

Phase Diagram for the Adsorption of Weak Polyelectrolytes at a Soft Charged Surface[†]Laurianne Vagharchakian,[‡] Bernard Desbat,[§] and Sylvie Hénon^{*,‡}

Matière et Systèmes Complexes, CNRS UMR 7057, Université Paris 7, case courrier 7056, 2 place Jussieu, 75251 Paris Cedex 05, France, and Laboratoire de Physico-Chimie Moléculaire, CNRS UMR 5803, Université de Bordeaux 1, 33405 Talence Cedex, France

Received: October 17, 2005; In Final Form: January 6, 2006

We have experimentally studied the adsorption of polyelectrolytes at oppositely charged surfaces. A weak flexible polyelectrolyte, poly(acrylic acid), was adsorbed from dilute solutions on a Langmuir film of a cationic amphiphile, dimethyldioctadecylammonium bromide. The polymer surface coverage, Γ , at equilibrium was measured by two reflectivity techniques—ellipsometry and polarization modulated infrared reflection absorption spectroscopy (PM-IRRAS)—as a function of the surface charge density, σ , and of the polymer ionization degree, α . Different adsorption regimes were evidenced. For weakly charged surfaces, $\sigma < \sigma^{\text{sat}}$, Γ increases with σ and with $1/\alpha$, as expected for a neutralization of the surface by the adsorbed polymers. For highly charged surfaces, $\sigma > \sigma^{\text{sat}}$, the adsorption of polyelectrolytes saturates. The mean orientation of the adsorbed chains also depends on the value of σ : it is parallel to the surface for $\sigma < \sigma^*$ ($< \sigma^{\text{sat}}$) and orthogonal to the surface for $\sigma > \sigma^*$. We have measured the values of σ^{sat} and σ^* as a function of α and compared the results with existing theories.

Introduction

Polyelectrolytes are important from the application point of view, because they constitute the main class of hydrosoluble polymers. They enter the formulation of numerous water-based manufactured products, such as suspensions of solid particles stabilized by the adsorption of oppositely charged polymers. Many biological mechanisms are also governed by the behavior of charged polymers (such as DNA or proteins) near charged surfaces (such as membranes). This is the main reason the adsorption of polyelectrolytes at oppositely charged surfaces has been the subject of much theoretical, numerical, and experimental work.^{1–9}

The comparison between experimental results and theoretical predictions is in general difficult, first because when working with polymers the equilibrium state is often difficult to be reached and second because much of the measurements have been performed with colloidal particles, in which the surface state is difficult to vary and to characterize, and moreover is often heterogeneous.

The present work describes an experimental quantification of polyelectrolyte adsorption at a single oppositely charged surface. To easily control the charges of the system, we have used a weak polyelectrolyte, poly(acrylic acid), and a Langmuir film of a charged amphiphile, dimethyldioctadecylammonium bromide, as a charged surface. The ionization degree, α , of the polymer is varied by changing the pH of the solutions, and the surface charge density, σ , is varied by compression/expansion of the Langmuir film. We have measured the amount of adsorbed polyelectrolyte as a function of α and σ , by two complementary reflectivity techniques: ellipsometry at the Brewster angle and infrared spectrometry.

Experimental Section

Polyelectrolyte Solution Preparation. Poly(acrylic acid) (PAA) and sodium polyacrylate were purchased from Sigma-Aldrich and used without further purification. The solutions of PAA were made in ultrapure water (18.2 M Ω ·cm, from a Millipore—Simplicity purifying system). The average degree of polymerization is about 70 ($M_w \approx 5000$ g/mol), and the polydispersity is 2.43. PAA is a flexible polymer, the monomer length, a , is about 0.25 nm, and at 25 °C it is close to θ -solvent conditions in water. The concentration of the polymer solutions was 12.5 ppm (1.7×10^{-4} mols of monomers per liter). At such a low bulk concentration and at pH > 4, PAA does not show any significant self-adsorption at the surface of water.^{10,11}

PAA is a weak polyacid. Its ionization degree, α —the fraction of dissociated carboxylic groups—depends on pH. The pH of the PAA solutions was varied from 4.8 to 8.5 by the addition of NaOH (Prolabo, Normapur), which corresponds to a variation of α from 0.12 to 0.78.

No salt was added to the solutions, except NaOH for pH adjustment: the salinity of the solutions was always low.

