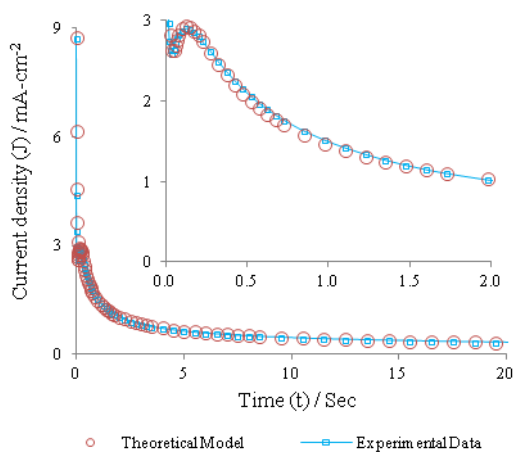
(100 mV)



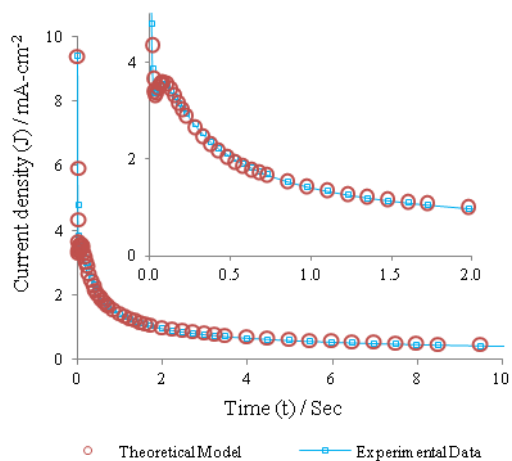
(120 mV)



(140 mV)



(160 mV)



(180 mV)

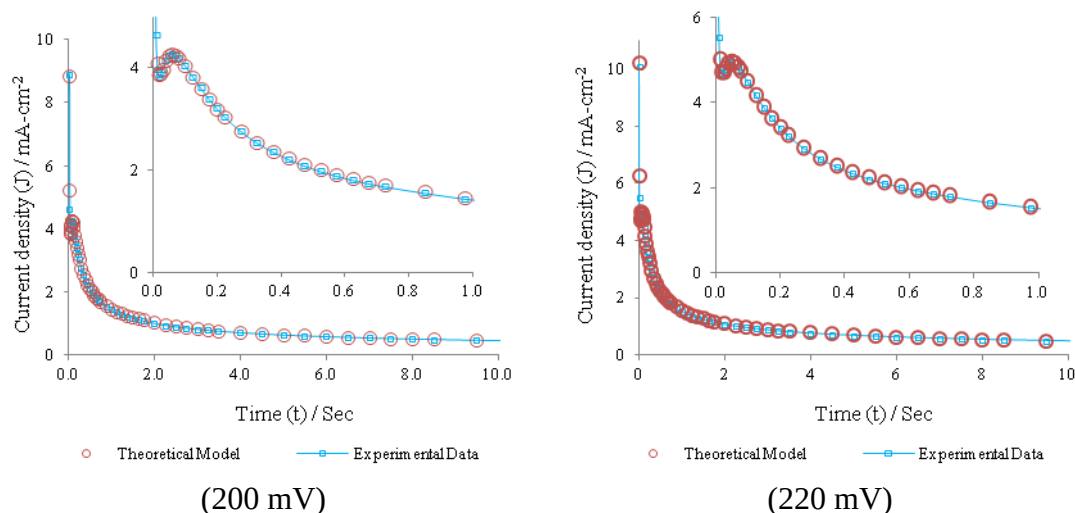


Figure 4.21: *The non-linear best fitting using equation 4.14 of the current density transients recorded at different step in 1:2 ChCl:urea containing Ag(I) and CTAB 50 and 5 mmol dm⁻³ respectively*

4.5.6 Variation of the number densities of active sites

The dependence of the number of active sites for the nucleation of silver on overpotential is shown in **Figures 4.22** and **4.23**. This shows that an exponential relationship exist between N_o and the overpotential. The nuclear number density remains unaffected by the addition of the additives in both the solvents. The values obtained from the two models are similar within the range of experimental error suggesting the kinetics of the nucleation of silver deposition can be explained by any of these models.

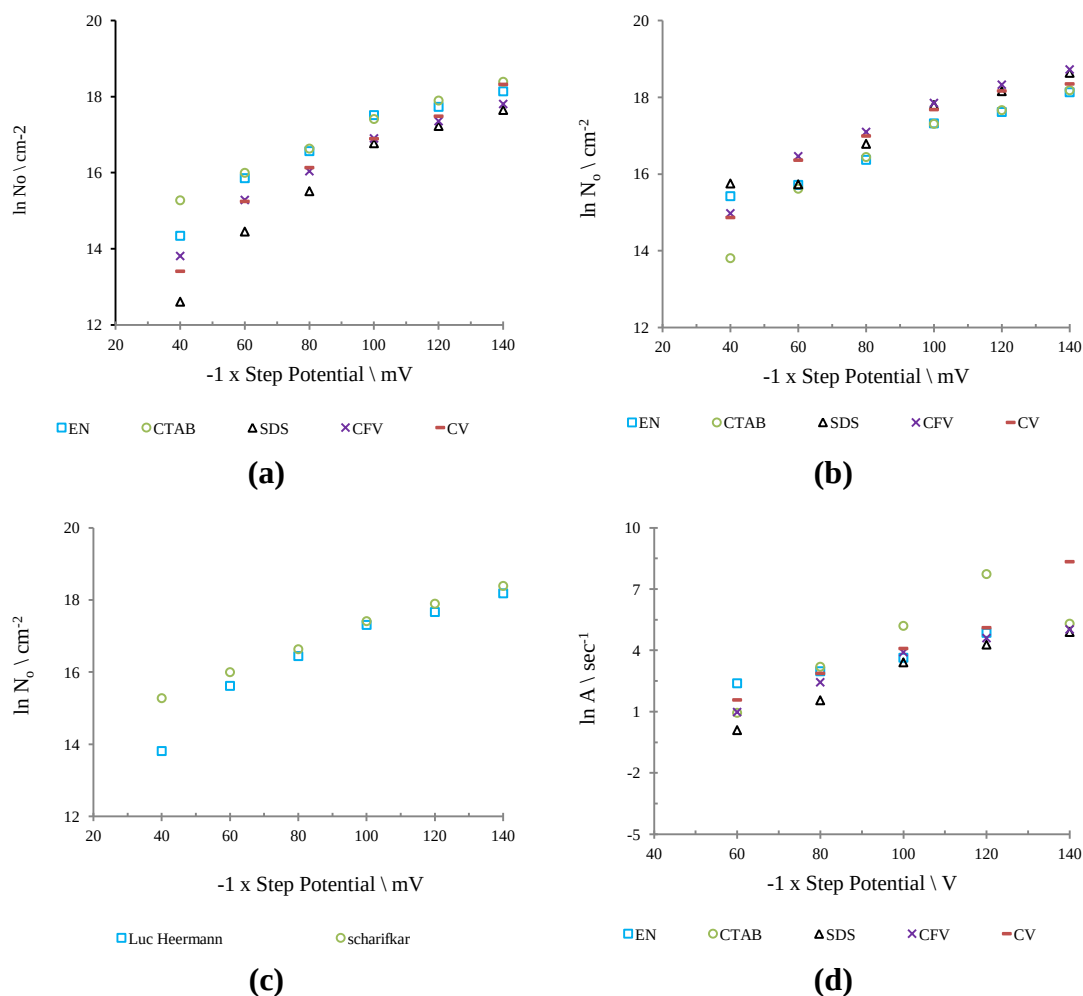
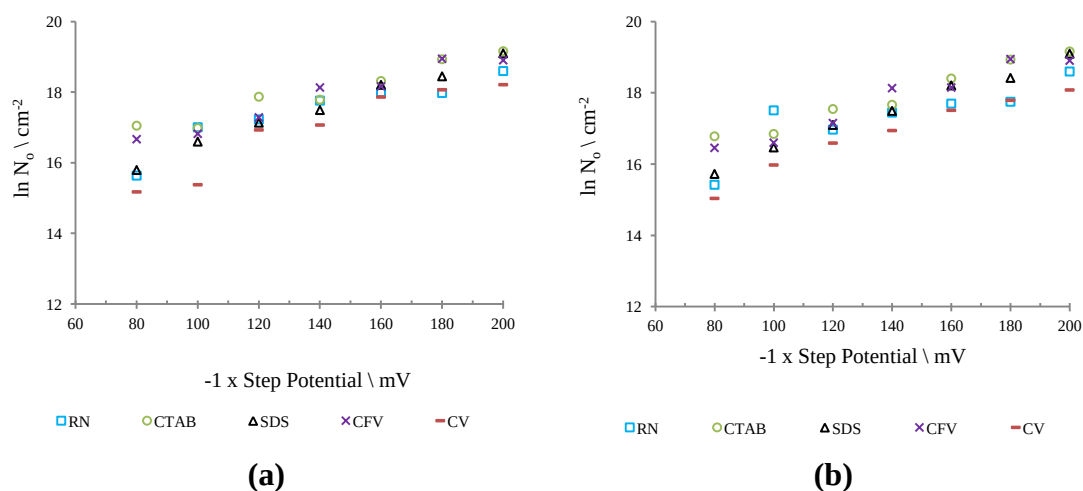


Figure 4.22: Overpotential dependence of the nuclear number density for AgNO_3 (50 mmol dm^{-3}) at various step potentials in 1:2 $\text{ChCl}:\text{EG}$ containing additives. The N_0 values obtained by non-linear best fitting of the experimental current transients (a) Scharifker and Mostany model (b) Heermann and Tarallo model (c) comparison of the N_0 values obtained from two models for solution containing CTAB 5 mmol dm^{-3} (d) rate of nucleation



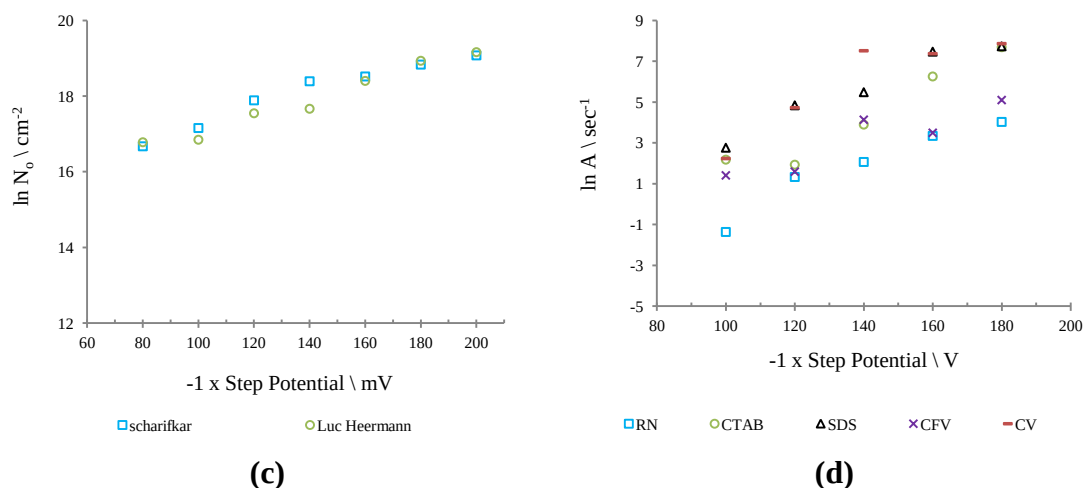


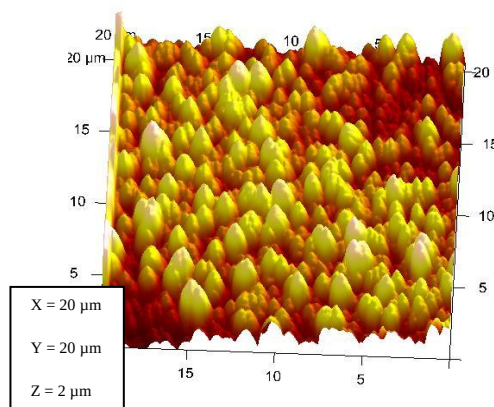
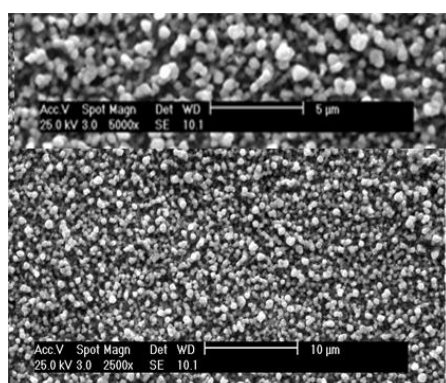
Figure 4.23: Overpotential dependence of the nuclear number density of AgNO_3 (50 mmol dm^{-3}) at various step potentials in 1:2 ChCl :urea containing additives. The N_0 values were obtained by non-linear best fitting of the experimental current transients (a) Scharifker and Mostany model (b) Heermann and Tarallo model (c) comparison of the N_0 values obtained from two models obtained for solution containing CTAB 5 mmol dm^{-3} (d) rate of nucleation

4.6 Characterization of deposit morphologies

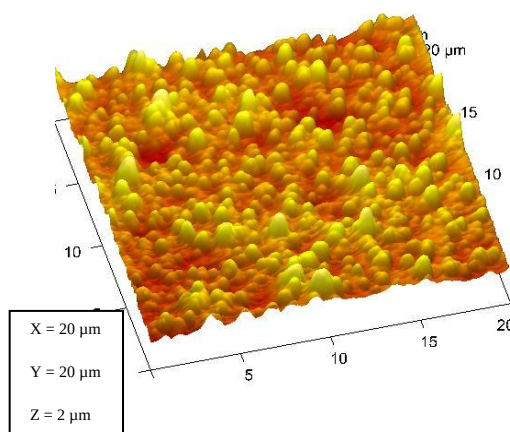
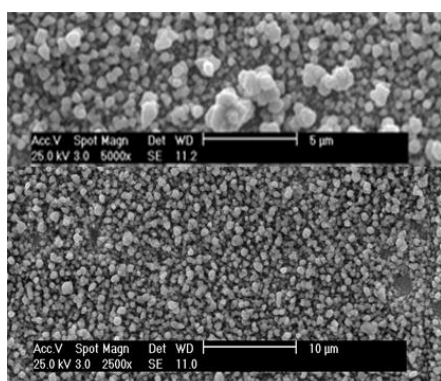
Silver was electrodeposited on the platinum substrate potentiostatically from 1:2 ChCl :EG in the presence of additives in concentration of 10 mmol dm^{-3} at -0.5 V for 30 minutes at 40°C and from 1:2 ChCl :urea at -0.6 V for one hour at 50°C . After deposition the substrate is thoroughly washed with deionized water followed by acetone and ethanol to completely remove the residual liquids. The potentiostatic reduction of Ag(I) yielded a silver white electrodeposit. The topography of the deposited silver layers was characterized by atomic force microscopy and scanning electron microscope coupled with EDX to explore the surface morphologies and composition.

Figure 4.24 show micrographs for a silver deposit from 1:2 ChCl :EG containing 100 mmol dm^{-3} AgNO_3 containing additives at a concentration of 10 mmol dm^{-3} . The micrographs reveal that the silver deposits in all cases consist of randomly sized silver grains and some large agglomerated crystallites formed from fine crystallites in the nanometer range. They vary from spherical to elliptical in shape. In some cases the deposit contained some nodular structures on the large silver grains, causing the facet

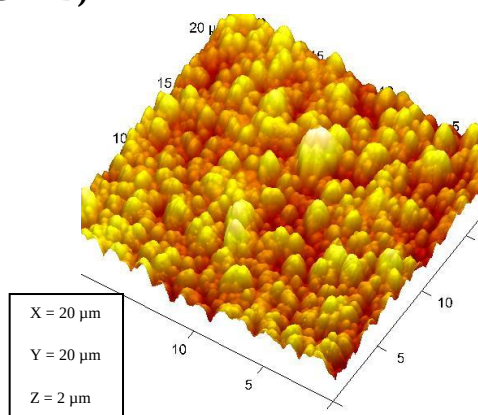
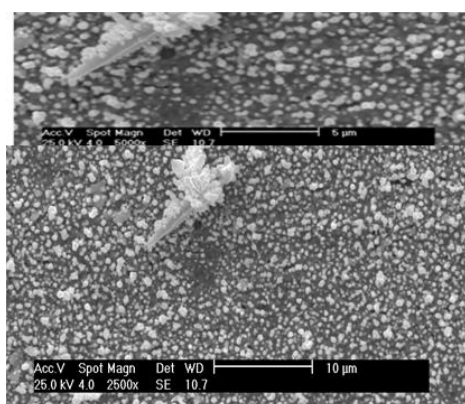
grains to lose their regular geometries. The silver surface appears porous with nanometre voids around the Ag grains. The additives affect the grain size and the deposits consist of small crystallites hence smooth and dense films are obtained as compared to the deposit from the solution without additives.



