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Adsorption of Weak Polyelectrolytes on Highly Charged Surfaces. Poly(acrylic acid) on Polystyrene Latex with Strong Cationic Groups

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ABSTRACT: We have studied the adsorption of the weak polyelectrolyte poly(acrylic acid) (PAA) on a positively charged polystyrene latex. The latex surface contained quaternary ammonium groups, so that the surface charge was independent of pH. Hence, when the pH was changed, only the degree of dissociation of the polymer varied. We found that the adsorbed amount is low at high pH, where PAA is fully charged. With decreasing pH the adsorption increases and passes through a maximum at about 1 pH unit below the intrinsic dissociation constant pK_0 of the carboxylic groups of the macromolecule. The ionic strength has little effect. The experimental results agree very well with a recent extension[1] of the model of Scheutjens and Fleer to polyelectrolyte adsorption.

Introduction

The adsorption of polymeric materials plays an important role in a number of technological processes such as waste water treatment, flotation separations, fine-particle recovery by selective flocculation, enhanced oil recovery, etc.[2-5] Much effort has been put into experimental and theoretical work to understand the behavior of polymers at interfaces. Gradually, the main trends in the adsorption behavior of neutral polymers and polyelectrolytes on charged and uncharged surfaces become clear.

For the adsorption of neutral polymers one generally finds thick adsorbed layers and long tails with many segments of the adsorbed polymer in loops. In good solvents the adsorbed amount is low and only weakly dependent on chain length. However, in poor solvents (Θ solvents) the adsorbed amount depends linearly on the logarithm of the molecular weight of the polymer. When the ionic strength is increased, the adsorption of a neutral polymer may increase because the solvent quality decreases with increasing salt concentration.[6,7] Charging the surface has only a minor effect on the interfacial behavior of uncharged macromolecules. However, the adsorbed amount on a charged surface is less than on an uncharged surface if the number of available sites for binding the polymer decreases on charging the surface. This is the case for the adsorption of poly(vinyl pyrrolidone) and poly(ethylene oxide) onto silica.[8] Those polymers adsorb by hydrogen bonding with SiOH groups, the number of which decreases with increasing pH. Another effect of the surface charge on the adsorption of uncharged polymers has recently been predicted theoretically.[1] If the surface charge is very high, the accumulation of counterions in the double layer prevents high polymer segment concentrations and decreases the adsorbed amount. As far as we are aware, no experimental study has, as yet, dealt with this effect.

For polyelectrolyte adsorption, we have to make a distinction between strong and weak polyelectrolytes. Some general trends in the adsorption of strong polyelectrolytes, for which the charge does not depend on pH, have been discussed by Cohen Stuart.[9] For media with relatively low ionic strength ($c_s < 0.2$ M) and a neutral surface, the charged polyelectrolyte will adsorb in a flat configuration. In this case the adsorbed amount is low, and there is no dependence on molecular weight or ionic strength. For media with a relatively high ionic strength ($c_s > 1$ M), the adsorption is a function of the ionic strength and the molecular weight. The trends of the adsorption are, in this ionic strength region, comparable to the adsorption of a neutral polymer. When the surface is oppositely charged, the adsorbed amount of a strong polyelectrolyte depends on the surface charge density, resulting in higher adsorbed amounts for surfaces with higher surface charge densities because of the electrostatic contribution to the adsorption energy of the segments.

For weak polyelectrolytes, the degree of dissociation, α, depends on the pH. At low pH, where $\alpha = 0$ (polyacid), the situation is similar to that for the adsorption of neutral polymers. In the limit of high pH, where $\alpha =$

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1, the adsorption behavior is like that of strong polyelectrolytes. For intermediate values of the pH, the situation is complex because the degree of dissociation might be a function of the distance from the surface. If the surface carries no charge, the transition between low pH (uncharged groups, thick layers) and high pH (highly charged groups, thin layers at low c_s) is smooth and situated around the pK_0 of the polyelectrolyte. For oppositely charged surfaces some recently developed theories,[1,10] which are extensions of the Scheutjens–Fleer approach,[11,12] predict a maximum in the adsorbed amount at a pH value below the pK_0 of the polyacid. These theories also predict that the adsorption of a weak polyelectrolyte on a highly oppositely charged surface depends only weakly on the ionic strength, unless $c_s > 1$ M.

To our knowledge a maximum in the adsorbed amount as a function of the pH has only been reported by Tanaka et al.[13] They studied the adsorption of polymers with weak cationic groups (modified starch) onto bleached kraft pulp. They found a maximum in the adsorbed amount at about 2 pH units below the pK_0 of their polymers.