Langmuir Film Preparation. Dimethyldioctadecylammonium bromide (DODA) was purchased from Sigma-Aldrich and used without further purification (purity > 99%). It was dissolved in chloroform at a concentration of about 0.5 mg/mL. The solutions were stored at 4 °C and frequently renewed to avoid aging problems. The Langmuir films were obtained by spreading with a microsyringe controlled quantities of the DODA solution at the free surface of the polyelectrolyte solutions, after cleaning the surface with a suction device. A small round Teflon trough ($\varnothing \approx 6$ cm) was used for ellipsometry experiments, and a Langmuir trough coated with Teflon (Nima, 6.5×12 cm²) was used for polarization modulated infrared reflection absorption spectroscopy (PM-IRRAS) experiments.

Since each DODA molecule carries a monovalent and permanent charge, the surface of the solutions is charged by the presence of the DODA Langmuir film. The surface charge

[†] Part of the special issue "Charles M. Knobler Festschrift".

^{*} Corresponding author. E-mail: henon@ccr.jussieu.fr.

[‡] CNRS UMR 7057, Université Paris 7.

[§] CNRS UMR 5803, Université de Bordeaux 1.

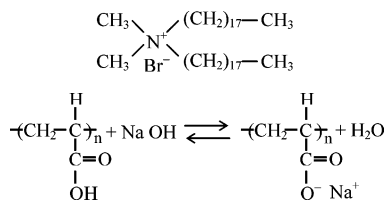


Figure 1. Chemicals used in this work: dimethyldioctadecylammonium bromide (DODA) and poly(acrylic acid) (PAA).

density is equal to σe , with σ being the DODA film density and e being the unit charge.

Surface Pressure and Compression Elasticity Measurements. The surface pressure measurements were held in a home-built thermostated Langmuir trough, $13 \times 30 \text{ cm}^2$, coated with Teflon, and equipped with a Wilhelmy plate system (R&K, Germany, resolution 0.1 mN/m). The compression rate was about $5 \text{ \AA}^2 \text{ molecule}^{-1} \text{ min}^{-1}$. The compression elastic modulus of a film is defined as $\epsilon = -S d\pi/dS = \sigma d\pi/d\sigma$, where π is the surface pressure, S is the total area of the film, A is the area per amphiphile molecule, and $\sigma = 1/A$ is the density of the film. The compression moduli were calculated directly from isotherms $\pi(A)$ as $\epsilon \approx -A[\pi(A + \Delta A/2) - \pi(A - \Delta A/2)]/\Delta A$, with $\Delta A \approx 5 \text{ \AA}^2/\text{molecule}$. Before these calculations, the isotherms were smoothed, by averaging the measurements over a few $\text{\AA}^2/\text{molecule}$.¹²

Ellipsometry. The instrument we used was described elsewhere in detail.¹³ We measured the ellipticity, ρ_B^{DODA} , of the DODA film on water and the ellipticity, ρ_B , of the DODA film on a PAA solution. The difference $\Delta\rho_B = \rho_B - \rho_B^{\text{DODA}}$ is directly proportional to Γ : $\Delta\rho_B = \beta\Gamma$.¹⁴ The constant β is equal to $2(\pi/\lambda)[\sqrt{(1+n_w^2)/n^2}]C$, where λ is the wavelength, n_w is the refractive index of water (1.33), and C is the refractive index increment, which characterizes the variation of the refractive index, n , of a PAA solution with its concentration, c : $C = (dn/dc)$. The values of C for different polymers are tabulated;¹⁵ C is equal to $1.6 \times 10^{-2} \text{ nm}^3/\text{molecule}$ for PAA, and we finally obtain $\beta \approx 2.0 \times 10^{-4} \text{ nm}^2/\text{molecule}$.

Infrared Spectrometry. PM-IRRAS. Polarization modulated infrared reflection absorption spectroscopy (PM-IRRAS) is an appropriate technique to evidence the presence and the organization of adsorbed molecules at the air–water interface.^{16–18} The intensity of an absorption band in a PM-IRRAS spectrum is proportional to the density of adsorbed molecules and to a function of their orientation with respect to the surface. In particular, with the experimental setup used in this study, a band is positive if the angle, γ , between the absorption moment and the normal to the water surface is greater than 38° (absorption moment close to the water surface) and negative if $\gamma < 38^\circ$ (absorption moment close to the water surface normal).¹⁶ The PM-IRRAS signal is also sensitive to the water in the subphase. To eliminate this contribution, the presented spectra are the normalized differences of spectra with and without DODA:¹⁶ spectra were first recorded on polyelectrolyte solutions without amphiphiles, DODA molecules were then spread onto the solutions, and spectra of the mixed films (DODA–PAA) were recorded for different densities of the DODA Langmuir film. In infrared spectra, one can clearly distinguish the bands corresponding to the acid form of a carboxylic acid from the bands corresponding to its basic (carboxylate) form, and thus, one can in principle have access to the ionization degree at the interface.^{18,19}

