Atomic Force Spectroscopy on Poly(*o*-ethoxyaniline) Nanostructured Films: Sensing Nonspecific Interactions

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Abstract: Atomic force spectroscopy (AFS) was used to measure interaction forces between the tip and nanostructured layers of poly(*o*-ethoxyaniline) (POEA) in pure water and CuSO₄ solutions. When the tip approach and retraction were carried out at low speeds, POEA chains could be physisorbed onto the Si₃N₄ tip via nonspecific interactions. We conjecture that while detaching, POEA chains were stretched and the estimated chain lengths were consistent with the expected values from the measured POEA molecular weight. The effects from POEA doping could be investigated directly by performing AFS measurements in a liquid cell, with the POEA film exposed to liquids of distinct pH values. For pH $\geq$ 6.0, the force curves normally displayed an attractive region for POEA, but at lower pH values—where POEA is protonated—the repulsive double-layer forces dominated. Measurements in the liquid cell could be further exploited to investigate how the film morphology and the force curve are affected when impurities are deliberately introduced in the liquid. The shape of the force curves and the film morphology depended on the concentration of heavy metal in the liquid cell. AFS may therefore be used to study the interaction between film and analyte, with important implications for the understanding of mechanisms governing the sensing ability of taste sensors.

Key words: atomic force microscopy, atomic force spectroscopy, conducting polymers, poly(*o*-ethoxyaniline), environmental sensors, force curve, nonspecific interactions

INTRODUCTION

The understanding of molecular-level interactions at interfaces may have an impact in a number of scientific and technological issues, as in the case of highly sensitive sensors obtained with nanostructured films deposited onto metallic electrodes (Da Silva et al., 2002). Recent developments in taste sensors using impedance spectroscopy as the principle of detection, for instance, point to a high performance governed by surface interactions (Riul et al., 2002). In these sensors, sensing units comprise nanostructured films of various materials—including conducting polymers—adsorbed onto interdigitated electrodes. Measurements of interactions between surfaces bearing polymer layers can provide insights into the mechanisms responsible for detection of trace amounts of analytes in a liquid, for example, pollutants in waters. Particularly suitable for studying these interactions is atomic force microscopy (AFM) (Binnig et al., 1986), which may provide images on specific locations of organic and inorganic materials (Frommer, 1996; Noy et al.,

1997; Azzaroni et al., 2003) and serve to investigate surface chemistry and adhesion using force curves through AFS (Weisenhorn & Hansma, 1989; Hudson & Abruña, 1996; Sirghi et al., 2000; Cappella et al., 2002; Drelich et al., 2004; Leite & Herrmann, 2005). AFS allows the study of inter- and intramolecular forces and has been applied to biological systems (Hoh et al., 1991; Gimzewski, 1999; Dufrene et al., 2001; Prazeres et al., 2003), polymers (Mizes et al., 1991; Aimé et al., 1994; Munz et al., 1998; Bliznyuk et al., 2002; Minko & Roiter, 2005), and interfacial phenomena (Beach et al., 2002; Mugele et al., 2002; Leite & Herrmann, 2003). This prompted us to choose it as a characterization method for studies of poly(*o*-ethoxyaniline) (POEA) in the form of layer-by-layer (LbL) films (Decher, 1997).

The behavior of electrolytes and conducting polymers at the molecular level is crucial for the design of new materials and technologies, as in high-performance sensors made from Langmuir–Blodgett films of conducting polymers (Ferreira et al., 2003), biosensors (Ngamna et al., 2005), and nanosensors with modified tips (Florin et al., 1995; Raiteri et al., 2001).

In this study, we measured force curves for a Si₃N₄ tip approaching POEA films in a liquid cell, aiming to demonstrate that AFS may serve to investigate nonspecific interface interactions responsible for the high sensitivity of taste

Figure 1. Schematic protonic acid doping of a POEA tetrameric unit. Units (i) and (ii) represent emeraldine base (EB) and emeraldine salt (ES), respectively, with A^- being the acid dopant counterion.

sensors based on the electrical properties of thin films. The article is organized as follows. After describing the experimental procedures for depositing the POEA films onto chrome electrodes and taking the AFS measurements, we discuss briefly the forces one expects to measure for these polymer samples in a liquid cell. The results are presented and discussed next, starting with force curves for POEA in water and then for aqueous solutions containing heavy metal ions. Special emphasis is given to the way force curves depend on experimental parameters, such as the speed with which the tip approaches the sample. Conclusions close the article.