(EN)



(EN + CTAB)



(EN + SDS)

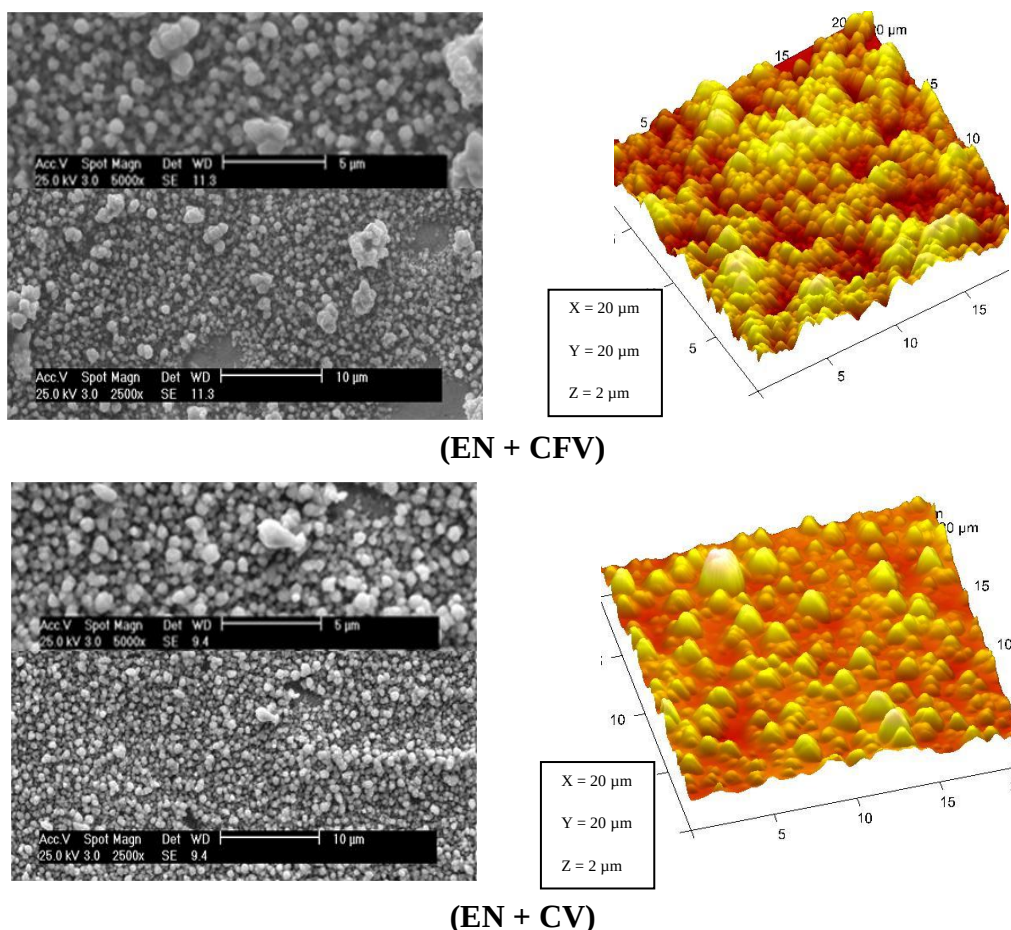


Figure 4.24: SEM and AFM images for silver deposit from 1:2 ChCl:EG containing 100 mol dm^{-3} Ag(I) and additive concentration 10 mmol dm^{-3} . The Z scale in AFM images is $1 \mu\text{m}$.

Figure 4.25 exhibits SEM images of silver deposited from AgNO_3 (100 mmol dm^{-3}) in 1:2 ChCl:urea. The additive concentration in all cases is 10 mmol dm^{-3} . The silver deposit is granular and the silver grain size is smaller than the similar deposit from 1:2 ChCl:EG and few multiply twined grains clusters are present. The additives do not have a marked effect on the morphology of the deposit.

The AFM images reveal a rough but fairly dense silver film corresponding to an island (Volmer-Weber growth) model⁶⁴. The EDX analysis shows a pure silver (90-94%) deposit.

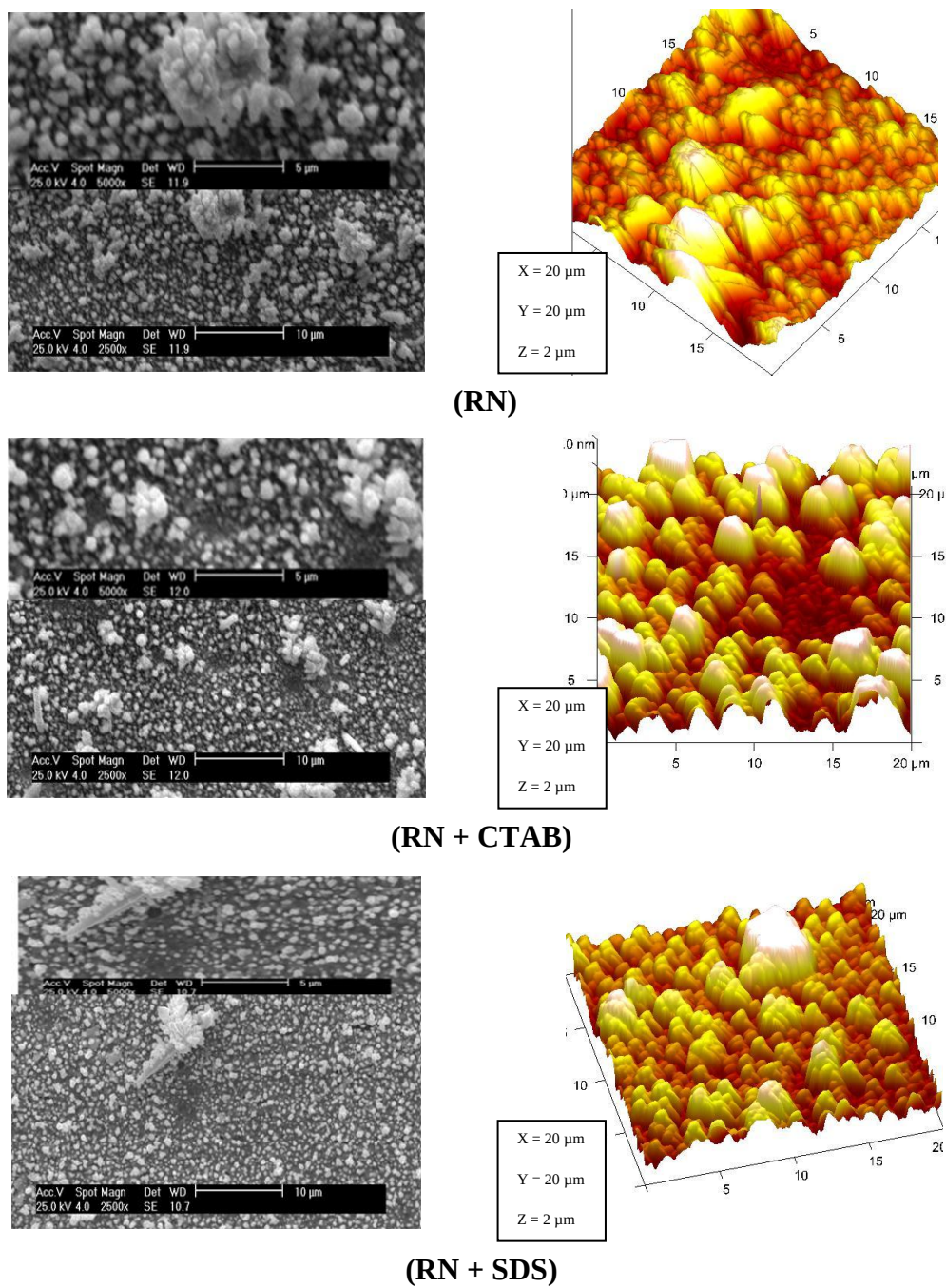


Figure 4.25: SEM and AFM images for silver deposited from 1:2 ChCl:urea containing 100 mol dm^{-3} Ag(I) and additive concentration 10 mmol dm^{-3} . The Z scale in AFM images is 1 μm .

4.7 Conclusion

The electrochemical reduction of Ag(I) to Ag(0) has been studied on a platinum electrode from solutions containing cationic and anionic surfactants (CTAB and SDS) as surface active agent and the basic dyes Cresyl fast violet and crystal violet as brighteners in the deep eutectic solvents 1:2 ChCl:EG and 1:2 ChCl:urea. The effect of these additives on the silver deposit is probed using electrochemical techniques and deposit morphologies are characterized using scanning probe microscopy as a function of the concentration of additives with a constant concentration of the Ag(I) in solution.

The additives show no effect on the physical properties of the solutions except the surface tension. The anionic surfactant changes the surface tension of the 1:2 ChCl:urea while the cationic surfactant showed a marked effect on the surface tension of 1:2 ChCl:EG. The cyclic voltammetric study revealed a slight anodic shift of the reduction peak with the addition of additive in 1:2 ChCl:urea. The peak heights remained almost unchanged in both the solvents.

A qualitative evaluation of the nucleation and growth mechanism and quantitative estimation of the kinetic parameters of silver electrocrystallization process was carried out using existing theoretical formalisms. To extract the nucleation parameters the whole current time transients are fitted by a non linear best fitting method using the Scharifker and Heermann models and varying nuclear number density (N_0), rate of nucleation (A) and diffusion coefficient (D). The extracted nucleation parameters are compared and it is found that both the models explain the nucleation kinetics of silver deposition equally well and can be used to describe the nucleation and growth behaviour. The analysis showed that additives had no effect on the nucleation and growth behaviour.

The surface topographical characterization of the silver deposits on the platinum reveals the top layers of silver are loosely packed with granular characteristics having a grain size in the nanometer region. The morphology of these deposits seems to be affected slightly by the counter ion of the salts and the type of DES. Deposits with small crystallite size and smooth deposits are obtained in the presence of additives.

4.8 References

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Chapter 5 : Microscopic Investigation of Silver Nucleation Kinetics in DES

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5.1 Introduction

The physicochemical properties such as magnetic, catalytic, optical properties *etc.* of metallic nanostructures deposited on a metal surface critically depend upon their size, morphology and crystal structure. The morphology and crystal structure strongly depend on the early stages of the metal deposition. Extensive fundamental studies on the initial stages of electrocrystallisation such as the formation of clusters and islands have been carried out concerning various aspects such as experimental¹⁻⁵, theoretical treatment^{4, 6-11} and practical applications¹²⁻¹⁴. The theoretical models proposed for explanation of the current transients rely at some point on simplifying assumptions or approximations. Research in this field stimulated different approaches to gain new insights into nucleation and associated processes. To test the validity of the theoretical models and statistical study of nucleation kinetics^{3, 7, 11, 15, 16} microelectrode studies, computer simulation and direct visual monitoring of the growth of nuclei using microscopic methods have been applied. Microscopic studies allow a direct comparison between the parameters extracted from analysis of current transients and the actual processes observed on the electrode surface. Studies of the number, size and spatial distribution of the developing nuclei have been made.

Prior to microscopic studies structural information about the electrified solid-liquid interface was inferred from the results of spectroscopic or electrochemical measurements. Markov and Stoycheva¹⁷ made the first *ex-situ* attempt to observe a growing droplet of mercury on platinum using a double potential step technique under an optical microscope. Milchev¹⁸ used the same procedure with an improved version of the double potential step technique. Serruya *et al.*¹⁹ deposited lead on glassy carbon for a long period and then observed under an optical microscope the distribution of nuclei on the surface.

The principles used with optical microscopy studies were applied to scanning probe microscopy (SPM) which also allows easy *in-situ* measurements. SPM techniques gave new impulse to the field^{20, 21} enabling the direct observation of atomic processes involved in the formation of a stable island but with much higher resolution and hence it became a useful and popular analysis tool for the early stages of nucleation. Initially *ex-situ* AFM and SEM studies were used for the investigation of the spatial and size distribution and the morphology of the deposit and gave a reliable atomistic

description of nucleation and growth for precise control of metal on metal homoepitaxy and heteroepitaxy^{22, 23}.

Although ‘*ex-situ*’ and ‘*non-situ*’ methods have yielded a considerable insight into the electrode structure and dynamics there is still the necessity to obtain information from the electrode surface, in solutions and under potential control. SPM techniques provide a hitherto unobtainable level of structural insight into surfaces in solution. A new approach of *in-situ* study is gaining importance and provides significant advantages over *ex-situ* microscopy because it allows

- ❑ Changes in the properties of a single area as a function of time to the studied.
- ❑ Avoids the possibility of morphological changes on removal of the electrode from solution.

Sonnenfeld and Hasma²⁴ were the first to use STM to image highly oriented pyrolytic graphite (HOPG) in solution under potential control. The first effort to use SPM for an *in situ* study was made by Gewirth and Niece²⁵ but they focused on the atomic scale appearance of electrochemically deposited adatoms rather than the determination of nucleation parameters. Mao *et al.*²⁶ for the very first time used AFM to image a single growing silver nucleus on a carbon micro-electrode and studied the nucleation dimensions. In 2002, Hyde *et al.*²⁷ used *in-situ* AFM to observe directly the appearance and growth of individual nuclei. Earlier in this group, Barron used *in-situ* AFM coupled with electrochemical quartz crystal microbalance (EQCM) to explore the early stages of Zn deposition from deep eutectic solvents (1:2 ChCl:ethylene glycol)²⁸.

The main motive for microscopic investigation is to reveal the morphological characteristics of silver deposits and mechanisms of deposition from deep eutectic solvents. For this purpose *ex-situ* AFM and *in-situ* DHM studies of the initial stages of silver deposition from 1:2 ChCl:ethylene glycol and 1:2 ChCl:urea are conducted and an effort is made to understand the complex interplay between the substrate, nucleation and surface chemistry.

5.2 *Ex-situ* AFM study

The electrochemical deposition of metals onto foreign substrates in the over-potential regime usually occurs through Volmer-Weber growth, resulting in the formation of three dimensional (3D) islands²⁹. The kinetics of island growth are strongly influenced by the nucleation over-potential which is defined as the potential corresponding to the onset of nucleation of metal M on substrate S, referenced to the equilibrium potential for the M^+/M couple³⁰. In the absence of under-potential deposition, the nucleation over-potential is usually several hundred millivolts so that after nucleation island growth is in the mixed diffusion/kinetic control regime^{31, 32}.

The island growth kinetics for silver on a platinum electrode in the deep eutectic solvent 1:2 ChCl:ethylene glycol containing Ag(I) 0.1 mol dm^{-3} is studied. The island growth kinetics are determined by analyzing the projected area and height of all the islands at different deposition times using scaling analysis³³. Analysis of the island dimension and the distribution of nearest neighbour distances is studied using *ex-situ* AFM micrographs.

The silver is deposited potentiostatically at 35 mV using a three electrode cell on platinum disc electrode (0.0707 cm^2), with a silver wire quasi reference electrode and a platinum flag counter electrode for times ranging from 10 to 6000 s. After each deposition the electrode is removed from the solution and thoroughly washed with deionised water followed by ethanol to ensure the complete removal of the residual solvents. AFM images ($20 \text{ }\mu\text{m} \times 20 \text{ }\mu\text{m}$) at five randomly selected locations were obtained. The island volume and the projected area of all the islands were calculated using the Digimizer image analysis software.

First, the platinum electrode surface was characterized. **Figure 5.1** shows the surface morphology of the bare platinum electrode, these micrographs show the typical polishing lines (scratches) on the whole surface of the substrate due to the mechanical polishing of the platinum electrode with alumina. These scratches are about 20-30 nm deep and about 70-100 nm wide. Occasional pits ($1.2 \text{ }\mu\text{m}$ in diameter) are also observed and arise due to air entrapped during the manufacturing of the electrode. The images also reveal that the electrode surface consists of nodule-like features with an average diameter of 30-50 nm and the surface is also enriched with a number of

surface features. However the surface is smooth enough to be used for the investigation of the early stages of silver deposition.

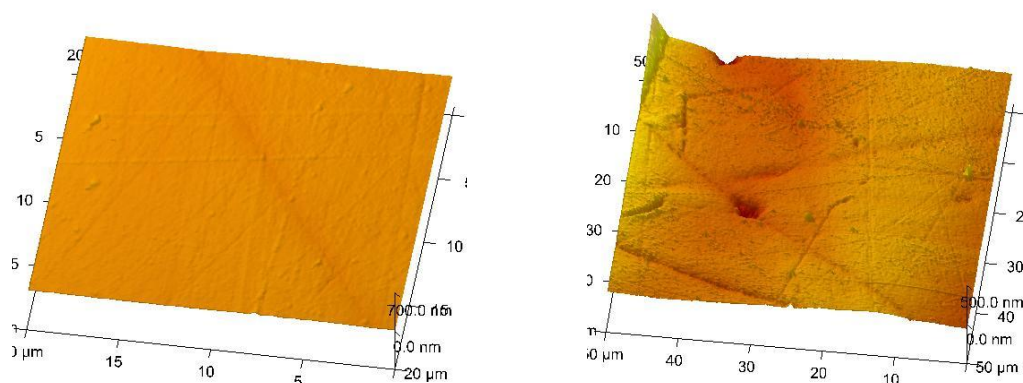


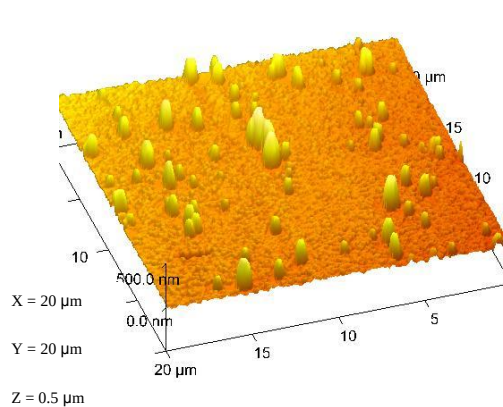
Figure 5.1: *AFM images of the polished bare platinum electrode surface with typical morphological characteristics*

5.2.1 Topographic characterization of deposited silver

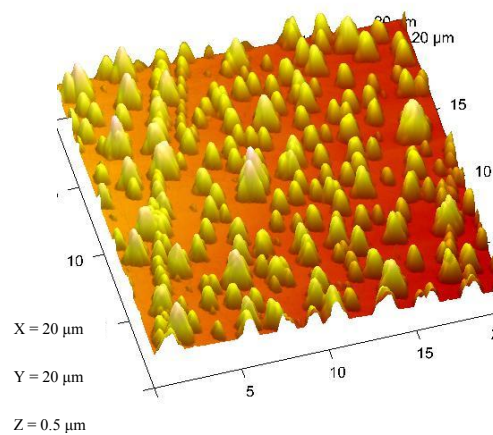
The topographic AFM images of silver deposited on the platinum electrode surface obtained at different time intervals ranging from 10 to 6000 s are shown in **Figure 5.2** while **Figure 5.3** shows the SEM images obtained after 20 and 50 s of silver deposition. These micrographs reveal the time evolution of island growth. The silver deposits through the formation of 3D hemispherical islands with more or less random spatial distribution over the substrate surface but some of the nuclei have aligned along the polishing line. The silver islands grow individually, both vertically and laterally with an aspect ratio of 0.5 that may indicate the absence of any adsorption of the anions (Cl^-) of the surface of the growing island. After 100 s the individual nuclei start to interact resulting in the formation of large silver clusters and this phenomenon continues until these clusters coalesce. A distribution of island sizes is observed up to 4500 s indicating the appearance of new nuclei and hence a progressive nucleation and growth mechanism. The coalescence of the islands at 4500 s gives the silver film an average thickness of around 3 μm .

