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Effects of Molecular Weight and Salt Concentration on the Thickness of Sodium Poly(styrenesulfonate) Adsorbed on a Metal Surface. 3.[†] Comparison with Scaling Concepts

Masami Kawaguchi,* Kasumi Hayashi, and Akira Takahashi

Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514, Japan.

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ABSTRACT: Replicate measurements of the adsorption of sodium poly(styrenesulfonate) from NaCl aqueous solutions onto a platinum plate at the polymer concentration in the plateau region were carried out by ellipsometry at 25 °C. In particular, the dependences of molecular weight and NaCl concentration on the thickness of the adsorbed layer were extensively investigated. Reproducibilities of the experiments were very good, with the error being less than 10%. The measured thickness, *t*, nearly corresponds to the diameter of the polyelectrolyte chains in solution. In a Θ solvent (4.17 M NaCl) the measured exponent of the molecular weight dependence was 0.5 while in good solvent conditions the exponent was 0.4. These values of exponents were in good agreement with those for adsorption of nonionic polymers and were interpreted by taking into account the central region of the concentration profile in the adsorbed layer derived from scaling concepts. The exponent of salt concentration dependence of the thickness of the adsorbed layer was found to be −0.2, and this exponent appears to hold for other experiments but was different from the predictions based on scaling concepts.

Adsorption of a polyelectrolyte onto interfaces plays an important role in science and technology. In the past 3 decades, efforts have been made to understand the fundamental nature of the adsorption of a polyelectrolyte. In the adsorption of a polyelectrolyte, factors such as the sign of the charges on the chain and the sign and number of charges on the substrate have an important effect, and three cases for polyelectrolyte adsorption have been considered: (1) adsorption on the oppositely charged substrate, where the driving force for the adsorption corresponds to the electrostatic attractive interaction between the oppositely charged polyion and substrate and the fraction of polymer segment adsorbed is expected to be large, (2) adsorption on the charged substrate of the same sign, where the driving force for the adsorption would be governed by a nonelectrostatic interaction between polymer segments and substrate, and hence the adsorption may be very weak due to the opposing effects of electrostatic repulsive forces not only between segments but also between segments and substrate, and (3) adsorption on the uncharged substrate, where the driving force is the nonelectrostatic interaction, and it is expected that the adsorption is moderate or strong depending on the strength of the nonelectrostatic force which is sufficiently larger than the electrostatic repulsive force between polymer segments.

A theory to describe quantitatively these features of polyelectrolyte adsorption has been reported by Hesselink[1,2] and only his theory is available to compare with experiments. Nevertheless, the quantitative studies for adsorption of polyelectrolyte were rare, and most works[3-8] were concerned with the determinations of the adsorbance of polyelectrolyte and the fraction of segments adsorbed.

For experimental measurements of the other important quantity such as the thickness of the adsorbed polyelectrolyte layer, which is necessary to infer the conformation of adsorbed polyelectrolyte, a few experiments have been reported. Pefferkorn, Dejardin, and Varoqui[9] reported the hydrodynamic thickness of alternative copolymers of maleic acid and ethyl vinyl ether adsorbed on the pore walls in cellulose ester filters. For adsorption of a polyelectrolyte onto an uncharged metal surface in added aqueous salt solution, we first extended the ellipsometry to the adsorption of a polyelectrolyte,[10] and in this work the adsorbance of a simple salt was measured besides the adsorbance of a polyion as well as the thickness of an adsorbed polyelectrolyte layer.

Recently, we measured the adsorption of sodium poly(styrenesulfonate) on a platinum plate using ellipsometry in NaCl aqueous solutions as a function of molecular weight at 25 °C.[11] It was found that the adsorbance of polyion is proportional to the square root of added salt concentration, in qualitative agreement with Hesselink's theory. The exponent obtained for the molecular weight dependence of the thickness of the adsorbed layer in good solvent condition was less than 0.5, but we could not determine precisely the exponent because of the lack of strict reproducibility of the data on the thickness.