MATERIALS AND METHODS

The nanostructured films were prepared with POEA, whose emeraldine salt and base forms have their chemical structures shown in Figure 1. At pH 3, POEA is not fully protonated, which leads to a chemical structure that is a mixture of emeraldine salt and base forms (MacDiarmid et al., 1987). POEA in the emeraldine base form (EB) was obtained by chemical polymerization and further deprotonation, according to the method described elsewhere (Mattoso et al., 1995). Solutions were prepared by dissolving POEA-EB in *N,N'*-dimethylacetamide (DMAC), after which distilled water was added until reaching a composition of DMAC/water 20:80 (v/v), and a polymeric concentration of 0.1 g/L. The pH of the solution in the liquid cell was adjusted by adding the doping acid (HCl) until required pH values. Aqueous solutions containing heavy metals were obtained by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at various concentrations.

POEA was immobilized onto the chrome surface by physical adsorption. The chrome films were obtained according to procedures described by Borato et al. (2006) and were cleaned with a piranha solution as the surface cleaning

agent. The films used here consisted of 10 POEA layers adsorbed by immersing the chrome substrate into the polymer solution for a period of 3 min. Between any two deposition procedures, the substrate + film was rinsed with pure water and dried under room conditions. Adsorption of POEA over POEA, with no alternating, oppositely charged layer, was possible because POEA can adsorb on itself via H-bonding (Pontes et al., 1999; Leite et al., 2005b), especially for films prepared at a high pH.

A Topometrix TMX 2010 Discoverer AFM, operating in the contact mode, was employed to measure the force curve and image the polymer surface. The images were analyzed using WSxM software (Nanotec Electronica S.L.). For quantitative force experiments the geometry of the tip and spring constant, k_c , of the cantilever need to be known. Several procedures have been applied to characterize the size and shape of tips and cantilevers (Neumeister & Ducker, 1994; Lévy & Maaloum, 2002; Drelich et al., 2004). Here we employed one of the most used ones, based on images from a Field Emission Gun–scanning electron microscope (FEG)–SEM (Butt et al., 2005), with the spring constants for the cantilever estimated with the equations suggested by Cappella (Cappella & Dietler, 1999) for rectangular and V-shaped AFM cantilevers. The spring constant of the cantilever was 2.5 ± 0.5 and 0.50 ± 0.07 N/m for the rectangular and V shapes, respectively. To estimate the radius of curvature of the tip, a zoomed-in section of each image that includes the probe apex and scale bar was printed out. Next, five different circles were fitted to the image and calibrated against the scale bar. The intermediate circle was selected as the average tip radius, whereas the smaller and larger circles were used to create a range of radii values. The tip curvature radius was 26 ± 5 and 56 ± 5 nm for the rectangular (Si) and V shapes (Si_3N_4), respectively.

Force curves were measured in solution with a cell developed by Topometrix consisting of a glass support with two orifices for the inlet and outlet of liquids and an O-ring for sealing it. The usual convention of (+) for repulsive forces and (−) for attractive forces was used in the analysis. Errors in force spectroscopy measurements are due to the piezo sensitivity ($\pm 5\%$), accuracy in measuring the spring constant ($\pm 15\%$), and nonlinearities of the photo-detector associated with the finite size of the laser spot ($\pm 2\%$).

Expected Tip–Polymer Forces for Samples Immersed in a Liquid

Force curves for samples immersed in a liquid depend on several factors, including the speed with which the tip is advanced or retracted toward the sample, sample roughness and hydrophobicity, solvent quality, and pH. In solution, the sample–tip interaction is dominated by forces with a length scale of 0.1–100 nm. These forces are frequently named *surface forces* because they control the interaction between materials in close proximity to each other (Leckband & Israelachvili, 2001). Derjaguin and Landau (1941)

Figure 2. Force curves for a POEA film adsorbed on a solid substrate and immersed in water ($\text{pH} \approx 6$) with frequency of jumps of $10^4 \mu\text{m/s}$ and $k_c = 0.07 \text{ N/m}$: A: no tip-film interaction; B–C: repulsive contact with the film; D: attractive peak due to surface adhesion; D–A: cantilever “pull-off” the surface.