The AFM images shown in **Figure 5.2** at longer times reveal a multiple step structure on the growing cluster indicating that the vertical growth of the silver cluster is associated with 2D nucleation and subsequent step flow on the cluster surface towards the terrace boundary. This type of behaviour is also observed at a solid / liquid

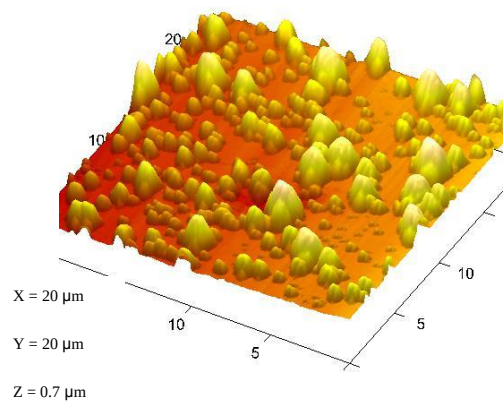
interface for homoepitaxial and heteroepitaxial systems including Cu on Cu{111},^{34, 35}
 Ag on Ag{111}³⁵ and Cu or Ni on Ag{111}^{36, 37}.



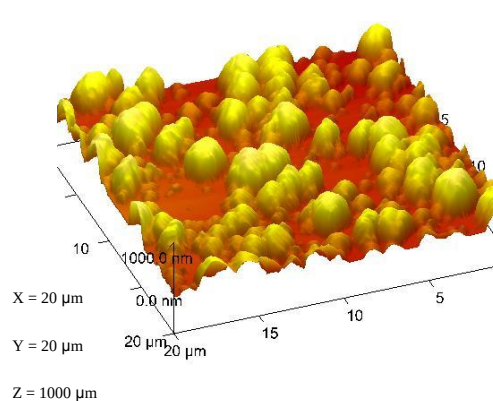
(10 s)



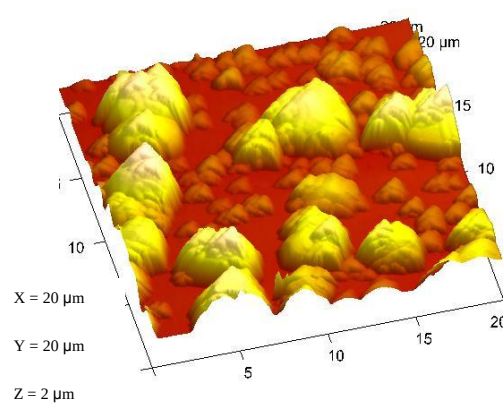
(20 s)



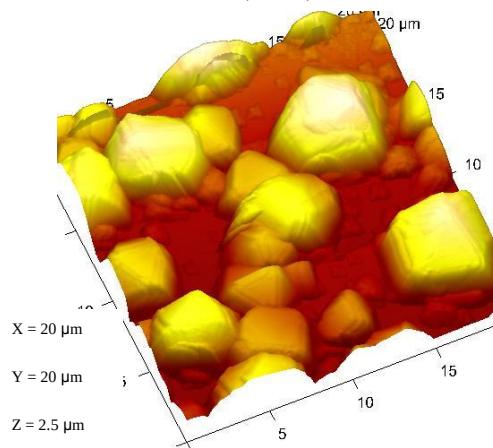
(50 s)



(100 s)



(500 s)



(1000 s)

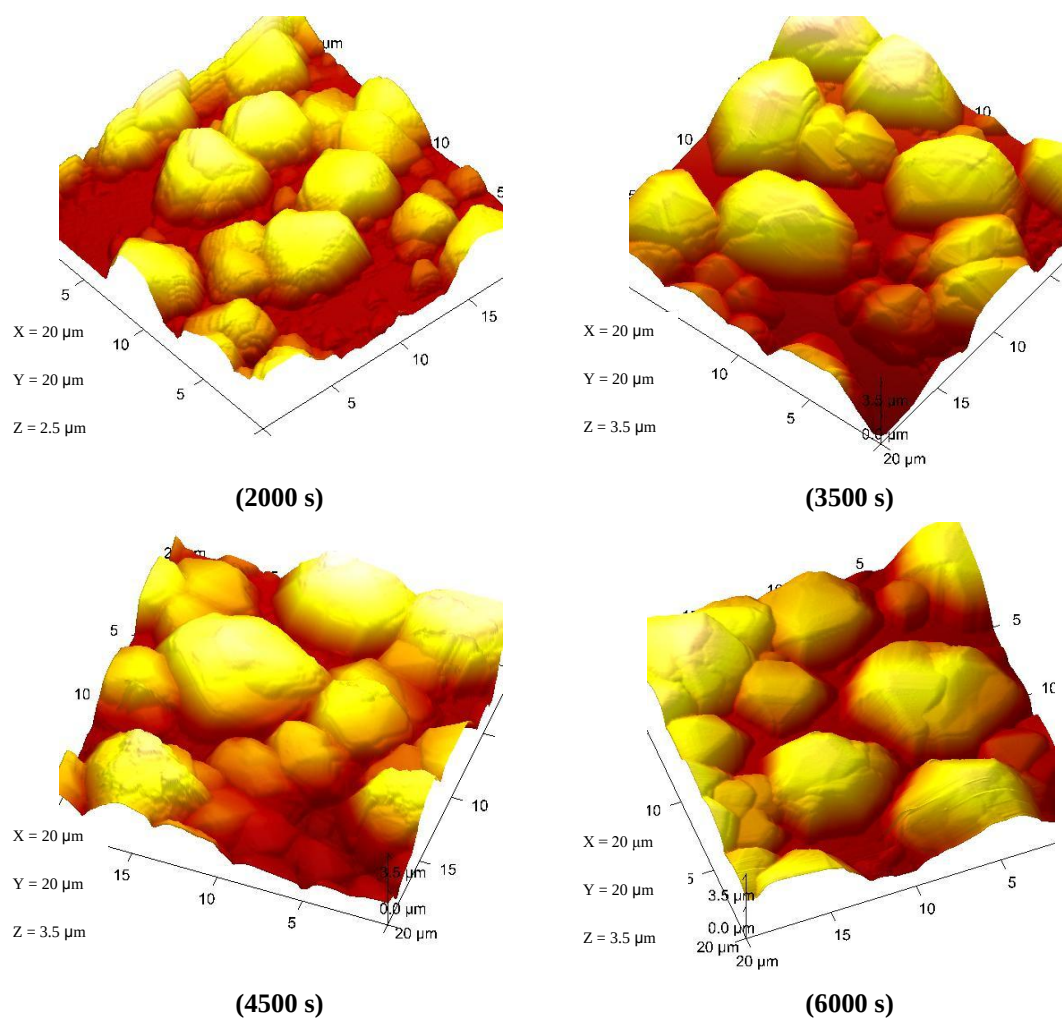


Figure 5.2: *AFM topography images of electrodeposited silver at 0.35V obtained at different time intervals as mentioned*

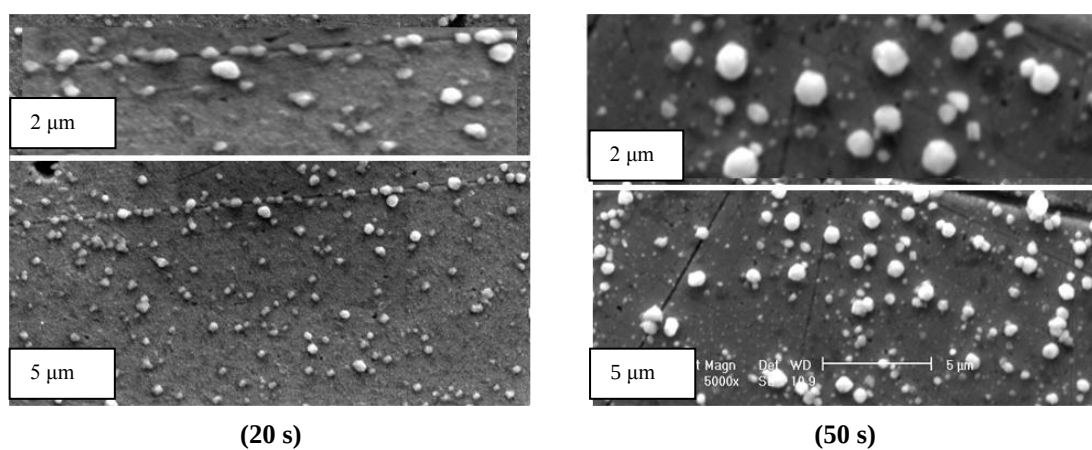


Figure 5.3: *SEM images of silver deposited on the electrode surface showing the spatial distribution of islands*

5.2.2 Charge density

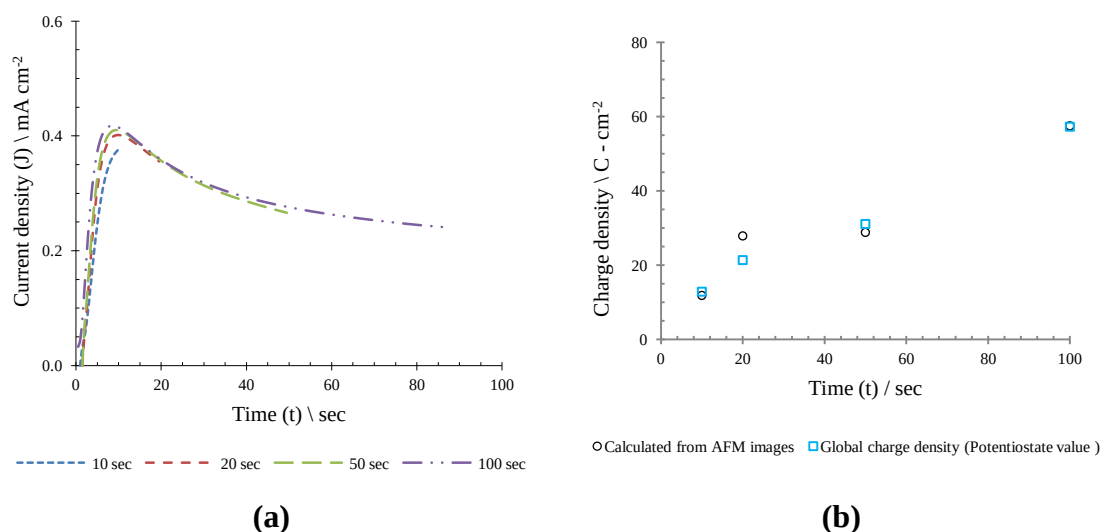


Figure 5.4: (a) Current transients for silver deposited on a platinum surface at 35 mV from a solution containing Ag(I) 100 mmol dm⁻³ (b) Comparison of the global charge density and the charge density calculated from the AFM images

The current transients for the deposition of silver (**Figure 5.4 (a)**) show the characteristics of diffusion limited growth having a t_{max} of about 10 s. The decay of current after t_{max} is slow which may be due to the small nucleation over-potential applied for the deposition resulting in a not purely diffusion limited growth but mixed kinetics. In order to show that the AFM images are a true representation of the whole surface, a comparison is made between the charge density obtained from the integration of the current transients and the charge density obtained from all the islands in AFM images. The mass of silver deposited is calculated from the sum of the volume of each of island and charge density is calculated using Faraday's law;

$$Q = \frac{nmF}{M} \quad (5.1)$$

where Q is the charge, n is the number of electrons involved in the process, m is the mass of silver in grams deposited, F is the Faraday's constant and M is the molar mass of the substance.

The calculated charge density is averaged over five AFM images (20 μm x 20 μm) randomly selected over the surface. The excellent agreement between the global charge density and the charge density calculated from the AFM images shows that the island distribution is uniform across the surface and the AFM images are representative of the whole substrate surface.

5.2.3 Nuclear number density

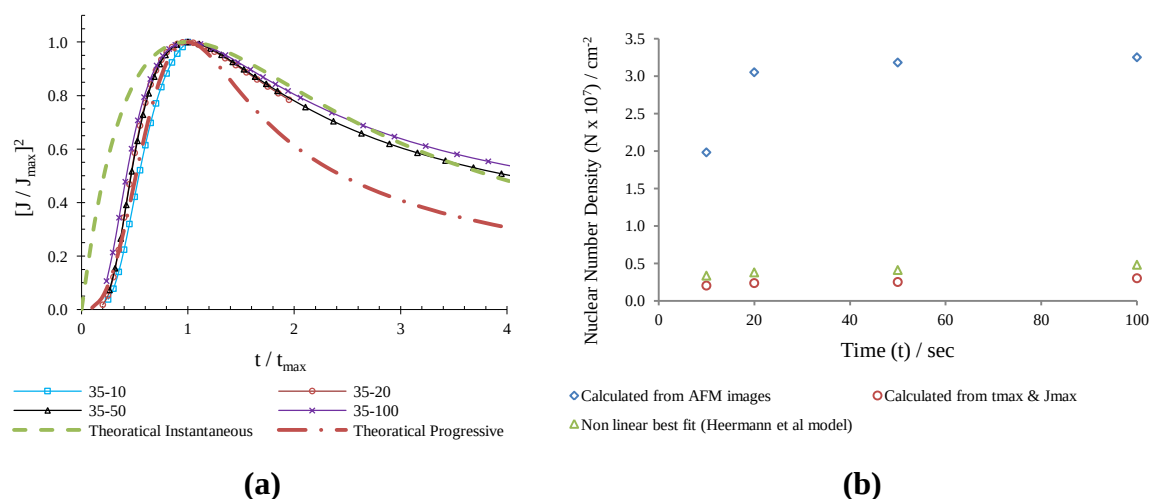


Figure 5.5:

(a) Dimensionless graphs of the current transients (b) Comparison of the nuclear number density calculated from the AFM images and calculated using Hill et al model and non linear best fit using Heermann et al model of the whole current transients

Figure 5.5(a) shows dimensionless graphs of the current transients for the deposition of silver for deposition times of 10, 20, 50 and 100 s. It shows a good agreement with the progressive nucleation and growth mechanism. This is consistent with analysis of the AFM images presented in **Figure 5.2** which shows the island size distribution. The time dependence of the island density for the deposition of silver before interactions of the individual nuclei is shown in **Figure 5.5 (b)**. The nuclear number density increases sharply up to 20 s and then slowly up to 100 s and reaches approximately $3.25 \times 10^7 \text{ cm}^{-2}$. The graph also shows the nuclear number densities calculated from the maximum coordinates ($t_{\max}$ and $J_{\max}$) using the growth law for progressive nucleation followed by diffusion limited growth (equation 3.16 and 3.18) and values ranges from 2.01 to $3.03 \times 10^6 \text{ cm}^{-2}$. The N values obtained from the non linear best fitting of the whole current transients using the Heermann et al model (equation 4.14) are also compared. The values are in the range of 3.2 to $4.8 \times 10^6 \text{ cm}^{-2}$. The nuclear

number densities calculated from the AFM images are about one order of the magnitude are larger than the values calculated from the analysis of the current transients. The similar discrepancies have also been observed for other system copper on TiN from pyrophosphate solution³⁸, lead on glassy carbon³⁹, gold on GaAs⁴⁰, and gold on Si⁴¹. The magnitude of the discrepancy is much less about 4 orders of magnitude in 1:2 ChCl:EG as compared to the aqueous systems. The reason for the discrepancy is not known and Searson et al³⁸ related this to the likely formation of the multiple nuclei within a single diffusion zone.

5.2.4 Spatial distribution

Figure 5.6 shows histograms of island nearest neighbour distances (nrd) at different times up to 100 s, which reveal the spatial pattern of dispersed islands on the electrode surface. At short times between 10 and 20 s the spatial distribution is narrow and random. At longer times the distribution of the islands becomes broad. This may be attributed to the formation of adatom depletion zones around the growing islands which suppress nucleation in these regions due to start of the coalescence and the competition for the adatoms between the adjacent growing islands. This phenomenon is consistent with surface diffusion mediated lateral island growth.

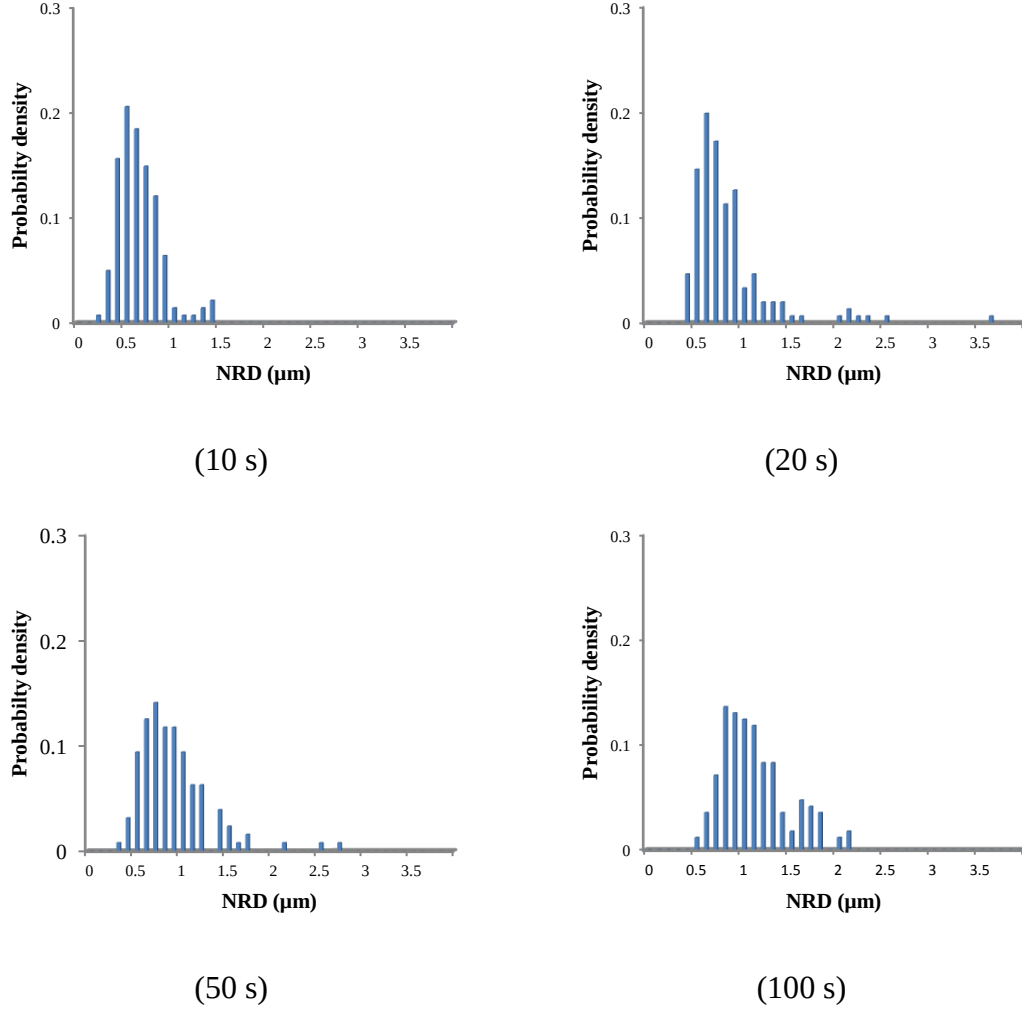


Figure 5.6: *Nearest-neighbour distance distributions at different times of deposition obtained after spatial analysis of 120 islands from the five randomly selected AFM images*

5.2.5 Island growth kinetics

The island growth kinetics are determined using scaling analysis³³ based on the evolution of island size and shape which is determined from volume and projected area of each island in five AFM micrographs. **Figure 5.7** shows plots of the volume versus the projected area of the islands. The solid line shows the isotropic growth of ideal hemispherical islands by the relationship in equation 5.2

$$V = \frac{2}{3\sqrt{\pi}} A^{3/2} \quad (5.2)$$

where V is the volume of the island, A is the projected area of the island and $3/2$ is the scaling exponent (m).