In this paper, replicate measurements of the adsorption of sodium poly(styrenesulfonate) onto platinum plates were carried out by ellipsometry to check the reproducibility of the experiments. The measuring concentrations are well in the plateau region as reported previously.[11] The exponents of the molecular weight and salt concentration dependences of the thickness of the adsorbed polyelectrolyte layer are determined, and then these exponents are quantitatively compared with those predicted from scaling concepts.[12]

Experimental Section

Materials. Four sodium poly(styrenesulfonates) (NaPSS) prepared by sulfonation of polystyrenes with a narrow molecular weight distribution were purchased from Pressure Chemical Co. Characteristics of NaPSS given by the manufacturer are listed in Table I.

Intrinsic viscosity measurements of NaPSS in NaCl aqueous solutions were carried out with an Ubbelohde viscometer at 25 °C, and the data are summarized in Table I.

Water was doubly distilled by an all-Pyrex apparatus. Analytical grade NaCl was used without further purification.

A platinum plate (12 × 57 × 0.5 mm) was used as an adsorbent. It was cleaned by soaking in a hot concentrated aqueous HNO_3–H_2SO_4 (1:1) mixture, washed thoroughly with distilled water, and then quickly dried in a dust-free box equipped with a heating lamp.

Ellipsometry. Adsorption measurements NaPSS onto a platinum plate were carried out by using a Shimadzu P-10 type ellipsometer. The platinum plate was vertically placed in a glass cell with a volume of 200 mL. The measuring temperature was controlled at 25 ± 0.1 °C by circulating thermostated water.

The light source was a Nihon Denchi SH-85 type high-pressure mercury lamp. The wavelength of the incident light was 546 nm, and the incident angle was 70°.

[†] Parts 1 and 2 are ref 20 and 21, respectively.

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Table I
Characteristics of Sodium Poly(styrenesulfonate)

sample	$M \times 10^{-3}$	deg of sulfonation	$[\eta]_{4.17\text{M NaCl}}$, 100 mL/g	$[\eta]_{0.5\text{ M NaCl}}$, 100 mL/g	$[\eta]_{0.1\text{ M NaCl}}$, 100 mL/g
NaPSS-1	88	0.89	0.068	0.260	0.286
NaPSS-2	177	0.81	0.107	0.430	0.640
NaPSS-3	354	0.99	0.126	0.610	1.14
NaPSS-4	1060	0.92	0.268	1.72	2.80

The ellipsometric data for the refractive index, n_f, and the thickness, t, of the uniform adsorbed layer were calculated by computer from the experimental values of the phase difference, Δ, and the azimuth angle, ψ, of the amplitude ratio.

Since the salt added polyelectrolyte solution consists of polyion, simple salt, and water, the components in the adsorbed layer are also considered to be the same as the bulk solution. For determinations of both adsorbances of polyion and simple salt from the measured n_f and t, we assumed the Donnan equilibrium between the bulk phase and the adsorbed layer as described in our previous papers.[10,11] The relationships used are as follows:

$$n_f = \left[\frac{\bar{M} + 2d\bar{R}}{\bar{M} - 2d\bar{R}}\right]^{1/2} \quad (1)$$

where $\bar{M}$ is the mean molecular weight, $\bar{R}$ is the mean molar refractivity, and d is the density of the adsorbed layer. $\bar{M}$ and $\bar{R}$ are given by

$$\bar{M} = \sum(X_iM_i) \quad (2)$$

$$\bar{R} = \sum(X_iR_i) \quad (3)$$

where X_i denotes the mole fraction of component i. The density, d, is expressed by

$$d = d_0 + (M_+ - d_0V_+^0)C_+/1000 + (M_- - d_0V_-^0)\ C_-/1000 + (M_p - d_0V_p^0)C_p/1000 \quad (4)$$