and Verwey and Overbeek (1948) proposed a theory (today known as the DLVO theory) in which these interactions could be explained by the interplay between van der Waals (vdW) and electrostatic double-layer forces. However, recent studies indicate that the DLVO theory cannot account for additional interactions detected by AFM and other surface techniques, such as hydration and hydrophobic interactions. An extended DLVO theory (i.e., EDLVO) was then developed (Churaev & Derjaguin, 1985; Yotsumoto & Yoon, 1993), which involves hydration repulsive forces between hydrophilic surfaces, hydrophobic forces, and steric repulsive forces between polymer samples. In ELDVO, the total energy between particles is $V_T = V_W + V_E + V_{HR} + V_{HA} + V_{SR} + V_{MA}$, where V_W is the van der Waals attractive potential, V_E is the electrostatic repulsive potential, V_{HR} is the hydration repulsive potential, V_{HA} is the hydrophobic attractive potential, V_{SR} is the steric stabilization energy, and V_{MA} is the magnetic attraction energy.

RESULTS AND DISCUSSION

Figure 2 shows a typical force curve for a POEA film immersed in distilled water, $\text{pH} \approx 6$, at which POEA is predominantly dedoped. Under such condition, the repulsive double-layer force should be absent, and hence one should measure the attractive van der Waals force. The curve features several regimes. As the piezoscanner extended upward approaching the tip from A to B, the tip was pulled down by the attractive force and jumped to contact with the surface at B. The small, attractive van der Waals

Figure 3. Force curves for the tip approaching and being retracted from a POEA film with distinct speeds, as marked in the figure. Note that for low speeds, the tip does not jump back immediately for a situation of nil force, thus indicating continuing interaction with the polymer sample for a considerable distance. In contrast, at higher speeds, especially at $10^4 \mu\text{m/s}$, the tip is detached from the sample abruptly.

force barely appears in the plot, but it may be clearly visualized if different scales for the force are chosen, as we shall do when discussing data for cells containing ionic solutions (see also Fig. 3). Upon continued movement of the piezoscanner, from B to C, the cantilever bent upward as the tip pressed onto the surface. The slope of the curve in the contact region is a function of the elastic modulus and geometry of the tip and sample. This slope can be used to derive information on sample hardness or investigate whether the sample response varies with the load, for example, in a transition from elastic to plastic deformation (Burnham et al., 1990). When the tip reached position C, the piezoscanner retracted from the tip and the cantilever relaxed (point D). As the sample continued to retract, the cantilever bent downward between points D and E, due to the adhesion force, until reaching the break point E at which the cantilever rebounded sharply upward to point F. The adhesion force measured between points D and F can be expressed as

$$F = k\delta_{\max}, \quad (1)$$

where F is the interaction force (in nanoNewtons) between the AFM tip and sample and k and $\delta_{\max}$ are the elastic constant and the maximum deflection of the cantilever, respectively. For a POEA film immersed in water, the adhesion force, F_{ad} , calculated with equation (1) was $6.1 \pm 1.3 \text{ nN}$, whereas the van der Waals force, F_{vdW} , was $0.17 \pm 0.02 \text{ nN}$ for measurements performed in three distinct regions.

The results showed no interaction between tip and sample until their surfaces were approximately 1.9 nm from contact, after which an attractive jump-in force was ob-

served on approaching the tip. The short jump-in that occurs when the force gradient exceeds the spring constant is consistent with the estimated magnitude for van der Waals attractive interactions (Kokkoli & Zukoski, 1999; Butt et al., 2006). The magnitude and distance range of the measured attraction agree with the theoretical values calculated with the van der Waals–Lifshitz model in which a nonretarded Hamaker constant (Israelachvili, 1992) is used, as in equation (2):

$$F_{vdW} = -\frac{H_{132}R_t}{6D_o^2}, \quad (2)$$

where H_{132} is the Hamaker constant for medium 1 (tip) and 2 (polymer) interacting across medium 3 (water), R_t is the tip radius, and D_o^2 is the distance when the tip contacts with the surface, estimated to be ≈ 0.2 nm (Cappella & Dietler, 1999). For the tip (S_3N_4)–water–polymer system, the force was ca. 0.2 nN, which compares well with the experimental results from the force curve of Figure 2 ($H_{132} \approx 9.5 \times 10^{-22}$ J and $R_t \approx 56$ nm). The influence from indentation on the pull-off force (adhesion force) was also investigated. The indentation was measured from the origin to the left edge of the force-versus-distance curve (Weisenhorn et al., 1992). In our work, the adhesion between the tip and polymer surface increased when indentation increased.