The graphs exhibit a broad distribution in both volume and area due to their different birth time (progressive nucleation). Due to the random spatial distribution of the growing nuclei it is assumed that each nucleus grows independently and hence

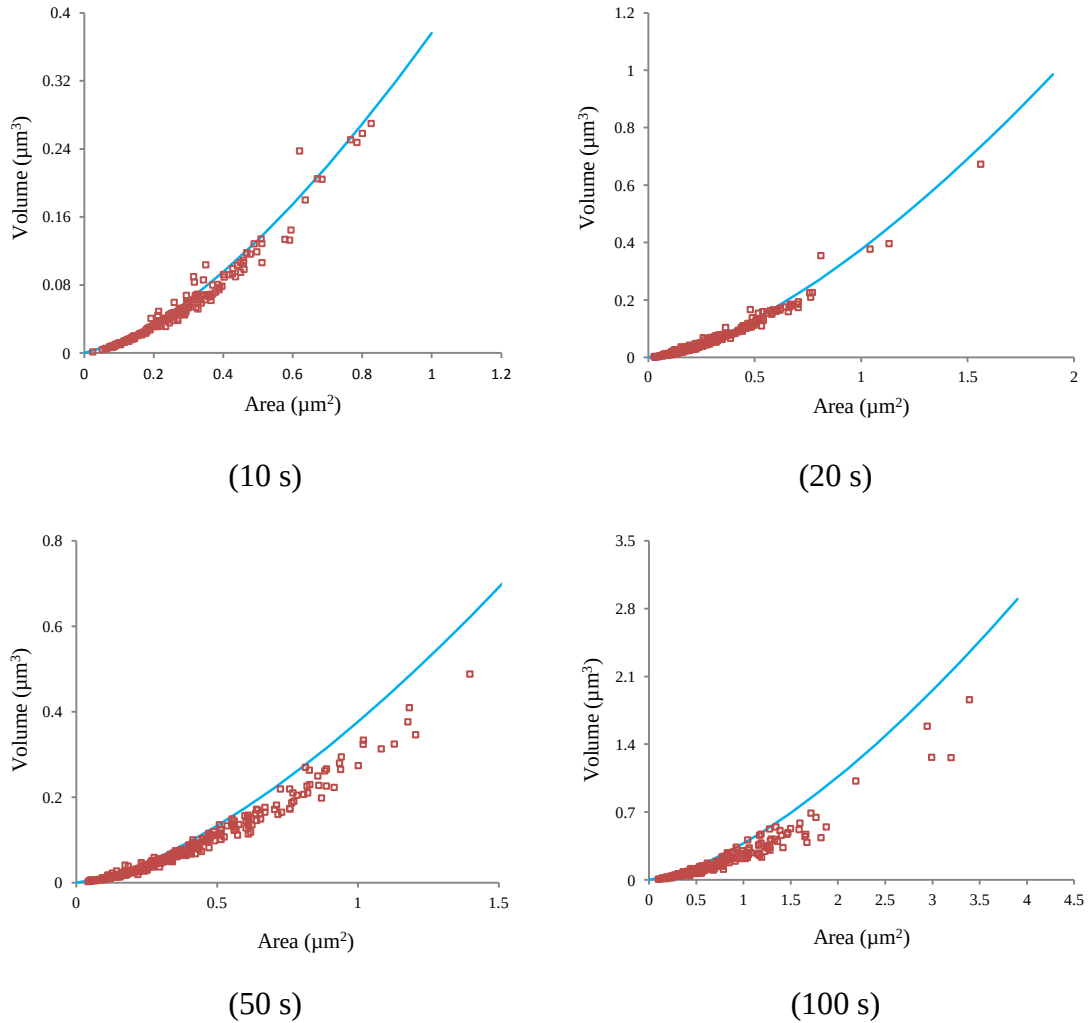


Figure 5.7: *Plot of Volume vs. projected area of silver hemispherical islands (120 islands at each time interval). The solid line shows isotropic growth.*

all the nuclei obey the same growth power law from which geometric information can be extracted. The scaling exponent (m) is determined by the slope of the double logarithmic plot and it comes to be 1.48 which indicates that the island growth is

isotropic. At 50 and 100 s there is slight deviation from the power law is observed that may be due to the onset of coalescence.

From the scaling relation $V \propto A^m$, the growth in each dimension can be described by a power law³³

$$L \propto t^a \quad (5.3)$$

$$h \propto t^b \quad (5.4)$$

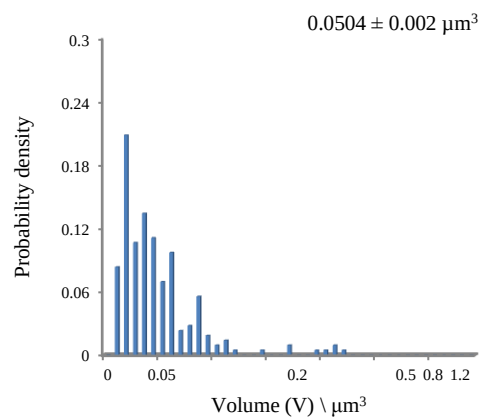
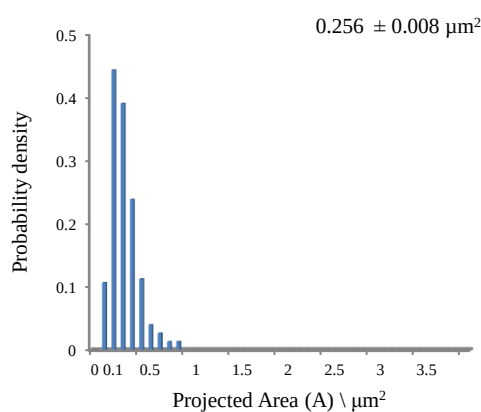
where L and h are the lateral and vertical dimensions respectively and ‘ a ’ and ‘ b ’ are the corresponding growth exponents which shows the time dependence of the island dimensions and not the magnitude of their dimensions. In our case $a = b$, *i.e.* the lateral and vertical growth exponents are equal.

The island width and height are calculated from the volume (V) and the projected area (A) of the individual islands from the recorded AFM images by the following equations

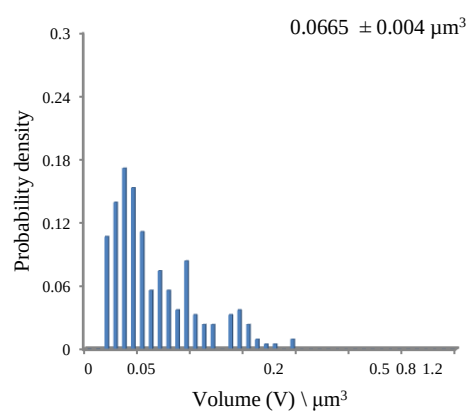
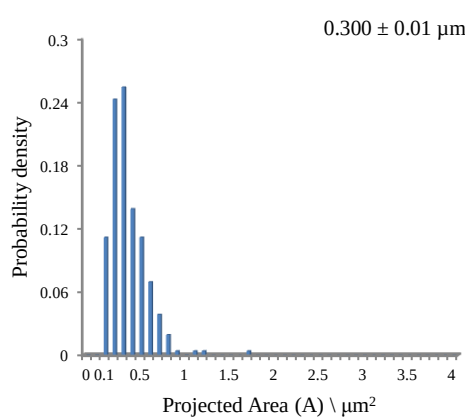
$$L = A^{1/2} \quad (5.5)$$

$$h = \frac{V}{A} \quad (5.6)$$

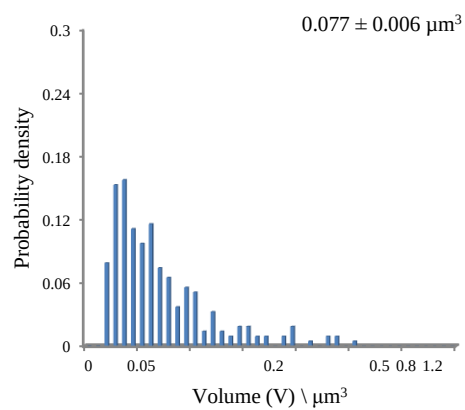
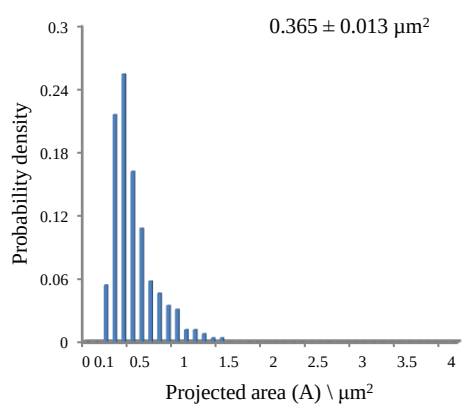
Figure 5.8 shows the projected area and volume of the individual islands at different time intervals. The AFM micrographs reveal that islands are narrowly distributed and the island size increases at a faster rate at short times but at longer times the increase in the size is a bit slower. At 100 s the distribution of island sizes becomes broader due to the onset of coalescence and the formation of depletion zones around adjacent islands. The increase in size dispersion of islands is indicative of progressive nucleation and growth.



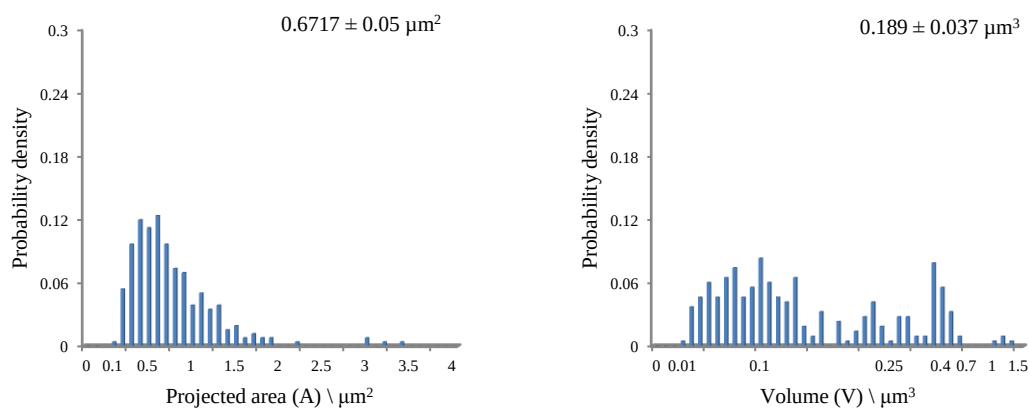
(10 s)



(20 s)



(50 s)



(100 s)

Figure 5.8: Projected area and volume histograms of islands at different times of silver deposition. The average values are also listed in each case. The number of islands analysed at each interval is 120.

5.3 In-situ DHM study

Hyde *et al.*²⁷ employed AFM to directly examine the properties of individual growing nuclei on an electrode surface and hence removed the need for *a priori* assumptions about the growth rate of diffusion zones, nucleation rate laws etc. and the dependence of interpretation of potentiostatic transients. However examine the properties this technique has some serious issues

- ❑ AFM is a slow technique and requires a long time to obtain the image. Electrochemical processes are faster than the acquisition rate of images which may results in loss of some information. To overcome this problem, Hyde *et al.* switched off the potentiostat after applying the short potential pulse. This repeated switching the cell on and off raises concern about the time taken for steady state diffusion to be achieved after the potential is applied.
- ❑ The probe tip may ‘shield’ the surface from unrestricted mass transport hence may result in disturbing the nucleation and growth rate.
- ❑ SPM techniques involve the movement of the probing tip over the surface which sometimes physically removes the deposited material and smears of the image due to dragging material across the surface.

- ❑ The precision of the control of moving parts, such as piezo-electric transducers is another limitation. Highly viscous solutions do not allow images to be obtained with acceptable levels of piezo-electric drift²⁸.

A new measurement system with nanometer scale resolution namely Digital Holographic Microscopy, DHM is used to investigate the initial stages of silver deposition from two deep eutectic solvents (1:2 ChCl:ethylene glycol and 1:2 ChCl:urea).

5.3.1 Digital Holographic Microscopy

Digital Holographic Microscopy is a fast, non-destructive and non-contact surface metrology technique. Digital Holographic Microscope systems are based on robust new technology allowing high frequency measurements at interferometric resolution. DHM gives Quantitative 3D information, Nanometric vertical resolution, Non invasive and non contact measurement, Rapid acquisition, Ease of use, Robustness and stability about the surface simultaneously

DHM uses the principle of classical holography.⁴²⁻⁴⁴ Holograms are generated by combining a coherent reference wave with the wave received from a specimen. The holograms are recorded by a video camera and transmitted to a computer for real time numerical reconstruction. DHM software allows computation by numerical algorithms⁴⁵ of the complete wave front emanating from an object. This provides intensity images with the same contrast as classical optical microscopy. The phase images provide quantitative data that are used for accurate and stable measurements. In reflection, the phase image reveals directly the surface topography with a sub nanometer vertical resolution. In transmission, the phase image reveals the phase shift induced by a transparent specimen, which depends on its thickness and refractive index.

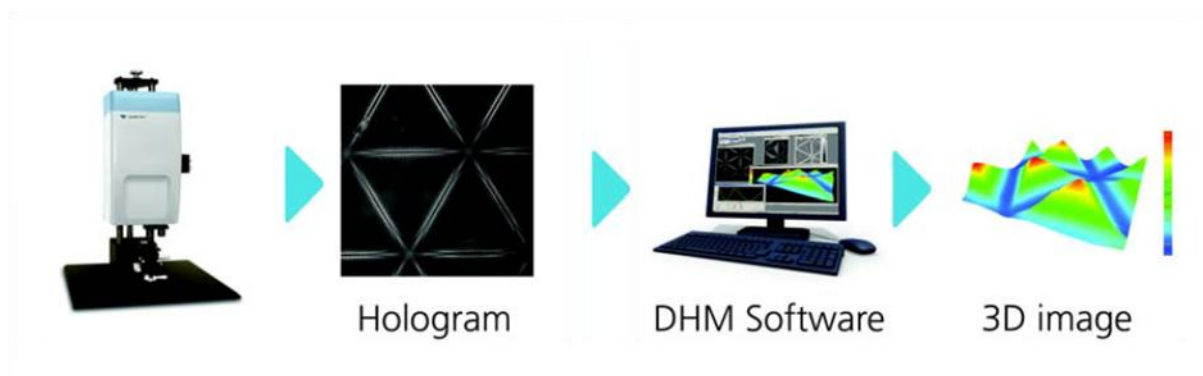


Figure 5.9: *Working of DHM: capturing of hologram and subsequent reconstruction of intensity and phase information using Koala software*

The strength of DHM lies in off-axis configuration by which the whole information about the surface can be retrieved by a single image acquisition ‘hologram’ within a few micro seconds. The extremely short acquisition time makes the system insensitive to vibrations and ambient light hence very stable. DHM can be used for shape and surface characterization of high aspect ratio micro optics, surface nanostructures and surface roughness.

Light interaction with a sample modifies two fundamental characteristics, intensity and phase, of the illuminating wave. The detector, usually a camera, is only sensitive to the intensity of the light therefore a part of the information carried by the light is lost. Gabor invented in 1948 a way to encode the phase modifications as an intensity variation: the “hologram”⁴³ which allows quantitative 3D information to be obtained. DHM captures holograms instead of intensity images. With the present performance of computers and the development of digital cameras, holograms can be numerically interpreted within a tenth of second to provide simultaneously:

- ❑ phase information, which reveals the object surface with vertical a resolution below 1° of the wave phase (the nanometer scale for homogeneous samples)
- ❑ intensity images, as obtained by a conventional optical microscope.

Both images are obtained with a diffraction limited resolution in the transverse (0 xy) plane and are “reconstructed” from the hologram in real time (more than 15 reconstructions per second for 512x512 holograms).

5.3.1.1 Principle

A collimated source beam (from a laser diode) is separated into two coherent beams with slightly different propagation directions (i) a 'reference beam' and (ii) an 'object beam'. The object beam illuminates the sample and the retro-diffused beam is collected by the objective of the microscope and then recombined with the reference beam to form a hologram in the camera. This is shown in **figure 5.9**.