FTIR Spectroscopy. Transmittance Fourier transform infrared (FTIR) spectroscopy was used to determine the complex optical indices of poly(acrylic acid) and sodium polyacrylate.²⁰ Using

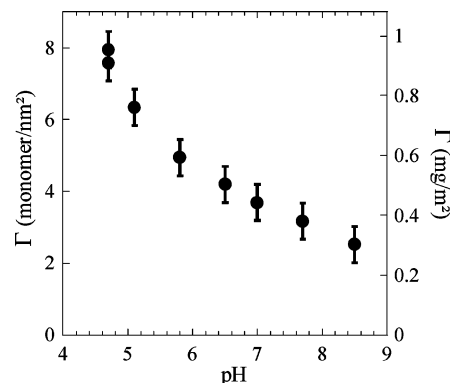


Figure 2. Quantity of adsorbed polymers, Γ , measured by ellipsometry, as a function of pH, for a surface charge density, σ , equal to $0.9 \text{ charge/nm}^2 \approx 0.14 \text{ mC/m}^2$.

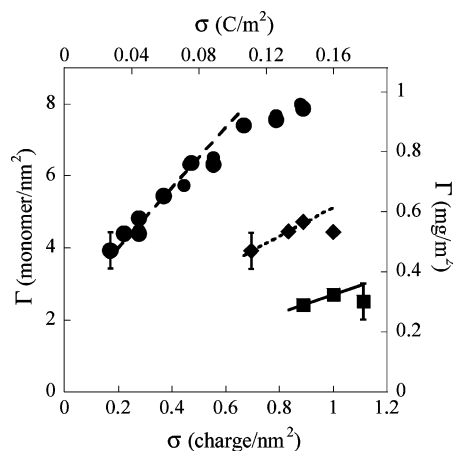


Figure 3. Quantity of adsorbed polymers, Γ , measured by ellipsometry, as a function of the surface charge density, σ , for three values of pH: 4.8 (circles), 5.8 (diamonds), and 8.5 (squares). The error bars are represented on one measurement at each pH.

the measured indices, PM-IRRAS spectra of the polymer film at the air–water interface can be simulated with homemade software and compared with the experimental ones.^{16–18} Our FTIR experiments were performed at normal incidence on thin films of poly(acrylic acid) and sodium polyacrylate deposited by spin-coating on a ZnSe substrate.

Results

Ellipsometry. Figures 2 and 3 show adsorbed amounts of PAA, Γ , as measured by ellipsometry. The values displayed are equilibrium values. Equilibrium is reached in a few minutes (for high pH values) to a few hours (for low pH values).^{12,14} In Figure 2, Γ (in mg/m^2 and monomers/nm^2) is plotted as a function of pH at a given surface charge density, $\sigma = 0.9 \text{ charge/nm}^2 \approx 0.14 \text{ mC/m}^2$. The polymer surface coverage decreases when the pH increases, that is, when the polymer charge density increases. The measured quantities are comparable with previous measurements of PAA adsorption on charged solid particles.²¹ In Figure 3, Γ is plotted as a function of σ at given pH values: 4.8, 5.8, and 8.5. The polymer surface coverage increases with the surface charge density. This is consistent with an adsorption governed by electrostatic interactions. More quantitatively, Figure 3 shows Γ (in mg/m^2 and in monomers/nm^2) as a function of σ (in C/m^2 and in charge/nm^2). At pH 4.8 and for low values of σ , the measurements are consistent with a neutralization of the surface charge by the adsorbed polymers with a small overcompensation: $\Gamma = (\sigma + \delta\sigma_0)/\alpha$.^{7,8,14} The fit displayed in Figure 3 gives $\delta\sigma_0 = 0.3 \text{ charge/nm}^2$ and $\alpha = 0.13 \pm 0.02$, a