The curve shown in Figure 2 was obtained with the tip approaching the sample and being withdrawn at a high speed of 10^4 $\mu\text{m/s}$, and with a low spring constant, 0.07 ± 0.02 N/m. In various experiments with POEA films, we observed that the force curves depended on these two parameters. Furthermore, the curves varied after several measurements had been performed in the same spot, due to the change in contact area and possible adsorption of polymer chains onto the tip. This occurs because the tip may be partially covered with POEA chains after a series of measurements, due to nonspecific interaction between the polymer and the tip, giving rise to the so-called bridge forces (Biggs & Proud, 1997; Fig. 4—see scheme). The adsorption of POEA to the AFM tip may be caused by attractive van der Waals forces and hydrogen bonding between the tip and the polymer chains. During separation of the tip, some POEA chains may be stretched, as we discuss later.

Adsorption is more likely when the tip approaches the sample at a low speed. At high speeds, the tip is detached from the sample almost immediately, whereas for low speeds detachment is gradual. The reason for such differences is that at high speeds the short times of contact decrease the probability of polymer adsorption onto the tip. This effect depends on the loading force applied by the tip, because for an elevated set point the tip penetrates deep into the sample. Figure 3 shows the influence of speed with force curves measured at various speeds and illustrates the appearance of the attractive van der Waals forces. The possible adsorption of POEA brings a number of consequences, the most impor-

Figure 4. Force curve obtained when extending chains of POEA from chrome surface in water with frequency of jumps < 1 $\mu\text{m/s}$: I: no tip-POEA interactions; II: film being compressed; III/IV: repulsive contact with the substrate; V: pull-off force due to surface adhesion; VI: cantilever “pulls off” the surface; VII: attractive peak due to stretching of POEA chains.

tant of which is that reproducibility of the results is considerably worse, as one should expect because the curves will depend on the amount of POEA adsorbed and how adsorption occurred. Among the possible results we get in a series of hundreds of measurements is the plot of Figure 4, obtained with frequency of jumps < 1 $\mu\text{m/s}$ and spring constant of 0.5 N/m. There is no sign in this figure of the van der Waals attractive force—though this contribution appeared in the majority of the curves because POEA is mostly dedoped in distilled water. As the cantilever approached the surface (region II), a nonlinear repulsive force started at $d \sim 293$ nm, corresponding to the compression of the film until reaching ca. 139 nm, where the chrome substrate surface was touched. The large repulsive force measured in region II is difficult to model theoretically because there may be several phenomena occurring simultaneously. These phenomena may include (1) electrostatic repulsion between the positively charged AFM tip (Bergstrom & Bostedt, 1990) and some islands of doped POEA (though the sample is primarily undoped, some doped islands may exist) or (2) polymer chain confinement between the tip and POEA during compression (Guffond et al., 1997).

A clear POEA adsorption could be identified in 15% of the force curves, which was denoted by the POEA–tip rupture in regions such as VI and VII of Figure 4. These withdrawal curves are similar to those in the literature (Mizes et al., 1991; Ortiz & Hadziioannou, 1999), characteristic of material adsorbed onto the tip. In subsidiary experiments with cantilevers of high elastic constant ($k \sim 3$ N/m)

and the same set point and withdrawal speeds, multiple events of POEA–tip rupture were observed (see inset of Fig. 4). In contrast, for lower loading forces ($k \sim 0.07$ N/m), the curve forces resembled those obtained with inorganic, flat substrates (Leite et al., 2003), with no rupture. In 40% of the measurements characteristic of POEA adsorption onto the tip, we may conjecture that a POEA single chain was being stretched and then use the cantilever's maximum extension, as calculated by Meadows (Meadows et al., 2003), as an estimate for the length of the chains. Obviously, several POEA chains could adsorb at the same time, or adsorption could occur through the middle of a chain, and in these cases no estimate can be done for the chain length. We obtained lengths in the range between 86 and 118 nm (backbone with $\sim 45 \pm 7$ tetramer units), with a most probable value of 102 nm, which are comparable to the length of a stretched POEA chain calculated using the average molecular weight obtained with high-performance size exclusion chromatography, namely, 90 ± 6 nm.