where d_0 is the density of water, V_+^0, V_-^0, and V_p^0 are the apparent molar volumes, M_+, M_-, and M_p are the molecular weights, and C_+, C_-, and C_p are the molar concentrations of cation, anion, and polyion, respectively. The Donnan equilibrium gives

$$C_s^0(C_s^0 + \nu\phi_pC_p^0) = [C_s^0 + (\Gamma_s + \nu\phi_\sigma\Gamma_p/t)](C_s^0 + \Gamma_s/t) \quad (5)$$

where C_s^0 and C_p^0 are the molar concentrations of uni-univalent salt and polyion in the bulk phase, respectively, ν is the number of charges per polyion, ϕ_p and ϕ_σ are the osmotic coefficients for the salt-free bulk polymer phase and the adsorbed layer, and Γ_p and Γ_s are the adsorbances of polyion and simple salt expressed in mol/cm^2. Equation 5 was first derived from Frommer and Miller[13] assuming the additivity rule for the osmotic factors.

From the measured refractive indices and densities for NaPSS in NaCl aqueous solution at 25 °C, the molar refractivities and the apparent molar ion volumes were calculated as follows: $R_{NaCl} = 9.23$ cm^3/mol, $R_{H_2O} = 3.73$ cm^3/mol, $R_{NaPSS} = 71.23$ cm^3/mol, $V^0_{Na^+} = -1.55$ cm^3/mol, $V^0_{Cl^-} = 18.3$ cm^3/mol, and $V^0_{NaPSS} = 127.81$ cm^3/mol. With $\phi_p = \phi_\sigma = 0.17$, which was reported previously[14] and the measured values of n_f, t, C_p^0, ν, and C_s^0, Γ_p, and Γ_s were calculated by solving eq 1–5.

Assessment of the adsorbance of NaPSS determined from ellipsometry an independent measurement of the adsorbance was attempted by determination of NaPSS concentration in the supernatant using UV spectroscopy, but the difference of NaPSS concentration between the supernatant and initial added solution was not observed. This may be attributed to too small an area of the metal surface used. In the future, we will attempt to directly determine the adsorbance.

Results

Typical examples of plots of adsorbance, A_p, of NaPSS against adsorption time are shown in Figure 1 for NaPSS-2 in 4.17 M NaCl aqueous solution at NaPSS concentration, $C_p^0 = 0.045$ g/100 mL, NaPSS-1 in 0.5 M NaCl at $C_p^0 = 0.05$ g/100 mL, and NaPSS-3 in 0.1 M NaCl at $C_p^0 = 0.04$ g/100 mL, respectively. The open, closed, and half-closed symbols represent separate runs. The A_p value first increases with adsorption time and then attains its equilibrium value after 1.5×10^3 min. Though data points for separate runs are somewhat scattered, they are represented by one curve for respective samples. The error of A_p in 4.17 M NaCl concentration is less than 5% and those in the lower NaCl concentrations are less than 10%.

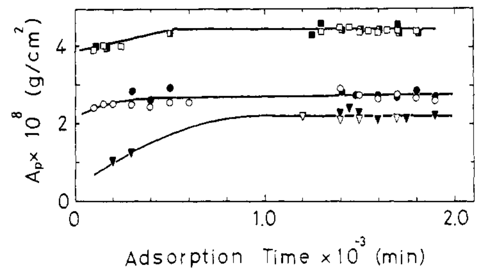

Figure 1. Adsorbance, A_p, of NaPSS as a function of time: (□, ■, ◧) NaPSS-2, NaCl concentration, $C_s^0 = 4.17$ M NaPSS concentration, $C_p^0 = 0.045$ g/100 mL; (○, ●), NaPSS-1, $C_s^0 = 0.5$ M, $C_p^0 = 0.05$ g/100 mL; (▽, ▼) NaPSS-3, $C_s^0 = 0.1$ M, $C_p^0 = 0.04$ g/100 mL. The open, closed, and half-closed points indicate separate measurements made on the same platinum plate.