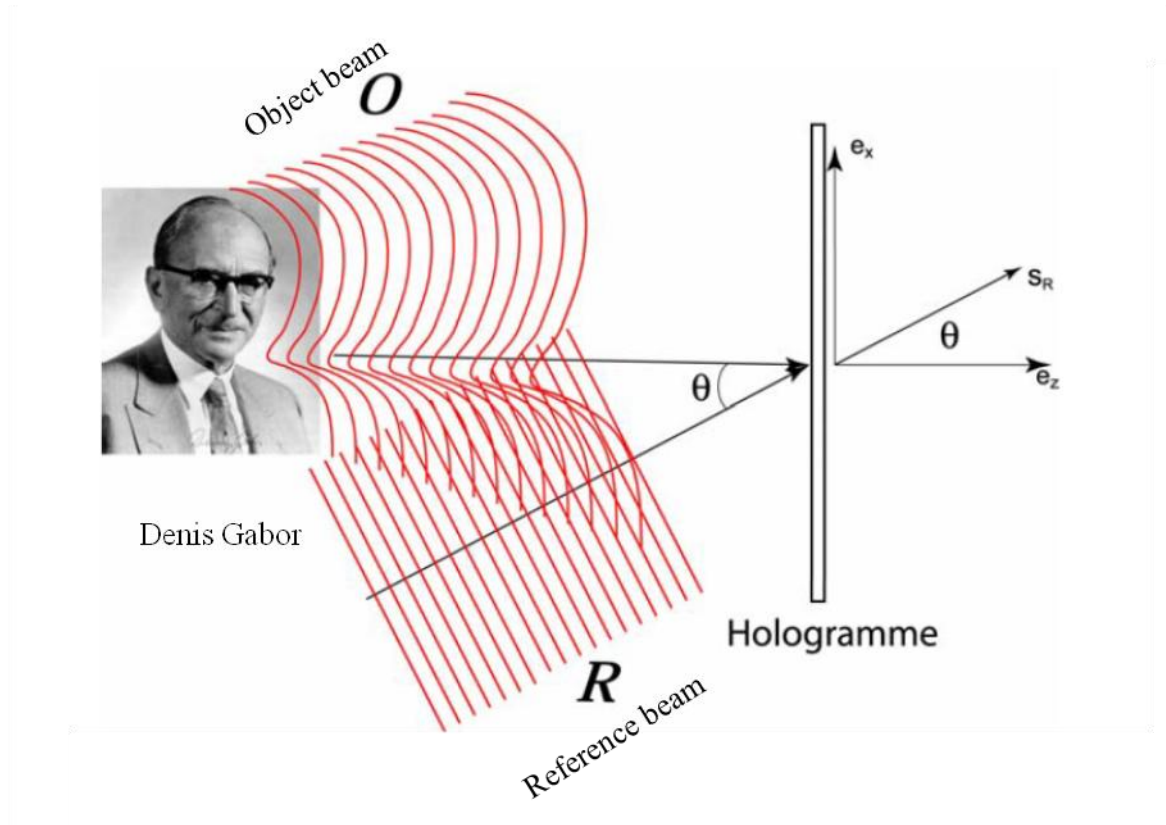


Figure 5.10: Principle of the formation of a hologram using off axis holography⁴⁶.

There are a few degrees (angle θ) between the reference (R) and the object beams (O). This off axis configuration enables the reconstruction of information using a single hologram acquisition while on-axis holography (i.e. $\theta = 0$) requires acquisition of several holograms.

5.3.1.2 Phase images

DHM can obtain two types of sample representation:

□ Intensity images or *amplitude contrast*.

These are the same images as those given by a classical optical microscope. As the images are obtained using the monochromatic source (laser) it does not give information about the colour of the sample. However sometimes it gives more contrast (the diffraction effect) than an image obtained with white light.

□ Phase images or *phase contrast*.

Figure 5.11 illustrates the principle of phase measurement by a DHM configured in reflection. The homogeneous reflective sample is lit by a monochromatic plane wave of wavelength (λ). The deformation of the reflected wave is measured in degrees of dephasing ($\Delta\varphi$) and directly connected to the 3D topology of the sample by

$$\Delta h = \frac{\lambda \Delta\varphi}{4\pi n} \quad (5.7)$$

where Δh is the height of the sample and n the refractive index of the immersion medium ($n = 1$ in air, 1.33 in water).

For non-homogeneous samples the physical characteristics of the surface must be taken into account when calculating its height as a function of the dephasing during reflection. However, a DHM does not measure the real dephasing but the modulo 2π

$$\varphi_{DHM} = \left[\frac{\Delta h 2\pi (n_2 - n_1)}{\lambda} \right] \text{Mod} 2\pi \quad (5.8)$$

This is a representation that is similar to that of the topography as described by the contour lines on a geographic map. In this case the equidistance is 360° (2π), where, using the equation:

$$\text{equidistance} = \frac{\lambda}{(n_2 - n_1)} \quad (5.9)$$

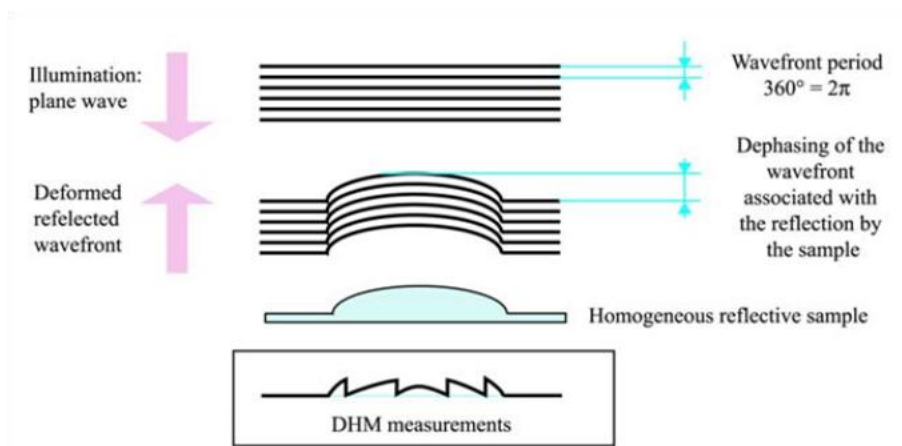


Figure 5.11: Principle of phase measurements by DHM in reflection mode⁴⁶

5.3.2 *In-situ* silver deposition

In-situ study of silver deposition was conducted using the Lyncee Tec's DHM R1000 reflection configured high precision optical profiler based on Digital Holographic Microscopy technology. The silver is deposited potentiostatically on the gold coated quartz crystal. The AT-cut polished (flat mirror) finish quartz crystal with a gold film thickness of $900 \text{ \AA}$, deposited in a keyhole shape on both sides with central disc active area of 0.211 cm^2 was used (International Crystal Manufacturing Co., Oklahoma City, USA.). **Figure 5.12(a & b)** shows intensity and 3D topographic images of the gold crystal. The figure reveals a flat surface without any surface defects such as

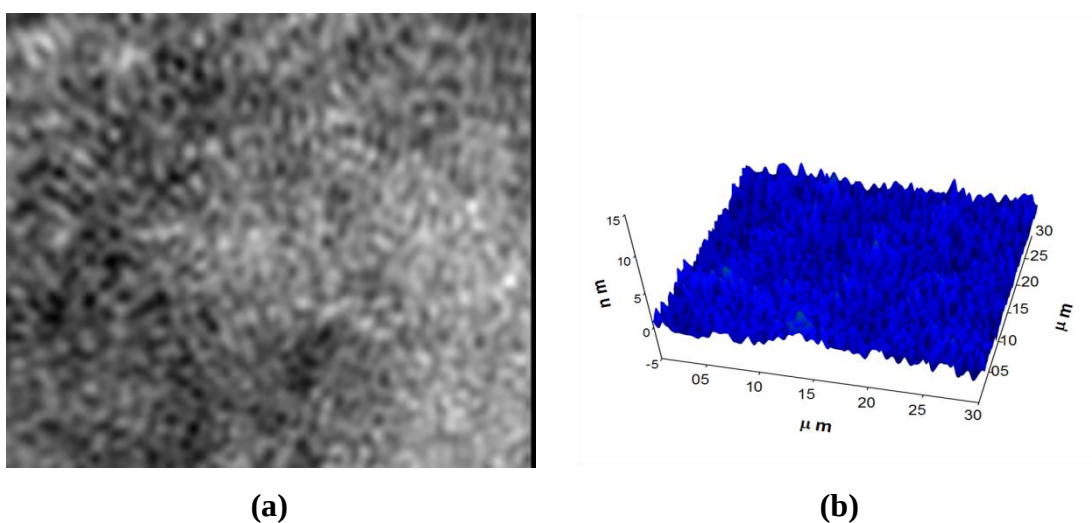


Figure 5.12: The surface topography of the polished gold coated quartz crystal (a) intensity image (b) 3D phase image

pits or polishing lines and the roughness of crystal is S_a 1.04 nm, S_p 5.28 nm, S_v -4.65 nm, S_t 9.92 nm. The polished gold coated crystal is used to minimize the effects of surface defects on the deposition and morphology of the silver deposit.

A standard three electrode configuration is used to deposit the silver consisting of a gold coated quartz crystal as working electrode, a platinum flag as the counter electrode and a silver wire as the quasi reference electrode. The electrochemical cell used for *in-situ* DHM study is constructed by attaching two O-rings (1 cm diameter and 4 cm diameter) to a flat polypropylene sheet. The smaller ring is pasted in the centre of the big ring and a polished gold coated quartz crystal is pasted on the small O-ring with insulating epoxy resin. The outer ring serves as the liquid reservoir. The schematic presentation is shown in **Figure 5.13**.

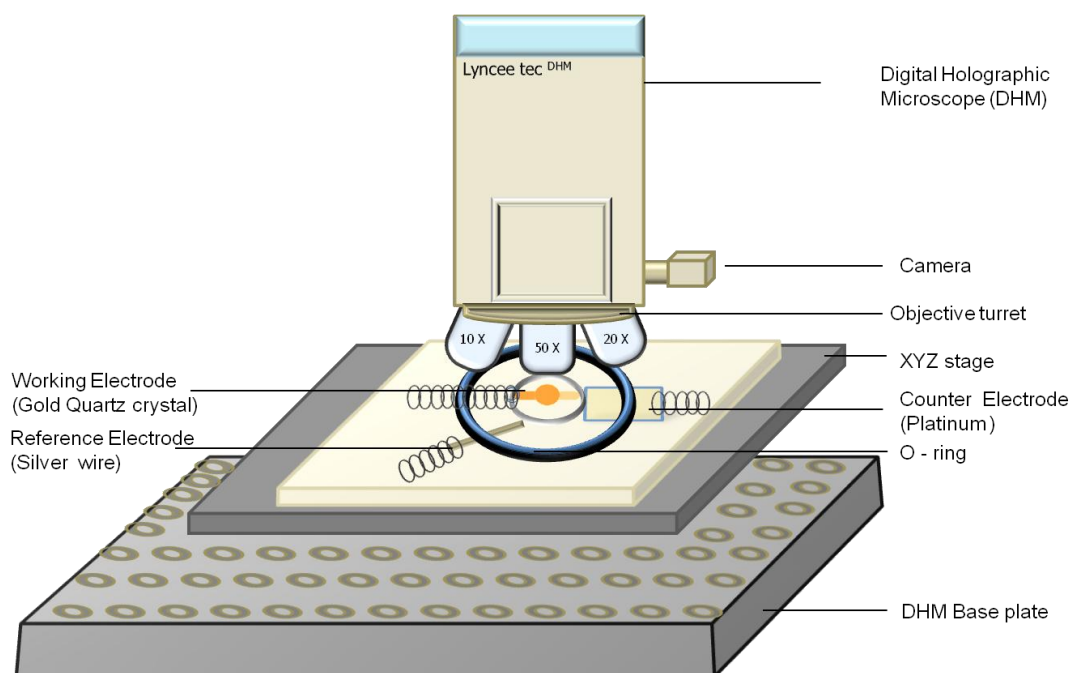


Figure 5.13: Schematic presentation of the *in situ* DHM cell placed under the DHM and submerged in liquid. The cell consists of a gold coated quartz crystal working electrode, a Ag wire pseudo reference electrode and a platinum counter electrode.

First the electrode surface was placed under the objective of the microscope and the surface was focused using 50x magnification. The solution was fed into the cell with the help of the syringe slowly and carefully to ensure that there was no bubble. This was done until the liquid form a thin layer over the whole substrate surface. After feeding the solution, the surface was again focused. Silver was deposited and the

sequential ‘holograms’ were obtained after every 100 milli-seconds. The obtained holograms were then reconstructed using Koala software to obtain the phase and intensity images.

The phase data thus obtained was plotted using sigma plot version 11 software and analysed using the image analysis software ‘Digimizer’. A temporal average over one second was obtained by taking the arithmetic mean of every ten phase images. The temporal average is used to reduce the noise and the image is shown in **Figure 5.14**. The image is still too noisy to extract information relating to the nucleation and growth kinetics. For this purpose the data is corrected by subtracting the blank substrate surface and setting a certain threshold height (10 – 15 nm) in all cases. **Figure 5.14(b)** shows the image obtained from the normalised data.

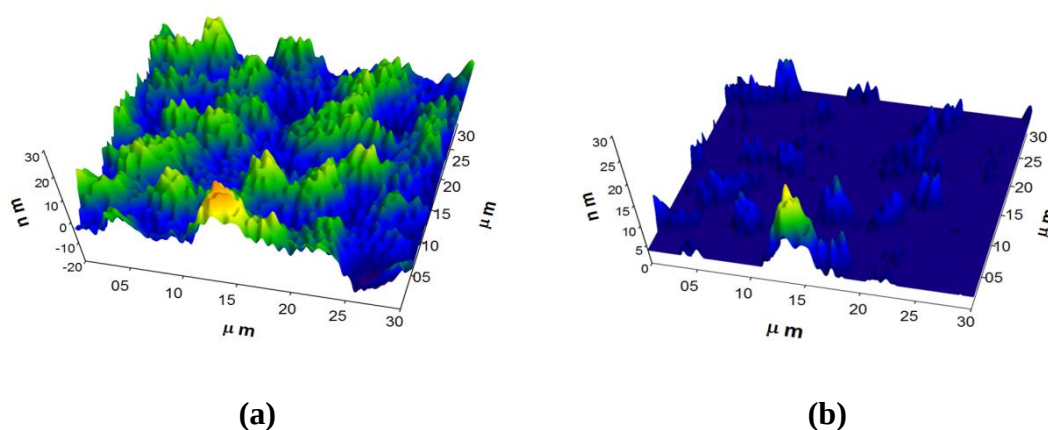
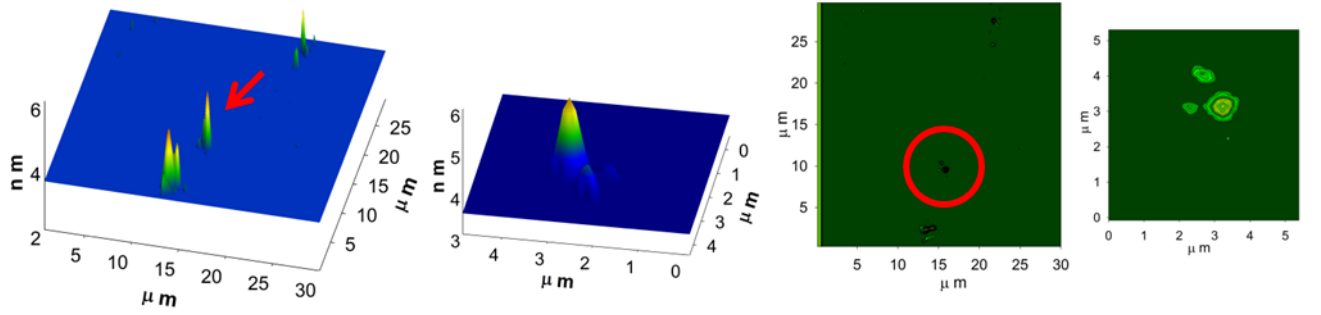


Figure 5.14: The 3D topography of silver deposited from 1:2 ChCl:EG after deposition for 37 s (a) raw data (b) corrected data

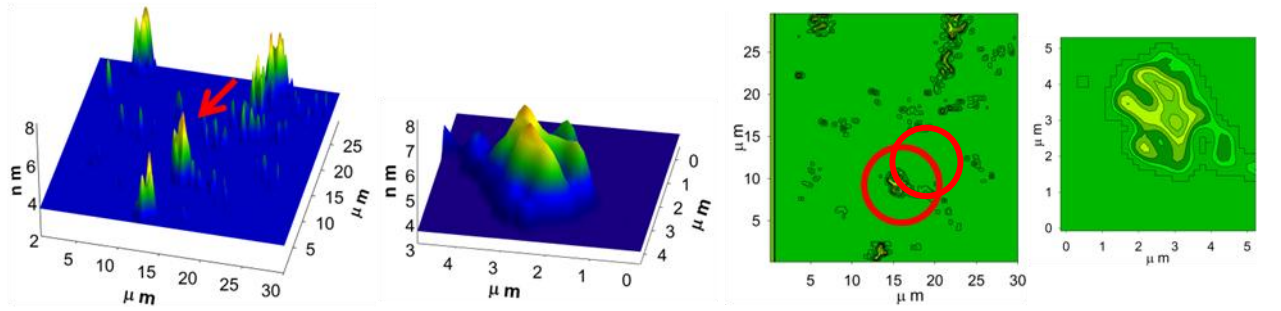
5.3.3 Silver deposition from 1:2 ChCl:ethylene glycol

Silver was deposited on the gold crystal from AgNO_3 in 1:2 ChCl:EG containing 100 mM Ag(I) at an overpotential of -100 mV for 60 s. The 3D topographic and the corresponding 2D projection images are shown in **Figure 5.15**. These images also show the growth of selected nucleus at different times. These images show that silver deposited through the formation of 3D hemispherical nuclei. The coalescence of these nuclei results in the formation of large silver clusters. Depletion zones develop

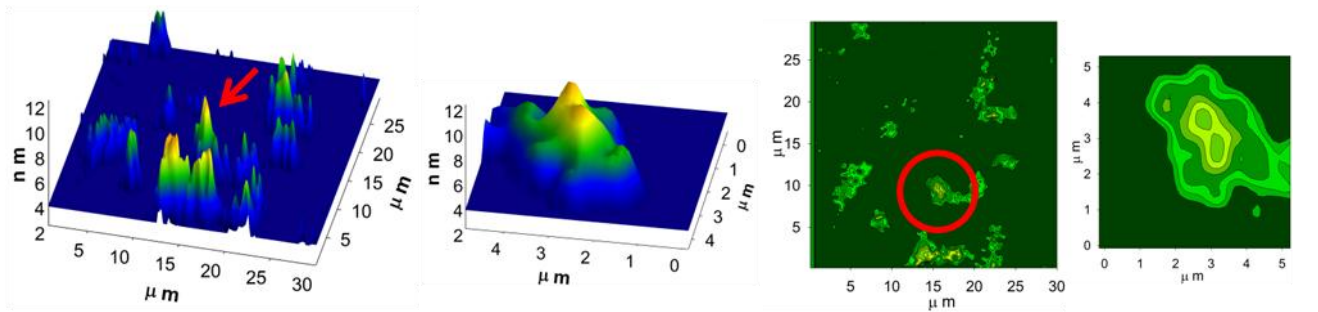
around the growing large clusters which minimize the chance of formation of new nuclei and these growing clusters also compete for adatoms at the perimeter. The coalescence of these growing clusters gives rise to the formation of a film. These observations are consistent with the *ex-situ* AFM study in the first section of this chapter and the morphological study of bulk silver deposition in Chapter 3.