In this paper we present experimental results for the adsorption of poly(acrylic acid) (PAA) onto highly charged polystyrene latices with strong cationic groups to test some of the theoretical predictions, especially the maximum in the adsorbed amount as a function of the pH, and the weak ionic strength dependence. The latter effect is, at first sight, somewhat surprising because it is known that the salt concentration affects the adsorption of strong polyelectrolytes considerably. In order to avoid unnecessary complications, we decided to use an adsorbent with a pH-independent surface charge and a weak polyelectrolyte that is as simple as possible.

We chose PAA because it has no hydrophobic side chains. It has been shown that especially those weak polyacids which carry such groups, e.g., poly(methacrylic acid),[14-16] poly(ethacrylic acid),[14] copolymers of maleic acid and alkyl vinyl ethers,[17] and copolymers of maleic acid acid and styrene,[18] undergo a conformational change on increasing the degree of deprotonization. It is believed that at low degrees of deprotonization these macromolecules find themselves in a tightly coiled compact conformation (hypercoil). The hypercoil is due to the hydrophobic interactions between the apolar side chains. Upon ionization the hydrophobic microdomains are disrupted and the macromolecule undergoes a conformational change resulting in a more random conformation. For PAA these effects are much weaker. Some authors[19-21] do report a conformational change, whereas others[14-16] state that PAA does not change its conformation on increasing the degree of deprotonization. Since PAA does not have hydrophobic side chains, the formation of hydrophobic microdomains is not possible. Presumably, if there exists any conformational change, it must be very subtle. Therefore PAA corresponds quite well to the simple polyelectrolyte presumed in the model. For the intrinsic dissociation constant K_0 (defined as the dissociation constant for an infinitely dilute solution in the limit $\alpha \rightarrow 0$) of PAA, Mathieson et al.[19] report, for media with an ionic strength between 0.02 and 0.2 mol/L, a value for pK_0 of 4.58. Spencer,[22] using the data of Gregor et al.,[23] arrives at pK_0 = 5.33 for PAA in water and at pK_0 = 4.52 in 0.1 M KCl. The dissociation constant pK_a for monomeric acrylic acid is reported as 4.25.[24] It is generally believed that at room temperature PAA is completely soluble in water even at low pH when all the carboxylic groups are protonated. Silberberg et al.[25] studied the temperature dependence of the light scattering of hydrogen-bonding polymers. They reported for PAA (molecular weight 420 000) in 0.2 N HCl a (lower critical solution) Θ temperature of 14 °C.

Theory

Before discussing the experimental data, we give some background of recent theory and a few typical predictions. An earlier version of a polyelectrolyte adsorption theory, in which the small ions are considered as point charges, had been published a few years ago.[10] A more recent theory, in which the volume of the ions is taken into account, has been published elsewhere.[1] For technical details we refer to these papers.

Physical Background. The models as proposed by Böhmer et al.[1] and Evers et al.[10] are extensions of the self-consistent-field (SCF) theory of Scheutjens and Fleer.[11,12] This theory is based on a lattice with equidistant lattice layers parallel to the surface. Both the electrical and nearest-neighbor interactions are averaged over the whole layer (mean-field approach). A polymer segment (not necessarily a monomer unit) occupies one lattice site. In the case of the adsorption from a solvent consisting of small molecules like water, a fixed number of solvent molecules fill one lattice site. These solvent molecules filling one lattice site are considered to behave as a cluster (entity). On adsorption one segment replaces such an entity. All the sites are filled either with a polymer segment, a solvent entity, or (if ions have volume) an ion.

The configuration of a polymer molecule can be modeled as a step-weighted walk in the lattice. The weighting factors for each step contain the nearest-neighbor contact energy, the electrical potential, and the mixing entropy. The contact energy for interaction between all the components is expressed through the Flory–Huggins χ parameter. The adsorption energy of a polymer segment (p) and the surface (S) is described by a similar χ_{pS} parameter. (The adsorption energy parameter, χ_s, as used in previous studies,[10-12] expressing the adsorption energy difference between a polymer segment and a solvent entity (o), is given by $-\lambda_1(\chi_{pS} - \chi_{oS})$, where λ_1 is the fraction of nearest neighbors in an adjacent layer; for a hexagonal lattice $\lambda_1 = 1/4$. In most cases χ_{oS} may be set equal to zero.) The mixing entropy accounts for the fact that the probability of a step toward a given lattice layer decreases as the segment concentration in this layer becomes higher.