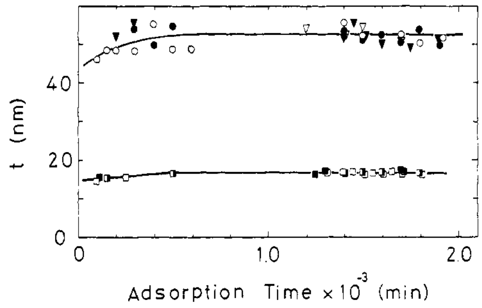

Figure 2. Thickness, t, of the adsorbed layer as a function of time. Symbols are the same as in Figure 1.

For the same samples and the same experimental conditions, typical results for the thickness, t, of the adsorbed layer are plotted (Figure 2) as a function of adsorption time. The t value also increases with increasing time and becomes constant after 1.5×10^3 min. The error of t in 4.17 M NaCl concentration is less than 3% and those in the lower NaCl concentrations are less than 10%. Reproducibility of the value t is also very good. As is seen from Figures 1 and 2, we regard the data on A_p and t determined after 1.5×10^3 min as the equilibrium value. Similar time dependences of A_p and t were obtained for other samples.

Average values of A_p, t, and adsorbance, A_s, of NaCl (negative value) in the highest NaPSS concentration over separate runs are summarized in Table II. The error of A_s is the same as that of A_p for respective NaCl concentrations.

The Θ condition for NaPSS prepared by radical polymerization of styrenesulfonic acid monomer was determined to be 4.17 M NaCl aqueous solution at 25 °C by Takahashi, Kato, and Nagasawa.[15] Though the NaPSS samples used here are not fully neutralized as seen from Table I, the proportinality between the intrinsic viscosities in 4.17 M NaCl aqueous solution and the square root of the molecular weight of NaPSS is obtained. Thus, we regard that

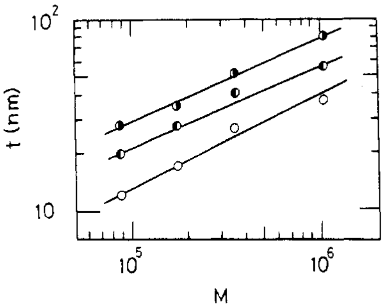

Figure 3. Double-logarithmic plots of thickness, t, and molecular weight, M. (○) NaCl concentration, C_s^0 = 4.17 M; (◐) C_s^0 = 0.5 M; (◑) C_s^0 = 0.1 M.

Table II
Adsorption Data of NaPSS onto a Platinum Plate and Twice the Radii of Gyration, $2\langle S^2\rangle^{1/2}$

sample	C_s^0, M	$A_p \times 10^8$, g/cm^2	$A_s \times 10^9$, g/cm^2	t, nm	$2\langle S^2\rangle^{1/2}$, nm
NaPSS-1	4.17	5.5	−1.4	12	$10._4$
	0.5	2.4	−0.55	20	$23._2$
	0.1	1.2	−0.25	28	$23._9$
NaPSS-2	4.17	4.4	−1.04	17	$15._3$
	0.5	2.4	−0.55	28	$34._6$
	0.1	1.5	−0.32	35	$39._6$
NaPSS-3	4.17	4.2	−1.2	27	$20._4$
	0.5	3.2	−0.85	41	$49._0$
	0.1	2.5	−0.72	52	$60._4$
NaPSS-4	4.17	9.0	−2.1	37	$39._8$
	0.5	2.8	−0.60	55	$99._8$
	0.1	2.0	−0.40	80	11_7

the 4.17 M NaCl aqueous solution at 25 °C is still a Θ solvent for the NaPSS samples.