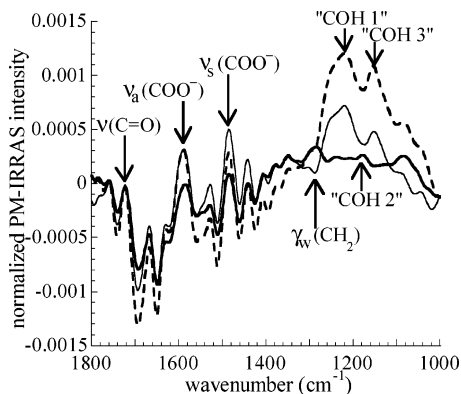


Figure 4. PM-IRRAS spectra of PAA adsorbed at a DODA Langmuir film from a PAA solution, 1.7×10^{-4} mols of monomers/L, pH 6.5, $T \approx 20$ °C, and for three different values of the surface charge density: $\sigma = 0.75$ molecules/nm² (thick plain line), $\sigma = 0.86$ molecules/nm² (thin plain line), $\sigma = 0.98$ molecules/nm² (dashed line). See text for the identification of the absorption bands.

value close to the ionization degree of PAA in solution: 0.12 ± 0.01 . For higher values of σ ($\sigma > 0.65$ charge/nm²), Γ seems to saturate.

For higher pH values, the resolution of the measurements is too low to allow a clear quantification of Γ . Nevertheless, the measurements are consistent with a regime of surface charge neutralization followed by a saturation of Γ . The fits displayed in Figure 3 give $\alpha = 0.25 \pm 0.03$ for pH 5.8 and $\alpha = 0.4 \pm 0.4$ for pH 8.5 ($\alpha = 0.26 \pm 0.02$ and 0.78 ± 0.02 , respectively, in solution).

PM-IRRAS. Experimental PM-IRRAS Spectra. Typical PM-IRRAS spectra are displayed in Figure 4. We have studied the bands specific to the carboxylic group in the 1000–1800 cm⁻¹ spectral range. The absorption bands relative to the basic form are the carboxylate antisymmetric (ν_a COO⁻) and symmetric (ν_s COO⁻) stretching vibration bands, located at 1590 and 1485 cm⁻¹, respectively.²² The absorption bands relative to the acid form are the carbonyl stretching vibration mode (ν C=O) at 1720 cm⁻¹ and three bands (denoted in the following as “COH1” to “COH3”) between 1100 and 1300 cm⁻¹ corresponding to interacting C—O stretching (ν C—O) and O—H deformation (δ OH) modes.²² The band in the 1325 cm⁻¹ region corresponds mainly to CH₂ “wagging” (γ_w CH₂),²² a collective vibration of the CH₂ groups along the polymer chain. Finally, the presence of a dip around 1650 cm⁻¹, corresponding to the dispersion of the water refractive index, is the signature of different optical responses of covered and uncovered water surfaces: penetration of water in the PAA film, changes in the orientation of the water molecules.¹² Only one minor band relative to DODA is also present in this range, the CH₂ stretching band (ν CH₂) located at 1450 cm⁻¹, which is too weak to be observed in the presented spectra.

Since the intensity of a PM-IRRAS band is directly proportional to the quantity of adsorbed molecules,¹⁶ the comparison between the COO⁻ and COOH bands should allow a determination of the ionization degree, α , of adsorbed polyelectrolytes. Unfortunately, the orientation of the adsorbed molecules (with respect to the surface) also contributes to the intensity of the bands.^{16,18} To evaluate the contribution of the molecular orientation, the experimental spectra were compared to simulated ones.

Simulated PM-IRRAS Spectra. Normalized PM-IRRAS spectra were simulated, using optical indices of PAA determined from experimental FTIR spectra, and by assuming an isotropic distribution of the orientation of the adsorbed monomers.^{16–18,20}

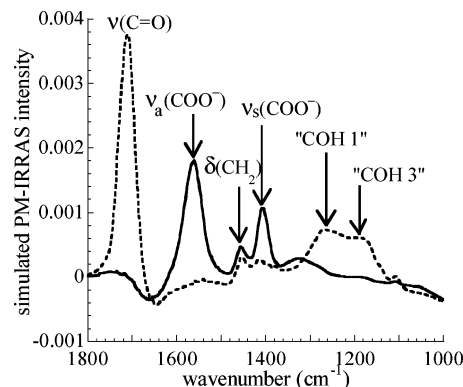


Figure 5. PM-IRRAS spectra of the acid form PAAH of PAA (dashed line) and of its basic form PAA⁻ (plain line) simulated at the air–water interface with the optical indices measured by FTIR spectroscopy. An isotropic distribution of the orientation of the adsorbed molecules is assumed.