The presence of impurities in the cell, deliberately introduced or not, is found to affect the force curves. Here we employed aqueous solutions of a heavy metal to investigate the interactions between the substrate (covered with polymer) and the solution, to mimic the experimental situation in taste sensors. Figure 5a is a typical force curve obtained in water with pH 3, which shows the level of noise and repulsive double-layer forces. In the inset, a force curve obtained in aqueous solution with high Cu^{2+} concentration (1 mol/l) is shown, which features a small van der Waals interaction of 0.5 nN. Figure 5b shows schematically how force curves for POEA adsorbed onto chrome are affected by different quantities of CuSO_4 dissolved in water. The trend in Figure 5b is similar to that of Butt (1991b) for different KCl and MgCl_2 concentrations, as we discuss later on.

It is known that silicon nitride is electrically neutral over a wide pH range, at least from 6 to 8.5, indicating equal densities of silanol and silylamine surface groups (Drummond & Senden, 1994). Therefore, if POEA film is exposed to distilled water, both tip and sample are neutral, and the force curve displays a region of attractive forces. To study effects from impurities on the force curve, we performed experiments at low pH. For pH 3, both POEA and AFM tip are positively charged, leading to electrical double-layer forces (Weisenhorn et al., 1992). An analytical expression of this force, for different tip and sample shapes, has been

Figure 5. a: Typical force-displacement curve for POEA film in aqueous solution (in the inset, a force curve is shown for 1 mol/l of Cu^{2+}). b: Approach curves for POEA in a pH 3 cell with various concentrations of CuSO_4 : 10^{-5} mol/l (i), 10^{-3} mol/l (ii), 1 mol/l (iii), and 2.5 mol/l (iv). c: Histogram showing the number of times a given repulsive interaction was observed.

Figure 6. AFM top view images ($3 \times 3 \mu\text{m}^2$) of a POEA film imaged in air (a), aqueous solution of CuSO_4 (1 mol/l) (b), and aqueous solution of CuSO_4 (2.5 mol/l) (c).

provided by Butt (1991a) on the basis of an equation of Parsegian and Gingell (1972). For a spherical tip and a flat sample, the force is given by

$$F = \frac{2\pi R}{\epsilon_l \epsilon_0 \kappa} [(\sigma_T^2 + \sigma_s^2)e^{-2\kappa D} + 2\sigma_T \sigma_s e^{-\kappa D}], \quad (3)$$

where D is the distance between the surfaces, σ_T and σ_s are the surface charge densities of tip and sample, respectively, ϵ_l is the dielectric constant of the liquid, R is the tip radius, and κ is the inverse of the Debye length. For a divalent salt of concentration C (in moles per liter) and at 22°C , the Debye length is (Cappella & Dietler, 1999)

$$\kappa^{-1} = \frac{0.152}{\sqrt{C}} \text{ nm}. \quad (4)$$

The surface charge is balanced by dissolved counterions that are attracted back to the surface by the electric field, but spread away from the surface to increase the entropy (Butt et al., 1995). When the AFM tip approaches the sample, the double layer is perturbed and the concentration of ions between the surfaces increases, resulting in a repulsive force.

The force curves were obtained at Cu^{2+} concentrations between 10^{-5} mol/l and 2.5 mol/l. At low CuSO_4 concentrations, ca. 10^{-5} mol/l CuSO_4 , the force curve of Figure 5b resembles that obtained with water at pH 3 (Leite et al., 2005a). When the ionic strength of CuSO_4 solution was increased to 1 mol/l, the repulsive electrostatic contribution was suppressed, leading to an attractive force of 0.7 ± 0.2 nN. According to equation (3), with increasing CuSO_4 concentrations the repulsive force is expected to decrease, and the contribution from the attractive, van der Waals force becomes visible, as shown in Figure 5a for a concentration of 1.0 mol/l. At concentrations >2.5 mol/l of CuSO_4 again a repulsive force was measured. This repulsion is not due to a double-layer force, because at concentrations of ca. 3 mol/l the Debye length is only ~ 0.09 nm. It may be ac-