Figure 3 displays a double-logarithmic plot of t listed in Table II against the molecular weight. Log t is linear with log M for respective NaCl concentrations, and the solid straight lines can be drawn in the figure. The slope of the solid line for Θ solvent (4.17 M NaCl) is nearly 0.5. The molecular weight dependency at Θ solvent condition is in good agreement with various experimental results[16-19] of nonionic polymer adsorption. In the lower NaCl concentrations, i.e., in good solvent conditions, the slopes are 0.4 ± 0.02 and definitely less than 0.5. The exponent 0.4 is in excellent agreement with the cases of polystyrene adsorbed onto a chrome plate in cyclohexane at 40 and 45 °C in carbon tetrachloride at 35 °C[20] and poly(ethylene oxide) adsorbed on cellulose ester filters in water at 35 °C.[21]

Figure 4 shows a double-logarithmic plot of t and NaCl concentration, C_s^0. The exponent obtained for the salt concentration dependency is −0.2 ± 0.02 for respective molecular weights. The solid lines with the slope of −0.2 are drawn in the figure.

Discussion

Theoretical descriptions for adsorption of polyelectrolyte are much rarer than those for nonionic polymer adsorption. Now Hesselink's theory[1,2] is the only available one to compare with the experimental data. In his theory particularly, the adsorbed amount of polyion is quantitatively calculated as functions of polymer concentration, simple salt concentration, and molecular weight of polyion. In our previous papers[10,11] we showed that a linear dependence between adsorbance of polyelectrolyte and the square root of salt concentration is in good agreement with the theoretical predictions of Hesselink.[1,2] However, the quantitative calculations for effects of molecular weight and salt concentration on the thickness of the adsorbed polyelectrolyte layer were not well performed, since the thickness of the adsorbed layer was clearly an overestimate.

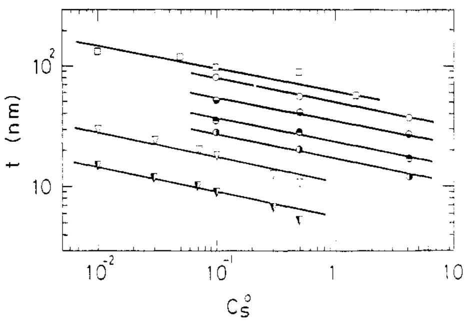

Figure 4. Double-logarithmic plots of thickness, t, and salt concentration, C_s^0. (○) NaPSS-1; (◒) NaPSS-2; (◓) NaPSS-3; (◑) NaPSS-4; (□) sodium poly(acrylate) with M_w = 950 × 10^3;[10] (▽) maleic acid and ethyl vinyl ether copolymer with M_w = 335 × 10^3;[9] (▼) maleic acid and ethyl vinyl ether copolymer with M_w = 160 × 10^3.[9] The solid lines indicate the slope of −0.2.

We reported successful results[20] that the exponent for the molecular weight dependence of the thickness of the adsorbed nonionic polymer layer in both Θ and good solvent conditions is quantitatively interpreted by de Gennes' adsorption theory[22] based on scaling concepts.

Recently, additional theoretical work has been reported,[24-26] since Eisenriegler, Kremer, and Binder[23] pointed out that the proximal region of de Gennes' concentration profile in the adsorbed layer[22] is incorrect. In response to Eisenriegler et al., de Gennes and Pincus[24] revised the earlier paper[22] and reached the same results as Eisenrielger et al.

Subsequently, Eisenriegler[26] made a detailed analysis of the earlier paper of de Gennes and showed that the central and distal regions in the concentration profile are the same as in de Gennes' earlier paper.

Both de Gennes and Pincus and Eisenriegler suggested that the proximal region is in principle important for weak adsorption, but the central region is an essential part for strong adsorption corresponding to most practical cases. For the strong adsorption, they showed that the same concentration profile still holds even if the adsorption is from dilute solution, since the polymer chains in the adsorbed layer are strongly overlapping. The bulk concentration of NaPSS in this experiment corresponds to dilute solutions.