Figure 5 shows the simulated signals as a function of wavenumbers, for PAAH and PAA⁻ adsorbed at the air–water interface, as a thin layer with a thickness of 10 Å and a density of 1. The intensity of the carbonyl stretching band (ν C=O) is expected to be almost 5 times greater than the ones of the C—O and O—H bands. The relative intensities of the bands in the experimental spectra (Figure 4) largely differ from that of the simulation (Figure 5). This demonstrates that the adsorbed COOH groups show a preferred orientation.¹² The contribution of the orientation is difficult to evaluate, and a quantitative determination of the adsorbed amounts from the analysis of the band intensities was not possible.

Nevertheless, it can be assumed that the variations in the intensities of the bands are representative of the variations of the amount of adsorbed monomers.

PM-IRRAS Measurements. In Figure 4, three PM-IRRAS spectra are displayed, for PAA solutions of pH 6.5 ($\alpha = 0.37$) and for three different values of the surface charge: $\sigma = 0.75$ charge/nm² (thick plain line), $\sigma = 0.86$ charge/nm² (thin plain line), and $\sigma = 0.98$ charge/nm² (dashed line). Almost all of the band intensities (with respect to the baseline) increase with σ , which shows that the quantity of adsorbed PAA increases with the surface charge. All of the bands are positive with respect to the baseline for $\sigma \approx 0.75$ charge/nm², whereas two bands are negative for higher values of σ : the (γ_w CH₂) and “COH2” bands. This demonstrates a change in the orientation of the adsorbed molecules. Since the transition moment relative to the CH₂ wagging band is parallel to the polymer chain,²² the angle between the adsorbed chains and the water surface is small at low density and large at high density. This is consistent with a change in the orientation of the adsorbed polymers, from lying flat at the surface for $\sigma < \sigma^*$ to forming a 3D adsorbed layer for $\sigma > \sigma^*$, with a mean orientation of the chains orthogonal to the surface,¹² as predicted by existing theories.^{7,8} The same transition in the orientation of the adsorbed polymers was observed for different pH values. The surface charge, σ^* , of this transition depends on pH: σ^* increases with increasing pH.¹²

Figure 6 shows the intensities of the (ν_s COO⁻) and “COH1” bands as a function of pH for a fixed value of σ : 1 charge/nm² (0.16 C/m²). Within the experimental resolution, the adsorbed amount of COO⁻ groups, Γ_{COO^-} , does not depend on pH. This is again consistent with an adsorption governed by electrostatic interactions: if the surface charge is neutralized by the adsorption of charged COO⁻ monomers, Γ_{COO^-} is expected to be independent of pH and equal to σ . The adsorbed amount of

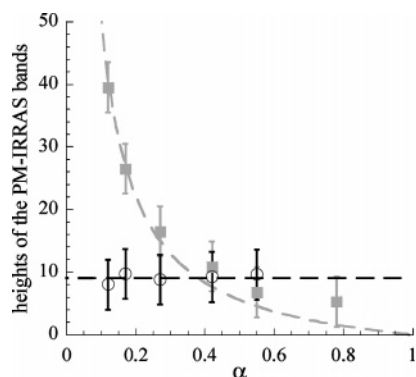


Figure 6. Heights of the ($\nu_s \text{COO}^-$) (circles) and “COH1” (squares) bands as a function of the ionization degree, α , of PAA and for a fixed value of the surface charge density: $\sigma = 1 \text{ charge/nm}^2$ (0.16 C/m^2).

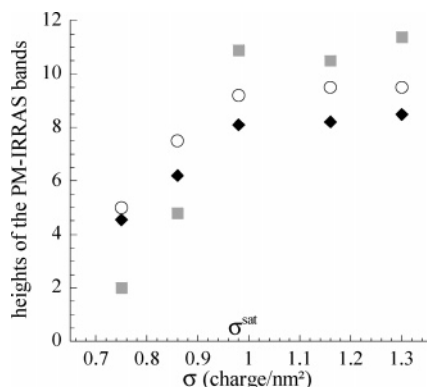


Figure 7. Heights of the ($\nu_s \text{COO}^-$) (circles), “COH1” (squares), and ($\nu \text{C=O}$) (diamonds) bands as a function of the surface charge density, σ , and for a fixed pH value of 6.5 (ionization degree $\alpha = 0.42$). The heights saturate for $\sigma > \sigma^{\text{sat}}$.

uncharged monomers, Γ_{COOH} , is thus expected to be equal to $\sigma[(1/\sigma) - 1]$. A plot of Γ_{COOH} by such a function of α is also displayed in Figure 6: it is consistent with the measurements for small values of α (< 0.3), but for higher values of α , the amount of adsorbed COOH groups is higher than expected.