counted for in detail by the EDLVO theory (Churaev & Derjaguin, 1985). For instance, Pashley (1981) explained the repulsion between two surfaces by assuming that divalent cations adsorb onto the surfaces and bind layers of water. When the surfaces approach each other, the cations have to be dehydrated, which increases the free energy of the system and causes a repulsive force. The strength of the repulsive force depends on the degree of hydration of the ion, according to the order $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Li}^+ \cong \text{Na}^+ > \text{K}^+ > \text{Cs}^+ \gg \text{H}_3\text{O}^+$ (Cappella & Dietler, 1999). The hydration forces are correlated with the low energy of wetting of surfaces with water; thus this interaction can also be attributed to the energy required to remove the hydration water or the surface-adsorbed species (secondary hydration). Figure 5c shows histograms from a statistical analysis of over 300 consecutive force curves for each concentration of CuSO_4 . The considerable broad range of the measured repulsive force is due to the variety of factors that contribute to the tip-sample interaction. When extrapolating the repulsive force to zero distance the average values of double-layer force for concentrations of 10^{-5} and 10^{-3} mol/l were 1.8 ± 0.5 and 0.86 ± 0.08 nN, respectively. The average value for the hydration forces for a concentration of 2.5 mol/l was 2.8 ± 0.4 nN.

The hypothesis of hydration forces in curve (iv) in Figure 5b may appear inconsistent with the distance range at which they operate (typically <10 nm). However, we remind the reader that the sample displacement in the abscissa does not correspond to the sample-to-tip distance, for the latter can only be estimated if the cantilever deflection is taken into account (Cappella & Dietler, 1999). In a subsidiary data treatment we verified that a repulsive force only appeared at tip-to-sample distances smaller than 10 nm. In any case, the existence of the hydration force could also be inferred from the experimental results showing that for $[\text{CuSO}_4] > 10^{-3}$ mol/l, the double-layer force disappeared.

The morphology of POEA film also is affected by the environment, as illustrated in Figure 6a,b, which compares AFM images obtained in air and in an aqueous solution. For

POEA in air, Figure 6a shows small globules and aggregates with sizes ranging from 100 to 200 nm and from 200 to 360 nm, respectively, forming a well-defined POEA carpet. However, the film surface in aqueous solution is rougher and the globules are larger (Fig. 6b) with sizes ranging between 150 and 370 nm. The larger roughness is not caused by artifacts associated with the tip because in water the tip-POEA interaction is reduced. Thus, changes in the surface morphology may be due to rearrangement of POEA chains in solution due to interaction between Cu^{2+} ion, water, and POEA film. Figure 6c shows that for a POEA film in contact with a 2.5 mol/l solution, the size of the globules may be increased fivefold, in comparison with the size observed for POEA in contact with 1.0 mol/l solution. This trend was affected by the time period of contact between solution and film, because for short times no morphological changes were noted.

CONCLUSIONS

Adhesion forces between an AFM tip and a 10-layer POEA film, obtained with the layer-by-layer technique, have been studied with atomic force spectroscopy (AFS). The force curves for POEA in a liquid cell were found to depend on the speed with which the tip approached the sample and on the load. With high speeds, there is no adsorption of POEA onto the tip, and the adhesion forces could be measured reproducibly (see discussion for Fig. 2). In contrast, reproducibility in the force curve measurements was considerably worse if a low speed or a high load were used, particularly because of adsorption of POEA onto the tip. Such adsorption varies with several factors, and the data indicate that a bundle of chains or a single chain could be attached, as indicated in Figure 4. In the latter case, we may hypothesize that upon withdrawing the tip, the POEA chain was stretched and its length could be estimated. Indeed, we showed that the estimated lengths were within the range expected based on high-performance size exclusion chromatography results for the POEA molecular weight. It is envisaged that AFS may allow the controlled manipulation of individual chains or specific interactions, which can be applied to measuring specific impurities, distinguishing between polymer chains of different conformations or molecular weight and contaminants in the liquid cell. We also demonstrated that AFS measurements serve to investigate interactions in a taste sensor. Using, by way of illustration, different concentrations of CuSO_4 in aqueous solutions, we observed that with AFS one is able to detect changes at the interface caused by the presence of heavy metals. Particularly important was the possibility of measuring double-layer and hydration forces for doped POEA films, in an aqueous solution of pH 3. Solutions of low electrolyte concentration showed the typical features of the DLVO theory, whereas the interaction force at high electrolyte concentration was dominated by the repulsive hydration force. This suggests that ions in the liquid cell somehow affect the film/liquid interface, possibly

through adsorption and desorption of molecules, which can be relevant for environmental sensors.

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