We expect that this experiment belongs to strong adsorption. The calculation for the concentration profile in the adsorbed layer follows our previous paper.[20] However, the correlation length, ξ, in polyelectrolyte solution with simple salt should depend on not only polyelectrolyte but also on simple salt concentrations. According to Odijk,[27] the value of ξ is given by

$$\xi \sim (L_t/\kappa)^{-1/4}(ac)^{-3/4} \qquad (6)$$

Here a is the length of a monomeric unit, c is the polyelectrolyte concentration, and κ^{-1} is Debye's screening length with the relationship of $\kappa^2 = 8\pi nQ = 8\pi ne^2/\epsilon_0 kT$, where n is the monovalent ion concentration, Q is the Bjerrum length, e is the elementary charge, ϵ_0 is the dielectric constant of the aqueous solution, k is Boltzmann's constant, and T is the absolute temperature. A persistence length, L_t, consists of a structural or intrinsic part, L_p, and an electrostatic part, L_e, arising from the screened charge interactions along the chain. The value of L_t is defined by

$$L_t = L_p + L_e = L_p + (Q/4\kappa^2A^2)f \qquad (7)$$

where A is the contour distance between the charges on the chain. The factor f takes into account the possibility that the strong interactions between the polyion and the counterion part of the charges on the chain are effectively reduced. If no effective charge compensation occurs, $f = 1$; otherwise $0 < f < 1$.

The polyelectrolyte concentration c is related to the volume fraction of polyelectrolyte ϕ as follows:[12]

$$\phi \sim ca^3 \tag{8}$$

Substitution of eq 8 into eq 6 gives

$$\xi \sim \phi^{-3/4}(L_t/\kappa)^{-1/4} \tag{9}$$

Equation 9 holds for the volume fraction of polymer $\phi(z)$ in the adsorbed layer at a distance z from the adsorbing wall. If one would know $\phi(z)$ and stand at a given distance z, one can construct a value of $\xi[\phi(z)]$. Then, the only possible function is $\xi[\phi(z)] \sim z$. Thus, $\phi(z)$ is derived by

$$\phi(z) \sim z^{-4/3}(L_t/\kappa)^{-1/3} \tag{10}$$

Equation 10 holds until the correlation length, ξ_b, in bulk solution. In general, we can calculate the average thickness, $\bar{z}$, of the adsorbed layer from the wall using eq 10

$$\bar{z} = \int_0^{\xi_b} z\phi(z)\,dz \sim \xi_b^{2/3}(L_t/\kappa)^{-1/3} \tag{11}$$

The upper limit ξ_b of the integration range depends on the polymer concentration in bulk solution.

The thickness of the adsorbed layer determined by ellipsometry corresponds to an average thickness of the uniform adsorbed layer, and ellipsometry does not give information on the concentration distribution in the adsorbed layer.

By assuming that the measured thickness, t, is proportional to the average thickness, $\bar{z}$, calculated from eq 11, a quantitative comparison of t and $\bar{z}$ is possible. Since the measuring NaPSS concentration corresponds to the dilute region, the integration range ξ_b in eq 11 is considered to be the radius of gyration $\langle S^2\rangle^{1/2}$. Two values of t and $2\langle S^2\rangle^{1/2}$ are comparable as seen from Table II, and this fact also supports letting $\xi_b = \langle S^2\rangle^{1/2}$ in eq 11. The values of $\langle S^2\rangle^{1/2}$ are calculated from the following equation.

$$[\eta] = 6^{3/2}\Phi\frac{\langle S^2\rangle^{3/2}}{M} \tag{12}$$

where Φ is Flory's universal constant. In the calculation of $\langle S^2\rangle^{1/2}$ from eq 12, we employ $\Phi = 2.87 \times 10^{21}$ for 4.17 M NaCl concentration and $\Phi = 1 \times 10^{21}$ for the lower NaCl concentrations.[15]