Figure 7 shows the intensities of the ($\nu_s \text{COO}^-$), ($\nu \text{C=O}$), and “COH1” bands as a function of σ for a fixed value of pH: 6.5 ($\alpha = 0.37$). Two adsorption regimes are observed. For small values of σ , $\sigma < \sigma^{\text{sat}}$, the amount of adsorbed polyelectrolytes increases with σ . For high values of σ , $\sigma > \sigma^{\text{sat}}$, the quantity of adsorbed polymer saturates.

Comparison between Ellipsometry and PM-IRRAS Measurements. The results of the two reflectivity techniques are compared in Figure 8. The total amount of adsorbed monomers, Γ , measured by ellipsometry and the amount of adsorbed COO^- monomers, Γ_{COO^-} , measured by PM-IRRAS are plotted together as a function of σ , at pH 4.8 ($\alpha = 0.12$). The variations of the adsorbed quantities obtained by the two techniques are consistent with each other and confirm the existence of two adsorption regimes: when $\sigma < \sigma^{\text{sat}}$, with $\sigma^{\text{sat}} \approx 0.67 \text{ charge/nm}^2$, both Γ and Γ_{COO^-} increase with σ ; when $\sigma > \sigma^{\text{sat}}$, the adsorbed quantities saturate. The same behavior was observed at different pH values. The density, σ^{sat} , for which the adsorbed quantities saturate depends on pH: σ^{sat} increases with pH.

Compression Elastic Modulus Measurements. Figure 9 shows the compression elastic modulus, ϵ , of mixed DODA–PAA films as a function of σ and for different values of pH: 5.1, 5.8, and 8.5, corresponding to $\alpha = 0.16$, 0.26, and 0.78. For low values of σ , $\epsilon = 0$ because the film shows a first-order phase transition.¹² Then, the film enters a homogeneous phase;

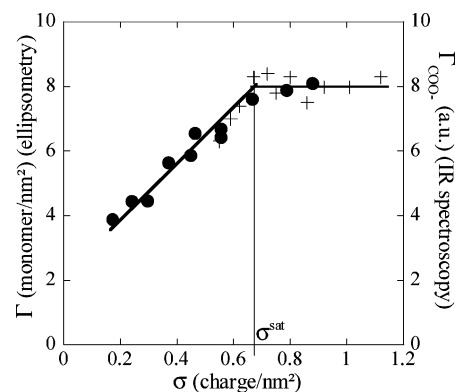


Figure 8. Amounts of adsorbed monomers, Γ , measured by ellipsometry and of adsorbed ionized monomers, Γ_{COO^-} , measured by PM-IRRAS, plotted as a function of the surface charge density, σ , for a fixed pH value of 4.8 ($\alpha = 0.12$). The adsorbed amounts saturate for $\sigma > \sigma^{\text{sat}}$.

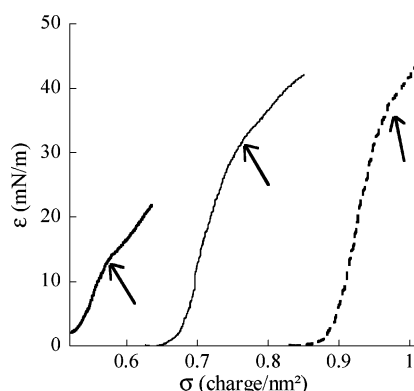


Figure 9. Compression elastic modulus, ϵ , as a function of the surface charge density, σ , for films adsorbed at the surface of PAA solutions, and for three different values of the ionization degree: $\alpha = 0.16$ (thick plain line), 0.26 (thin plain line), and 0.78 (dashed line). The arrows point to kinks in the curves.

its compressibility steps to a nonzero value and rapidly increases with σ (here, the step is smoothed because ϵ is calculated from smoothed isotherms). The DODA film remains homogeneous and does not show any phase transition until high values of σ (> 1.2 – $1.6 \text{ molecules/nm}^2$, depending on pH).¹² The $\epsilon(\sigma)$ isotherms show a kink for $\sigma = \sigma_0$, and for $\sigma > \sigma_0$, ϵ increases with σ about 4 times less rapidly than for $\sigma < \sigma_0$ (once again, the kink is smoothed because ϵ is calculated from smoothed isotherms). A comparison with the PM-IRRAS measurements shows that $\sigma_0 = \sigma^*$: the regime change in the compressibility is the signature of the transition from a dense two-dimensional adsorbed layer, difficult to compress, to a three-dimensional adsorbed layer, which is easier to compress by changing its thickness.¹²

Figure 10 shows the values of σ^{sat} , as measured by ellipsometry and by PM-IRRAS, and of σ^* , as measured by PM-IRRAS and elasticity measurements, as a function of the ionization degree, α , of PAA. Both increase with α and saturate for high values of α .