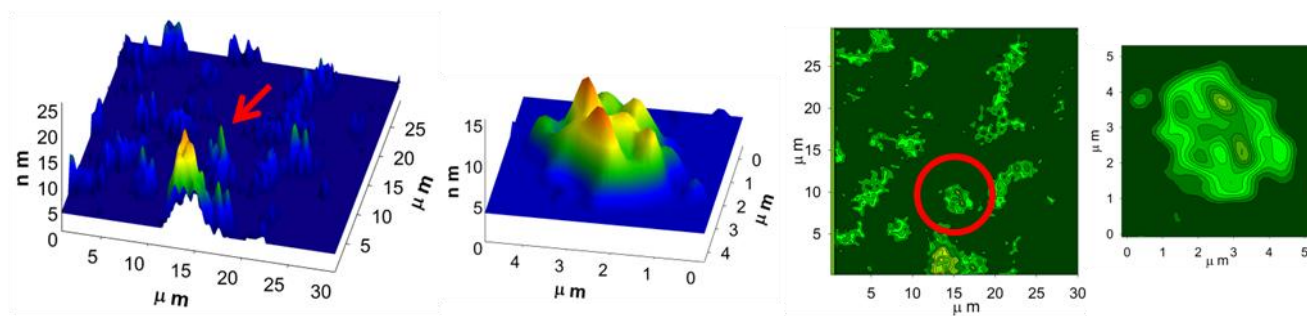
(2 s)



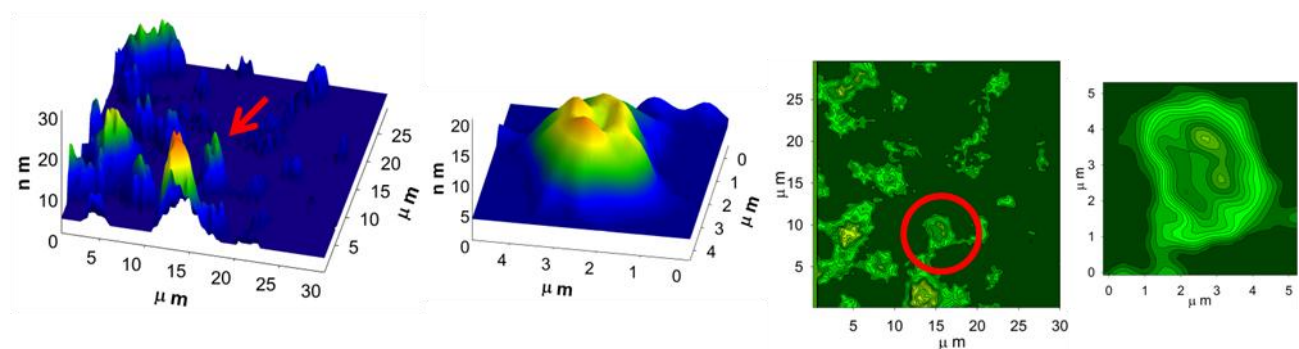
(7 s)



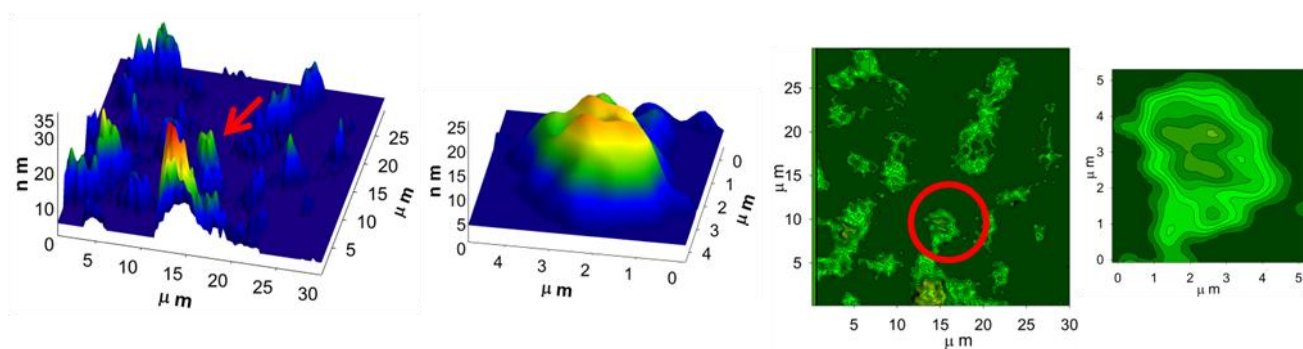
(17 s)



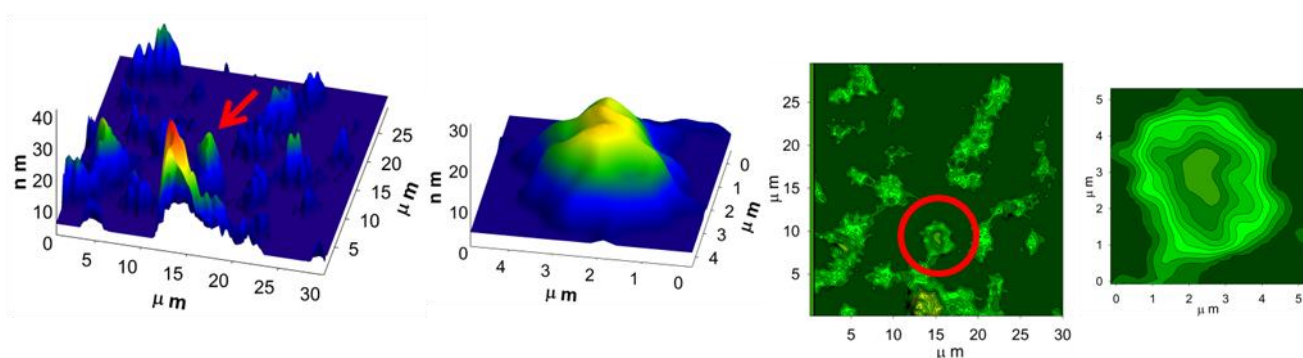
(27 s)



(37 s)



(47 s)



(52 s)

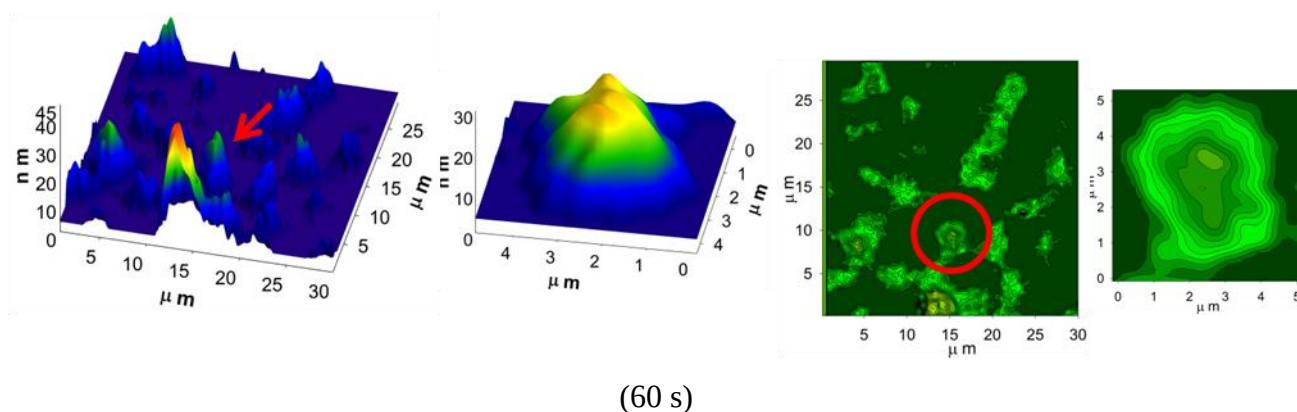


Figure 5.15: Successive *in-situ* images of Ag(I) deposition from 1:2 ChCl:ethylene glycol at -100 mV for 60 s.

5.3.3.1 Island growth rate

Figure 5.15 shows the time dependence of the average island diameter (width), the average island height and the volume of the nuclei. The analysis involved the selection of growing nuclei from the final image and tracing back the growth of the selected nuclei until they disappear. **Figure 5.16(b)** shows the volume of the growing clusters (9 clusters) plotted versus the time elapsed. The volume plotted here is the sum of all the individual nuclei at different times involved in the formation of the cluster. **Figure 5.17** shows the formation of a typical cluster in real time.

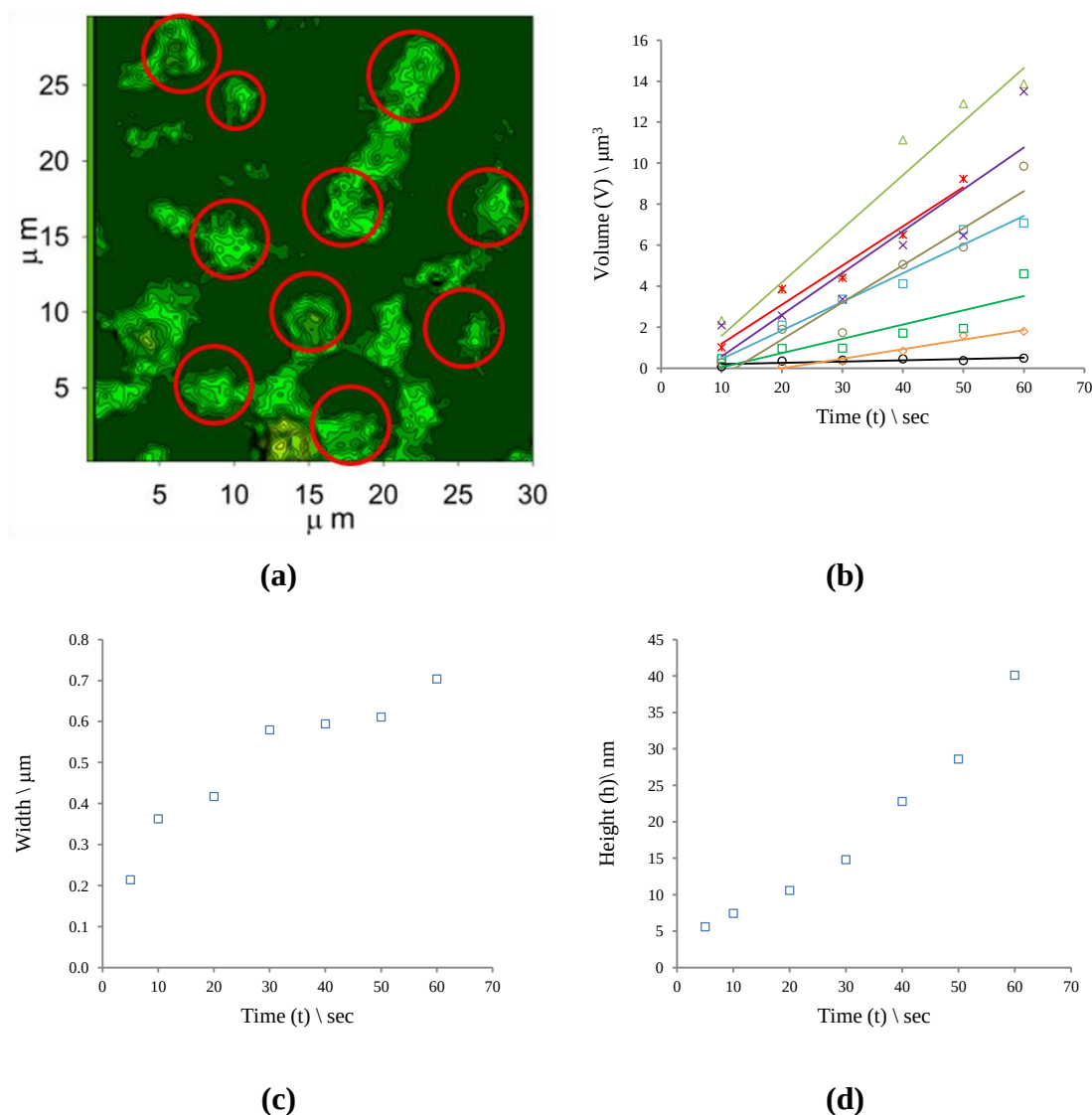
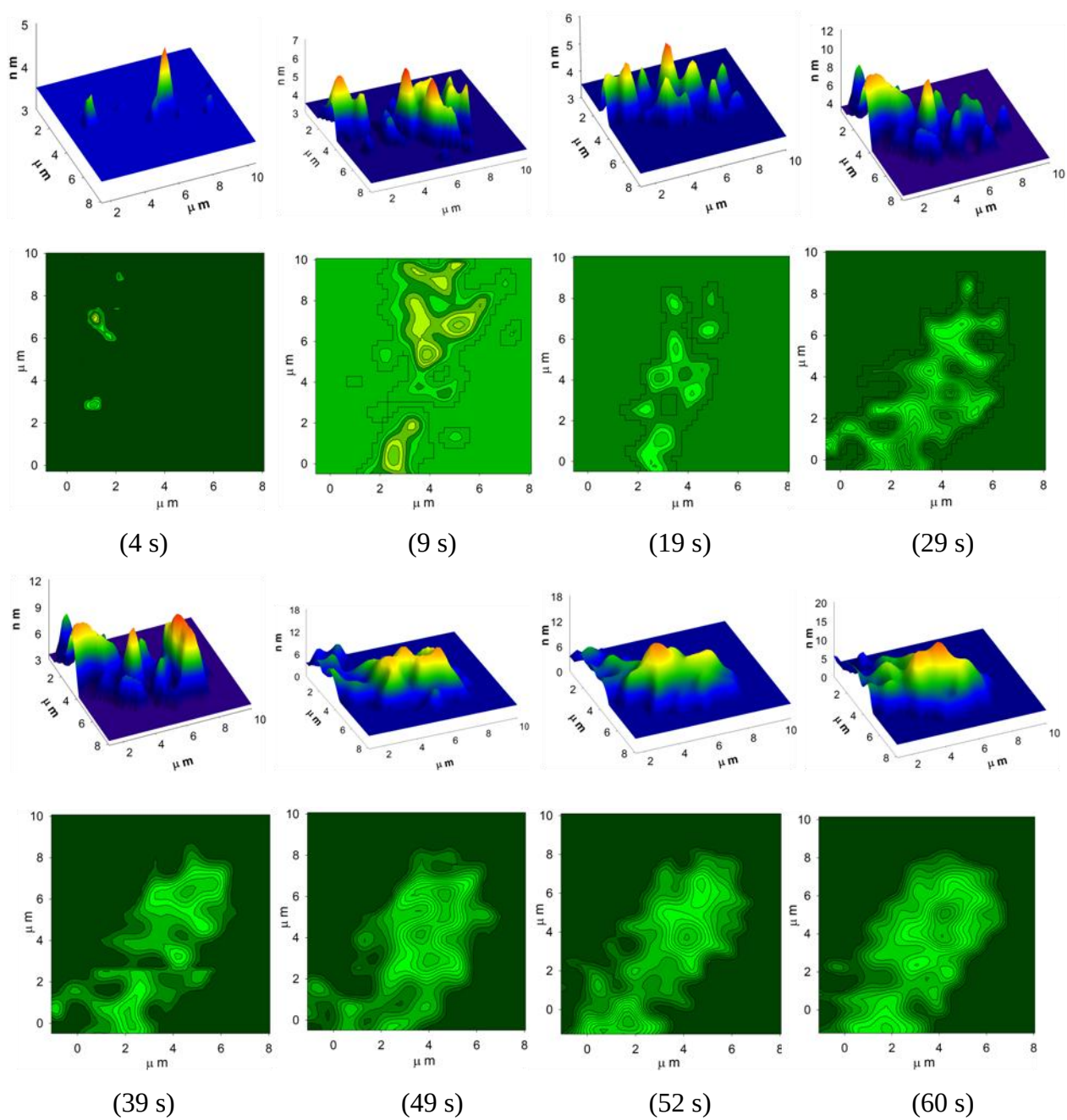


Figure 5.16: (a) The islands selected for the analysis. Time dependence of (b) the volume of the island (c) the average island diameter (width) and (d) the average island height of silver deposited from 1:2 ChCl:EG at -100 mV.