According to Odijk, the value of $\langle S^2\rangle^{1/2}$ for a polyelectrolyte chain in salt solution is approximated by $\langle S^2\rangle^{1/2} \sim N^{3/5}(L_t/\kappa)^{1/5}$, where N is the degree of polymerization. The effects of molecular weight and salt concentration of the average thickness, $\bar{z} \sim t$, are calculated by substitution of $\langle S^2\rangle^{1/2}$ into ξ_b in eq 11. We obtain

$$t \sim \bar{z} = \int_0^{\langle S^2\rangle^{1/2}} z\phi(z)\,dz \sim \langle S^2\rangle^{2/3}(L_t/\kappa)^{-1/3} \sim N^{2/5}(L_t/\kappa)^{-1/5} \tag{13}$$

Note that at constant salt concentration the thickness of the adsorbed layer is proportional to $N^{2/5}$. This molecular weight dependency is the same as for nonionic polymer adsorption in good solvent conditions.[20]

Figure 5 displays the plots of the measured value t against $M^{0.4}$ for two NaCl concentrations. The plots satisfy the linear relationship between t and $M^{0.4}$. Therefore, the exponent for the molecular weight dependence of t is quantitatively interpreted by the central region of the concentration profile in the adsorbed layer derived by scaling concepts.

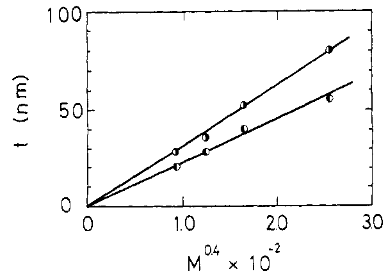

Figure 5. Plots of thickness, t, against $M^{0.4}$. Symbols are the same as in Figure 3.

On the other hand, we obtain the salt concentration effect on the thickness of the adsorbed layer at constant molecular weight from eq 13. From $\kappa^2 = 8\pi nQ$ the term κ is proportional to the square root of salt concentration. The value of $(L_t/\kappa)^{-1/5}$ in eq 13 is not expressed as a simple function such as a power of salt concentration. However, eq 13 indicates that t increases with increasing salt concentration at constant molecular weight.

As is seen from Figure 4, the negative value of the exponent for the salt concentration dependence of the measured thickness of the adsorbed layer is not in agreement with the prediction of scaling concepts. This discrepancy is difficult to interpret quantitatively and may be attributed to the fact that the salt concentration in the adsorbed layer is not equivalent and lower than the bulk salt concentration due to the negative adsorption of salt (Table II).

To further substantiate the exponent, plots of log t against log C_s^0 for available data on sodium polyacrylate adsorbed on a platinum surface in NaBr aqueous solution[10] and alternative copolymers of maleic acid and ethyl vinyl ether adsorbed on cellulose ester in NaCl aqueous solution[9] are also illustrated in Figure 4. The former thickness was determined by ellipsometry, while the latter was measured by a hydrodynamic method. For both polymers, log t linearly decreases with log C_s^0 and the exponent obtained for the salt concentration dependence of t is -0.2 ± 0.03. In the figure the slopes of the solid lines are -0.2. Therefore, we will stress that a good coincidence for the effect of the salt concentration on the thickness of adsorbed polyelectrolyte layer is obtained, irrespective of polyions and experimental methods. The measured salt concentration dependency means that the thickness of the adsorbed layer increases with better solvent condition. Such a solvent effect on the thickness of the adsorbed layer is in good agreement with the case of nonionic polymers.[20,28] Therefore, this experimental result may suggest that the effect of salt concentration on polyelectrolyte adsorption should be theoretically reconsidered, in particular for the thickness of the adsorbed layer.