Discussion

A major difficulty arising when working with adsorbed layers of polyelectrolytes is that their density and their structure depend on history.^{23,24} Such an effect does not appear in this work: the state reached by the film is the same whether it has been obtained by direct adsorption, or by compression, or by expansion of a previously adsorbed film.¹⁴ Moreover, the

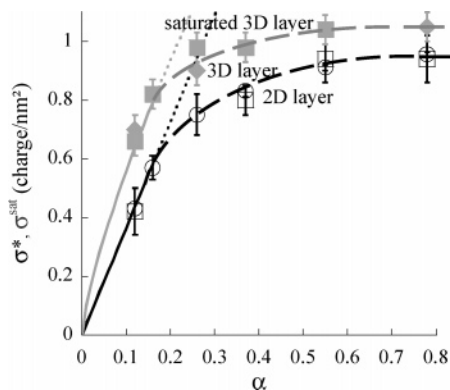


Figure 10. Surface charge densities of the two regime changes as a function of the PAA ionization degree, α : σ^* (change in the orientation of the adsorbed chains) and σ^{sat} (saturation of the adsorbed amounts). The measurements were obtained by ellipsometry (squares), PM-IRRAS (circles), and elasticity measurements (diamonds). Predicted values of σ^* and σ^{sat} are also displayed: $\sigma^* \approx f/a^2$ and $\sigma^{\text{sat}} \approx f^{3/4}/(a^3 l_B)^{1/2}$ (plain and dotted lines). The dashed lines are guides for the eyes which underline the saturation of σ^* and σ^{sat} .

equilibrium state is reached within a few minutes to a few hours, rather than days. This is probably because the polyelectrolytes we use are very short. This allows us to compare our results with theoretical predictions for equilibrium states.

Our measurements evidence different regimes for the adsorption of PAA at DODA films: in a first regime, the adsorbed polyelectrolytes neutralize the surface charge with a small overcompensation, and in a second regime, the polymer surface coverage is independent of the surface charge value; the conformation of the adsorbed polyelectrolytes also shows two regimes: at low surface density, they lie flat at the surface, forming a 2D layer, whereas, at high surface density, they form a 3D layer, with a mean orientation of the adsorbed chains orthogonal to the surface. The corresponding phase diagram is shown in Figure 10. Both σ^* and σ^{sat} steeply increase with α for low values of α and saturate for high values of α , presumably because α saturates. There are several possible explanations for such a saturation of the ionization degree. The value of α is governed by both the local pH and the local electric field,²⁵ the values of which differ at the surface and in solution, and α has different values for adsorbed PAA and PAA in solution.²⁶ Values of α smaller for adsorbed polymers than in solution, or values of pH smaller at the surface than in solution, have indeed already been observed.^{23,18} Furthermore, the values of σ^* and σ^{sat} are governed by the polymer charge fraction, f (fraction of charged monomers), rather than by the polymer ionization degree, α (fraction of dissociated monomers); f could be smaller than α for adsorbed PAA, as it is for PAA in solution because of the Manning counterion condensation.²⁷

The results of our measurements differ from the ones of other groups on similar systems.^{28,29} In particular, we do not observe a strong charge overcompensation. The main differences here are that we work at very low salinity, with short polyelectrolytes, and in θ -solvent conditions,^{15,25} whereas strong overcompensations are expected to be observed at intermediate salinity⁵ or when there is a short range attraction between the monomers and the interface.^{5,28} A study of the dependence of the adsorbed quantities on the salinity would have been desirable.^{7,8} Unfor-

tunately, when we add salts to the system, we face classical problems met when working with polyelectrolytes—very slow dynamics, metastable states of the films—and we are unable to obtain reproducible results.