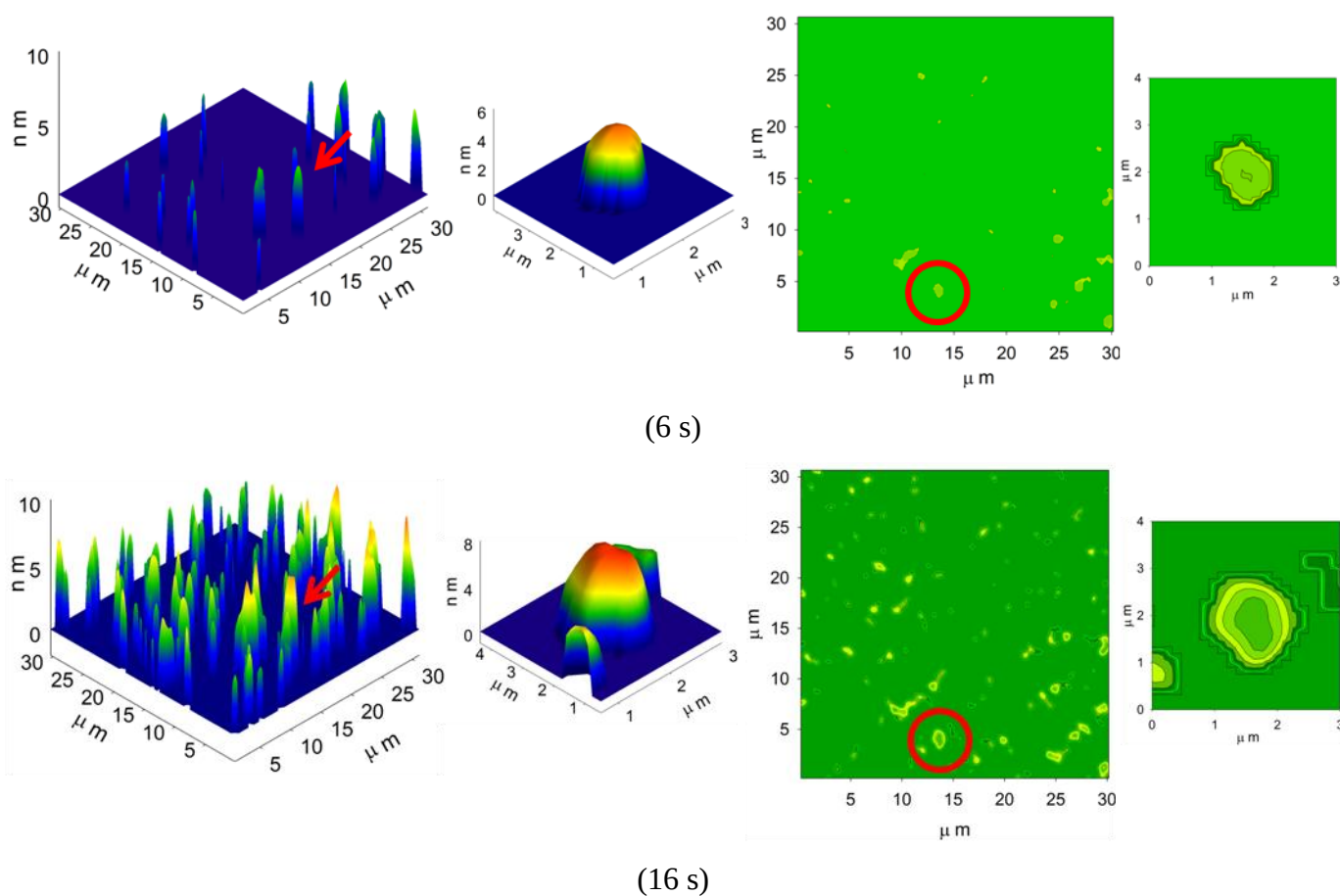
Figure 5.16(c and d) show the average lateral and vertical dimensions of the growing islands (30 nuclei) and their variance with time. In both the cases the two kinetic regimes observed are consistent with isolated island growth up to 30 s and then coupled growth after 30 s. In an isolated island growth regime, the growth for lateral and vertical dimensions is independent and the vertical growth rate is less than the lateral growth rate. After 30 seconds coalescences of individual islands starts which results in slow down of lateral growth due to the impingement of the growing island while the vertical growth speeds up due to the suppression of the lateral growth.

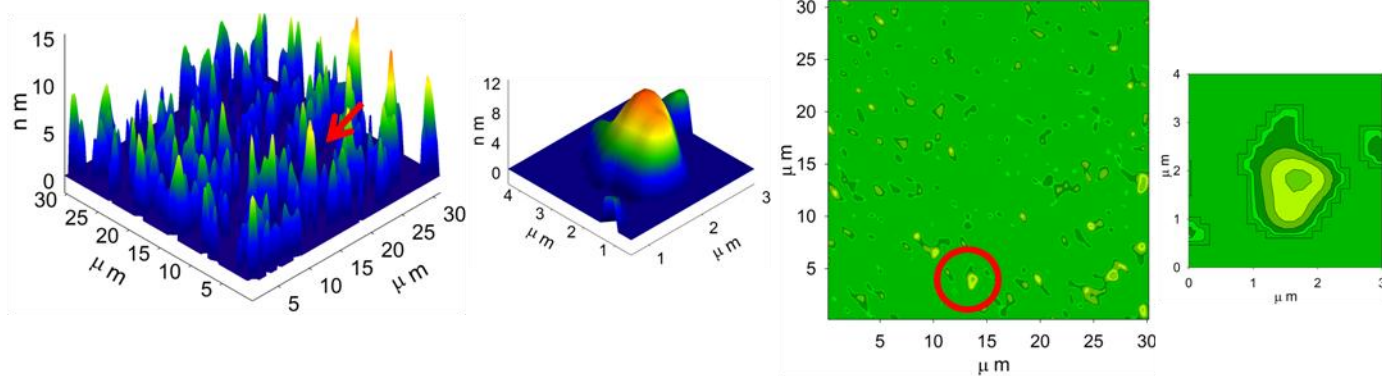
**Figure 5.17:**

The formation of a silver cluster

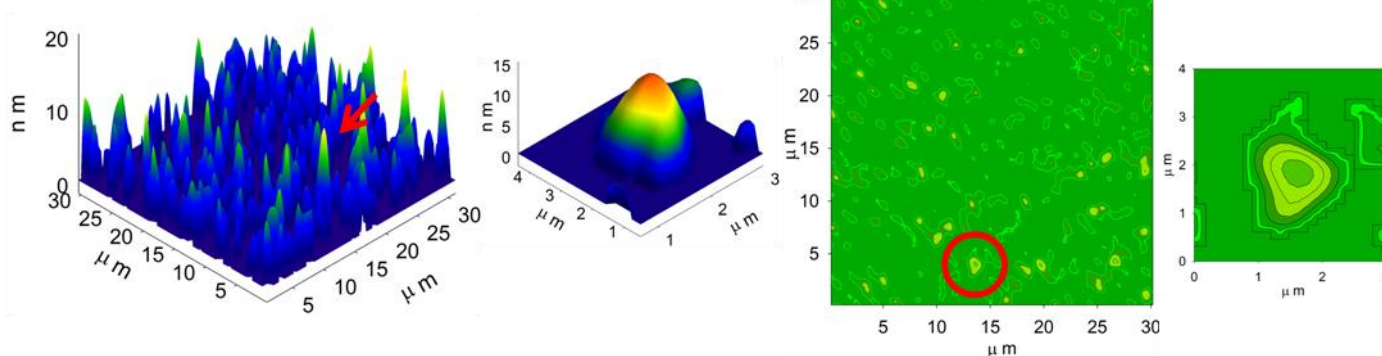
5.3.4 Silver deposition from 1:2 ChCl:urea

Figure 5.18 shows topographic images obtained for the deposition of silver from 1:2 ChCl:urea at a step potential (-140 mV) for 100 s. The silver is deposited from a solution containing $0.1 \text{ mol dm}^{-3} \text{ AgNO}_3$. Deposition occurs through the formation of 3D hemispherical islands. In contrast to the deposition of silver from 1:2 ChCl:ethylene glycol, no large silver cluster formation is observed and the growth takes place through individual nuclei and small crystallites. This observation is consistent with the morphological study of bulk deposition in Chapter 3.

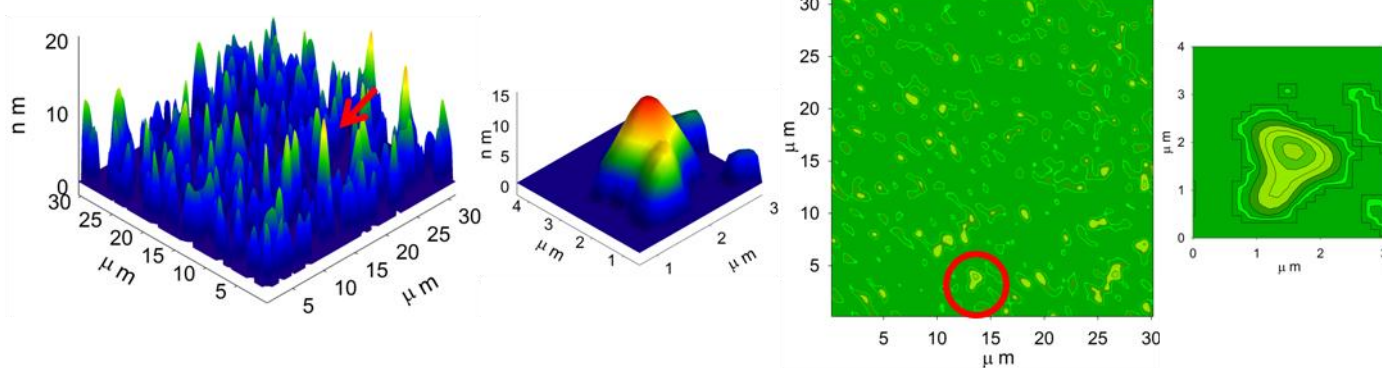




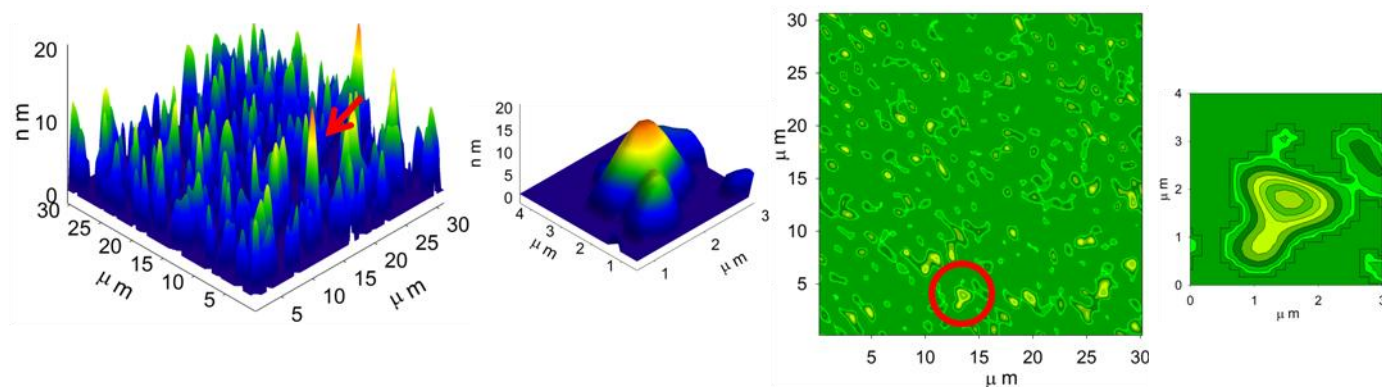
(36 s)



(56 s)



(76 s)



(92 s)

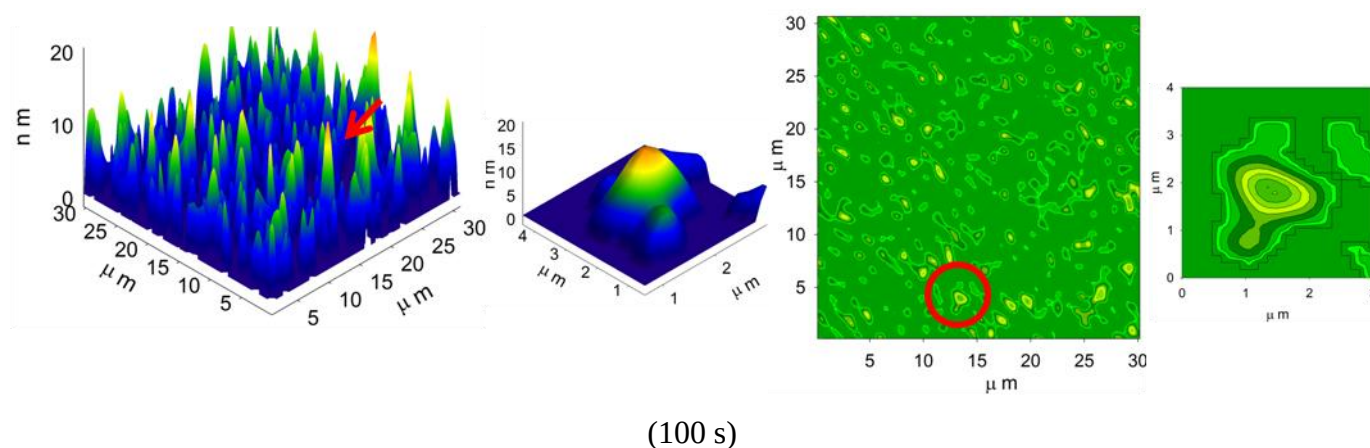


Figure 5.18: Sequential *in-situ* images of the topography of silver deposited from 1:2 ChCl:urea at -140 mV from a solution containing Ag(I) 100 mM dm⁻³

5.3.4.1 Island Growth kinetics

The time dependence of the growth of the silver crystallites is shown in **Figure 5.19**. The average lateral and vertical dimensions of the growing islands (30 islands) are shown in **Figure 5.19(c & d)**. Unlike silver growth from 1:2 ChCl:EG, there is only one kinetic regime observed indicating the absence of the coalescence of the growing nuclei. Moreover the vertical growth rate is slightly greater than the lateral growth rate. **Figure 5.19(b)** shows the variation of the volume of the growing nuclei (10 nuclei) with time. It shows that the induction time for nuclei appearance and the corresponding growth rate is less than for 1:2 ChCl:EG which may be attributed to high viscosity of 1:2 ChCl:urea hence the slow mass transport rate.

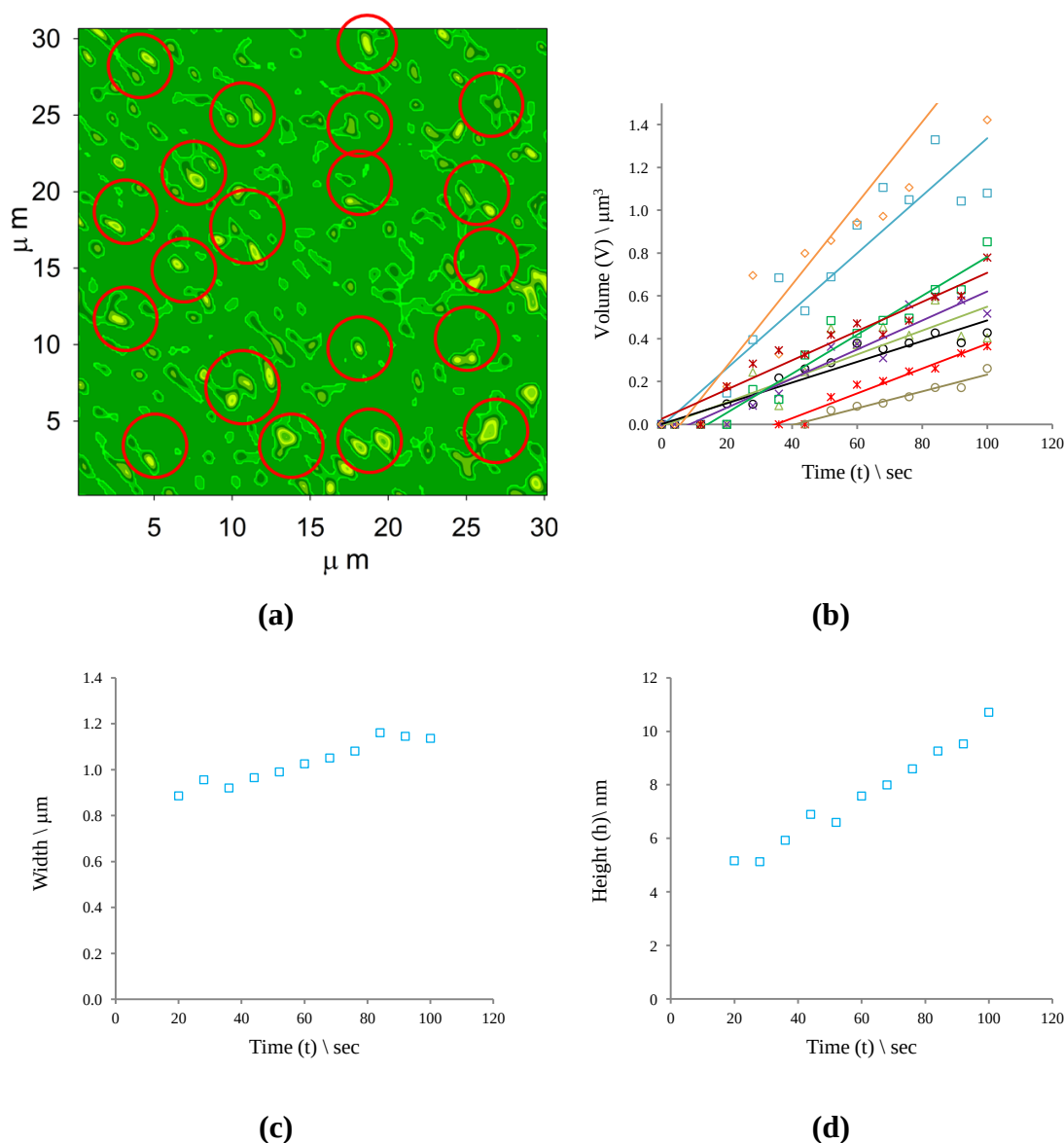
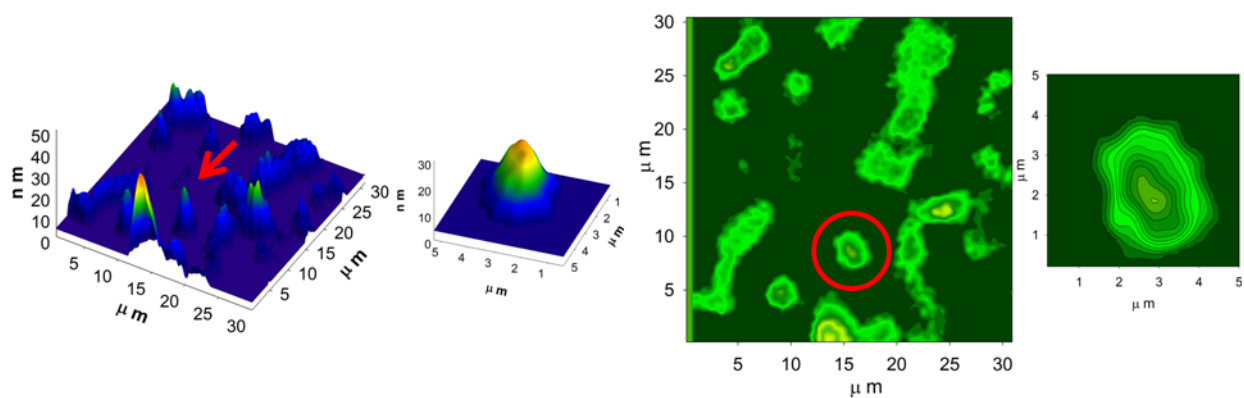


Figure 5.19:

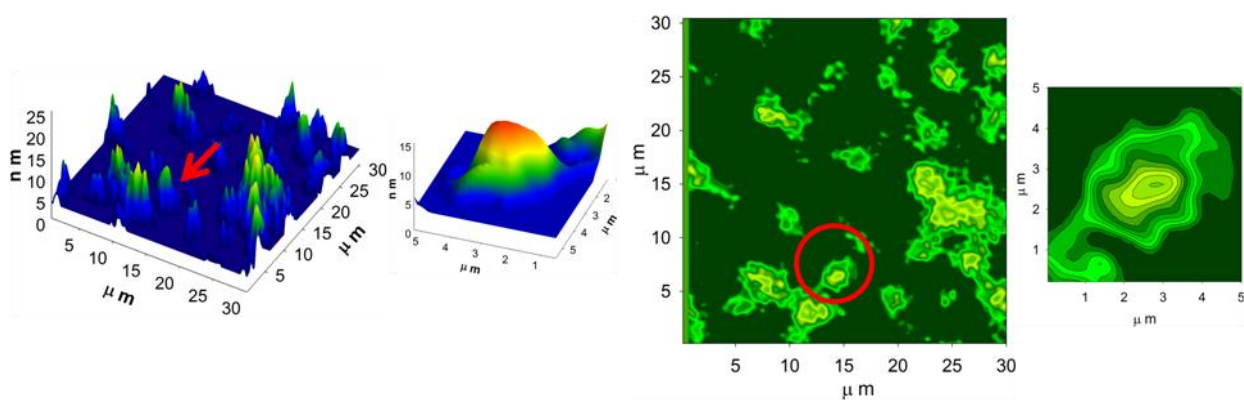
The growth kinetics of the silver crystallites deposited from 1:2 ChCl:urea (a) nuclei selected for the analysis (b) the volume dependence of the growing nuclei with time (c) the lateral growth of the nuclei versus time and (d) the vertical growth dependence on time

5.3.5 Stripping of deposited silver in 1:2 ChCl:ethylene glycol

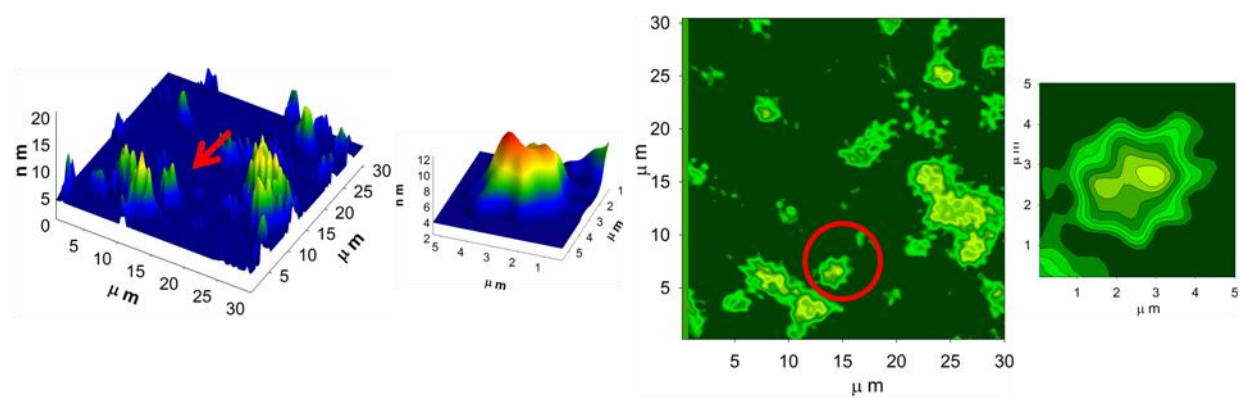
Figure 5.20 shows the stripping of silver deposited from 1:2 ChCl:ethylene glycol with time. Analysis of the images reveals that the stripping is isotropic like the deposition of the silver *i.e.* the rate of reduction in height and width of the silver islands is almost identical.



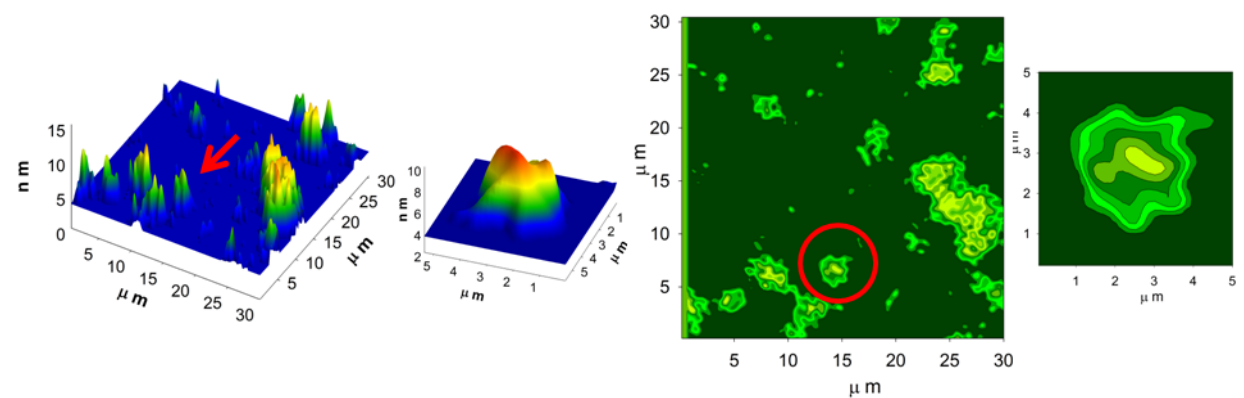
(0 s)



(10 s)



(20 s)



(30 s)

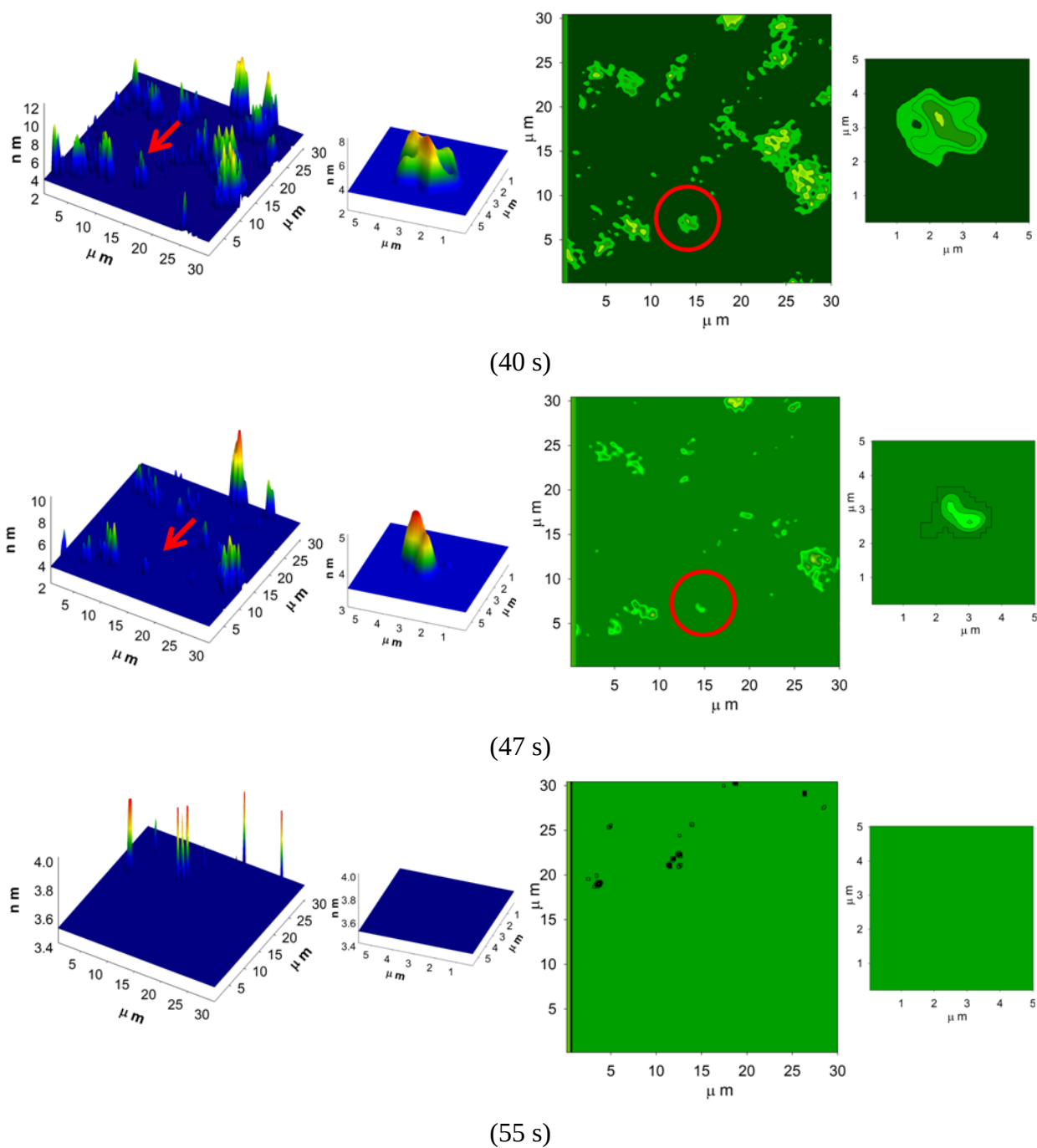


Figure 5.20: The removal of deposited silver in 1:2 ChCl:ethylene glycol at +100 mV in a solution containing Ag(I) 100 mM dm^{-3} .

5.4 Conclusion

The initial stages of the deposition of Ag(I) from deep eutectic solvents have been investigated directly to probe the nucleation and growth mechanism using microscopic techniques. For this purpose *ex-situ* AFM and *in-situ* DHM studies were carried out. SPM techniques used for *in-situ* observation of an electrified electrode surface suffer from limitations such as slow scan rate, lack of precise control of the movement of the tip and sometimes the smearing of the deposited surface due to the moving tip.

DHM is a new measurement approach which provides interferometric resolution (nanometer vertical scale) with short acquisition time. It is a non destructive and non contact surface metrology technique which enables the retrieval of a lot of information about a 3D phase from a single hologram, acquired using a conventional digital camera. DHM has been applied for the first time to investigate directly the electro-crystallization of a metal on a substrate in real time (*in-situ*) and its results are compared with an *ex-situ* AFM study of the deposition process. The *in-situ* DHM results show good agreement with the *ex-situ* AFM results.

The microscopic study reveals that island growth of silver deposited from deep eutectic solvents follows power law kinetics in both lateral and vertical directions. In 1:2 ChCl:EG two growth rates are observed, at short times the lateral growth rate is greater than the vertical growth rate while at longer times the vertical growth speeds up and the lateral growth slows down due to the coalescence of the growing islands which suppress the lateral growth. The microscopic study also removes the need for the analysis of the chronometric transients to extract the kinetic parameters such as nuclear number density and nucleation rate etc. This therefore removes the need for any arguable assumptions made for the nucleation and growth rates.

5.5 References

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Chapter 6 :**Summary and Future Directions**

6.1 Introduction**6.1 Summary**

- 6.1.1 Electrodeposition of silver in deep eutectic solvents
- 6.1.2 Effect of additives on silver deposition in deep eutectic solvents
- 6.1.3 Microscopic investigation of silver nucleation kinetics in DES

6.2 Future Directions**6.3 References**

6.1 Summary

Electrochemical deposition is the most economical and most widely used technique for surface finishing. Other techniques such as physical vapour deposition (PVD), chemical vapour deposition (CVD) and sputtering have limited use due to high capital cost and slow deposition rates. The present electro-deposition baths are based on aqueous media and are under tremendous pressure due to their strong negative impact on the environment. Non-aqueous baths include molecular solvents consisting of polar and non-polar molecules or ionic fluids consisting of high-temperature molten salts and lower-temperature ionic liquids. Ionic liquids are a prospective alternative electro-deposition medium due to their unique electrochemical properties but research is at a preliminary stage and is the subject of considerable investigation.

In this thesis, silver was used as a well behaved system for gaining an insight into the deposition mechanism *i.e.* nucleation and associated processes in ChCl:hydrogen bond donor deep eutectic solvents. For this purpose a systematic study of silver deposition in 1:2 ChCl:EG and 1:2 ChCl:urea was conducted on the following lines to develop on understanding of the way in which materials nucleate and grow on the substrate

- ❑ Qualitative evaluation of nucleation and growth mechanism using existing theoretical formalisms
- ❑ Computer simulation to quantitatively estimate the kinetic parameters of electrocrystallisation using the ‘non-linear best fitting’ approach of the whole potentiostatic current time evidence.
- ❑ Direct surface analysis using *ex-situ* AFM and *in-situ* DHM.

6.1.1 Electrodeposition of Silver in deep eutectic solvents

The effect of silver salts and the concentration of the electroactive species on the physical properties and the electrochemical behaviour of silver in 1:2 ChCl:EG and 1:2 ChCl:urea were studied. Physical properties like conductivity, viscosity, surface tension and density of these liquids were not affected by the concentration of silver salts which is in contrast to a previous study of Zn deposition where the concentration of the ZnCl_2 affected the physical properties of the same liquids.¹

The electrochemical window for both solvents was found to be 2 V extending from +1.2 V to -0.8 V. The electrochemical behaviour of silver salts in these solvents was

studied using potentiodynamic, potentiostatic and electrogravimetric techniques. These studies revealed that silver deposition is a slow process in 1:2 ChCl:urea which may be related to its high viscosity and low conductivity.

Qualitative, graphical, non-dimensionless comparison of the early part of the current transients showed that the nucleation mechanism of Ag(I) deposition was independent of liquid and is a function of overpotential. At low applied potential it most closely corresponded to 3D progressive nucleation whereas at higher applied potentials it resembled 3D instantaneous nucleation. At intermediate potentials it deviated from the two limiting cases and showed intermediate behaviour and was considered as instantaneous nucleation with growth controlled by mixed kinetics and diffusion. Kinetic parameters like nuclear number density, rate of nucleation, diffusion coefficient and critical nuclear size were quantitatively estimated by the analysis of the maximum coordinates and non linear best fitting of the current transients. The nuclear number densities (N_o) showed on exponential dependence on the over potential and critical nuclear size (n_k) values varying from 0 to 1 atom suggesting that each adsorbed silver atom acted as stable cluster.

SEM and AFM topographical characterization revealed the granular morphologies of the silver deposit similar to deposits obtained from other ionic liquids.

6.1.2 Effect of Additive on Silver deposition in deep eutectic solvents

The effect of additives on the electrochemical behaviour of silver in 1:2 ChCl:EG and 1:2 ChCl:urea electrolytes and deposit morphologies was investigated using both electrochemical and microscopic methods. The additives used were the surfactants hexacetylammonium bromide and sodium dodecylsulphate and brighteners cresyl fast violet and crystal violet.

The study revealed that the surfactants changed the surface tension of the solvents while other physical properties were insensitive to the addition of additives. The electrochemical behaviour of silver in 1:2 ChCl:ethylene glycol was not affected while in 1:2 ChCl:urea the reduction of silver was slightly shifted to more anodic potentials with the addition of additives. The nucleation kinetic parameters were calculated using the Scharifker *et al.* and Heerman *et al* models by varying nuclear number density, nucleation rate, diffusion coefficient and the influence of double layer

charging by simulating k_1 and k_2 to fit the whole current transients. The extracted parameters were compared and good agreement was obtained suggesting that both models described the nucleation and growth of silver in deep eutectic solvents equally well.

Surface characterization of the deposit by AFM and SEM revealed a slight change in the deposit morphologies and granular smooth deposit with small grain size was obtained with additives.

6.1.3 Microscopic investigation of silver nucleation kinetics in DES

Few efforts have been made to probe directly in real-time the development of the surface with nucleation and growth of the metal using scanning probe microscopy (SPM)². In this study a novel microscopic technique, digital holographic microscopy with nanometer vertical resolution and short acquisition time was successfully used to image the electrified surface to probe the nucleation and growth mechanism of silver deposition in real time. The results showed good agreement with the findings of the *ex-situ* AFM study and the morphological studies of bulk deposition.

The microscopic study revealed that island growth of silver deposition can be explained in terms of power law kinetics in deep eutectic solvents. Two kinetic regimes were detected in the lateral and vertical growth. At short times before the coalescence of the growing nuclei, the lateral and vertical growth rates were the same while the impingement of the growing islands after coalescence suppressed the lateral growth and speeded up the vertical growth. The microscopic study also removes the need for the analysis of the chronometric transients to extract kinetic parameters such as nuclear number density and nucleation rate etc. This therefore removes the need for any arguable assumptions made about nucleation and growth rates.

6.2 Future Directions

Digital Holographic Microscopy is a new metrology measurement approach with nanometer scale resolution in vertical scale. Unlike scanning probe microscopy (SPM) techniques which suffer from limitation of slow scan rate, precise control of the movement of the tip and sometimes the smearing of the deposited surface due to the moving tip, it is fast, non-destructive and non contact surface analysis technique. It

was successfully applied for *in-situ* investigation of the initial stages of silver deposition from 1:2 ChCl:ethylene glycol and 1:2 ChCl:urea.

The electrodeposition process is a complex interplay between the substrate, nucleation and surface chemistry. A range of additives in the electrolyte bath are introduced as leveller, brighteners and complexing agent etc. and their mode of action is solvent dependent. Little is known about their effect and mode of action in ionic liquids. *Ex-situ* AFM and *in-situ* DHM study could be applied to gain insight into the mode of action of the additives and their effect on the nucleation and growth mechanism of the metal in deep eutectic solvents.

The *in-situ* DHM studies may be applied to other system like Zn deposition where the previous study by Barron *et al.*¹ showed different electrochemical behaviour in two deep eutectic solvents (1:2 ChCl:EG and 1:2 ChCl:urea). A single phase of Zn was deposited in 1:2 ChCl:urea while two phase of Zn were deposited in 1:2 ChCl:EG. This divergence of behaviour was attributed to the activity of free chloride ions and their specific adsorption at growing Zn crystal faces. The *in-situ* study may be applied to further investigate the double layer structure and chloride activity to allow a more quantitative understanding of the Zn electrodeposition process at the substrate interface.

A large number of alloy electrodeposits have been reported from deep eutectic solvents. Very little is known about the alloy phase formation and the relative structure of the co-deposit. *Ex-situ* AFM and *in-situ* DHM study can be carried out to investigate the nucleation and growth mechanism of metals in the co-deposit and the correlation of the electrolyte composition and the electrodeposition parameters to the structure of the co-deposit at the early stages of deposition.

6.3 References

1. J. C. Barron, University of Leicester, 2009.
2. M. E. Hyde, R. Jacobs and R. G. Compton, *The Journal of Physical Chemistry B*, 2002, **106**, 11075-11080.