In Θ solvent condition both scaling[20,29] and mean field approaches[30-32] lead to the same conclusion that the thickness of the adsorbed layer is proportional to the square root of the molecular weight. As is seen from Figure 3, the data on the thickness of NaPSS layer in 4.17 M NaCl aqueous solution, i.e., in Θ solvent, satisfy the theoretical prediction.

Conclusions

Data on the thickness of the adsorbed layer for NaPSS–NaCl–Pt system were accumulated as functions of NaCl concentration and molecular weight by ellipsometry. Reproducibility in the adsorption experiments was extremely good. By consideration of only the central region of the concentration profile in the adsorbed layer derived by scaling concepts the dependence of the molecular weight on the measured thickness of NaPSS was quantitatively interpreted in both Θ and good solvent conditions. These molecular weight dependences of the thickness were in excellent agreement with the case of nonionic polymer adsorption.

However, the effect of NaCl concentration on the thickness of the adsorbed layer was different from that predicted by scaling concepts. The exponent of salt concentration dependence on the thickness was obtained to be around −0.2, and this absolute value was common among the available data. These coincident results, irrespective of polyion and experimental method, will be helpful in developing the theory.

The measured thickness t and $2\langle S^2\rangle^{1/2}$ are comparable, and this fact indicates that ellipsometry is sensitive to polymer segments at the periphery of the adsorbed layer.

Registry No. NaCl, 7647-14-5; platinum, 7440-06-4; (maleic acid)·(ethyl vinyl ether) (copolymer), 41315-86-0.

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Solvent Effects in Polyelectrolyte Solutions. 1. Potentiometric and Viscosimetric Titration of Poly(acrylic acid) in Methanol and Counterion Specificity

Nicolaas Th. M. Kloester, Frans van der Touw, and Michel Mandel*

Section of Physical and Macromolecular Chemistry, Department of Chemistry, Gorlaeus Laboratories, University of Leiden, 2300 RA Leiden, The Netherlands.

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ABSTRACT: Poly(acrylic acid) (PAA) in methanol at room temperature is shown to exhibit a conformational transition in the range $0.10 < \alpha < 0.25$ when neutralized with CH_3ONa. Viscosity measurements suggest that after this transition the polymer behaves as a small compact particle. Neutralization with CH_3OLi leads to a qualitatively different behavior without such a transition. This behavior is more analogous to that of PAA in water without added salt. However, neither the potentiometric nor the viscosimetric titration by CH_3OLi of PAA in methanol without added low molar mass electrolyte can be deduced from the results in water by the classical polyelectrolyte theory taking into account the change of the electric permittivity only.

I. Introduction

In polyelectrolyte theories electrostatic interactions are primarily assumed to determine the solution behavior. The solvent is considered as a continuum that influences these interactions only through its relative permittivity ϵ. Although this assumption seems to be quite reasonable in aqueous solutions and in agreement with experimental observations, the importance of nonelectrostatic interactions—particularly through specific solvent effects—cannot be ruled out altogether.[1]

In order to obtain a better understanding of the influence of the solvent on polyelectrolyte properties, an experimental study was undertaken on the behavior of a synthetic polyelectrolyte of very simple structure (poly(acrylic acid) (PAA)) in methanol. Methanol was chosen because it is in general a suitable solvent for electrolytes, and weak acids can easily be titrated in it. The physical and chemical properties of water and methanol do not differ too much[2,3] although the dielectric constant ϵ is only 31.4 in the latter at 25 °C as compared to 78.5 in the former. PAA was chosen for its very simple structure, the ease with which fractions of different molar mass can be prepared, and its good solubility in methanol. In aqueous solution it has been considered to behave as a typical weak polyacid without any complications.

We have investigated the solution behavior of PAA and partially ionized polyacrylates in methanol by several techniques. Ionization was performed by titration with a strong base, for which we have used lithium methoxide (CH_3OLi) and sodium methoxide (CH_3ONa). In the different parts of this series of papers the results obtained with the different techniques will clearly demonstrate that

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