The two regime changes observed in this study have been predicted theoretically:^{7,8} σ^* is predicted to be equal to f/a^2 and σ^{sat} to $f^{3/4}/(a^3 l_B)^{1/2}$ in θ -solvent, with f being the polymer charge fraction, a the size of the monomer, and l_B the Bjerrum length. This is indeed consistent with the experimental measurements but only for very low values of α , with $f = \alpha$ and $a \approx 0.5$ nm (expected value: 0.25 nm). Note that in the predicted values of σ^* and σ^{sat} all numerical prefactors have been omitted. For higher values of α , the measured values of σ^* and σ^{sat} are smaller than predicted; this is consistent with a saturation of α or of f .

Acknowledgment. The authors are indebted to J. Meunier and D. Bonn for the use of the ellipsometer.

References and Notes

- (1) Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at interfaces*; Chapman and Hall: London, 1993.
- (2) Eisenriegler, E. *Polymers Near Surfaces*; World Scientific: Singapore, 1993.
- (3) De Gennes, P.-G. *Scaling concepts in Polymers Physics*; Cornell University Press: Ithaca, NY, 1973.
- (4) Borukhov, I.; Andelman, D.; Orland, H. *Macromolecules* **1998**, *31*, 1665.
- (5) Joanny, J.-F. *Eur. Phys. J. B* **1999**, *9*, 117.
- (6) Netz, R.; Joanny, J.-F. *Macromolecules* **1999**, *26*, 32.
- (7) Dobrynin, A. V.; Deshkovski, A.; Rubinstein, M. *Phys. Rev. Lett.* **2000**, *84*, 3101.
- (8) Dobrynin, A. V.; Deshkovski, A.; Rubinstein, M. *Macromolecules* **2001**, *34*, 3421.
- (9) Netz, R.; Andelman, D. *Phys. Rep.* **2003**, *380*, 1.
- (10) Ishiyama, Y.; Ueberreiter, K. *Colloid Polym. Sci.* **1980**, *258*, 928.
- (11) Okubo, T. *J. Colloid Interface Sci.* **1988**, *125*, 386.
- (12) Vagharchakian, L.; Hénon, S. *Macromolecules* **2004**, *37*, 8715.
- (13) Meunier, J. In *Colloides et Interfaces*; Cazabat, A.-M., Veyssié, M., Eds.; Les Editions de Physique: Les Ulis, France, 1984.
- (14) Vagharchakian, L.; Hénon, S. *Langmuir* **2003**, *19*, 7989.
- (15) *Polymer Handbook*, 4th ed.; Brandrup, J.; Immergut, E. H., Grulke, E. A., Eds.; Wiley-Interscience: New York, 1999.
- (16) Blaudez, D.; Buffeteau, T.; Cornut, J.-C.; Desbat, B.; Escafre, N.; Pezolet, M.; Turlet, J.-M. *Appl. Spectrosc.* **1993**, *47*, 869.
- (17) Blaudez, D.; Turlet, J. M.; Dufourcq, J.; Bard, D.; Buffeteau, T.; Desbat, B. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4, 525.
- (18) Le Calvez, E.; Blaudez, D.; Buffeteau, T.; Desbat, B. *Langmuir* **2001**, *17*, 670.
- (19) Sukhishvili, S. A.; Granick, S. *Langmuir* **2003**, *19*, 1980.
- (20) Buffeteau, T.; Desbat, B. *Appl. Spectrosc.* **1989**, *43*, 1027.
- (21) Blaakmeer, J.; Höhmer, M. R.; Cohen Stuart, M. A.; Fleer, G. J. *Macromolecules* **1990**, *23*, 2301.
- (22) Leyte, J. C.; Zuiderweg, L. H.; Vledder, H. J. *Spectrochim. Acta, Part A* **1967**, *23*, 1397.
- (23) Sukhishvili, S. A.; Dhinojwala, A.; Granick, S. *Langmuir* **1999**, *15*, 8474.
- (24) Théodoly, O.; Ober, R.; Williams, C. *Eur. Phys. J. E* **2001**, *5*, 51.
- (25) Mandel, M. In *Chemistry and Technology of Water Soluble Polymer*; Finch, C. A., Ed.; Plenum Press: New York, 1983.
- (26) Cohen Stuart, M. A.; Fleer, G. J.; Lyklema, J.; Norde, W.; Scheutjens, J. M. H. *Adv. Colloid Interface Sci.* **1991**, *34*, 477.
- (27) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 954.
- (28) Ahrens, H.; Baltes, H.; Schmitt, J.; Mohwald, H.; Helm, C. A. *Macromolecules* **2001**, *34*, 4504.
- (29) Schnitter, M.; Engelking, J.; Heise, A.; Miller, R. D.; Menzel, H. *Macromol. Chem. Phys.* **2000**, *201*, 1504.