The additional feature as compared to the Scheutjens–Fleer theory is the electrical potential. In the approach of Van der Schee et al.[26] and Papenhuijzen et al.[27] for strong polyelectrolytes and in that of Evers et al.[10] for weak polyelectrolytes, the salt ions are considered to be point charges that occupy no volume. The polymer charges are localized in a plane in the middle of the lattice layer and their charge is smeared out over that plane. The small ions are distributed on both sides of the plane over the whole layer and an electrical double layer is formed. The electrical potentials are now obtained by solving the Poisson–Boltzmann equation. In the recent theory of Böhmer et al.,[1] the ions are considered to occupy a lattice site just like polymer segments and solvent entities. All charges are assumed to be in a plane in the middle of a lattice layer. The space between the planes is free of electrical charges. In this case the electrical potential in every plane is obtained by a multi-Stern-layer approach. The potential difference between the equidistant planes does not only depend on the charge on each plane but also on the separation distance, d, between the planes and on the dielectric constant. Hence, not only the lattice geometry but also the spacing of the lattice layers

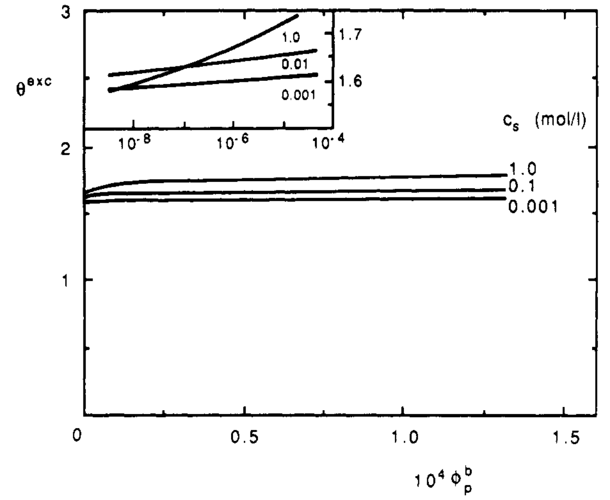

Figure 1. Excess adsorbed amount, expressed in equivalent monolayers, as a function of the bulk volume fraction of weak polyelectrolyte, $\phi_p{}^b$, at different salt concentrations (c_s), as calculated with the model of Böhmer et al.[1] The inset is the adsorbed amount as a function of the concentration polyelectrolyte on a logarithmic scale. The computations were performed with: $\chi_{pS} = -8.0$, $\chi = 0.5$, $r = 500$ segments, $d = 0.6$ nm, $Z = 12$, $pK_0 = 4.25$, $\sigma_0 = 160$ mC/m^2, and pH = 4.0.

has to be specified. The dielectric constant in a lattice layer is taken as a linear combination of the dielectric constants of polyelectrolyte, salt, and water.

In the multicomponent theory of Böhmer et al.,[1] each type of ion constitutes a separate component. In principle, one should then assign χ_{ij} and χ_{iS} parameters for the interactions between ions and solvent, ions and polymer segments, and ions and surface. In order to keep the number of parameters as low as possible, all the ions are considered to have identical properties as a solvent entity, except for their charge.

In these models[1,10] for the adsorption of weak polyelectrolytes the degree of dissociation, α, is not only a function of the pH but also of the distance z from the surface, since the local electrical potential varies with z.

The most severe drawback of these models for (weak) polyelectrolyte adsorption is the fact that the electrical potential is smeared out over the whole layer. Especially for polymers with a low charge density, the local electrical potential will be higher (in the vicinity of a charged segment) or lower (far away from a charged segment) than predicted by these two models. This smearing out of the electrical potential leads in the bulk solution (where the electrical potential is 0) to a prediction of the titration curve of a weak polyacid, which is identical with that of a weak monomeric acid.

Model Predictions. In Figure 1 we show three adsorption isotherms at salt concentrations of 0.001, 0.1, and 1 M, respectively, as calculated with the model of Böhmer et al.[1] The excess adsorbed amount, θ^{exc}, expressed in equivalent monolayers, is plotted as a function of the bulk volume fraction, $\phi_p{}^b$, of polyelectrolyte. In the inset we show the adsorption isotherms with the concentration axis on a logarithmic scale to illustrate what happens at very low concentrations polyelectrolyte. The calculations were performed for pH = 4, a surface charge density (σ_0) of 160 mC/m^2, and an intrinsic dissociation constant pK_0 of 4.25. The values of the adsorption energy (χ_{pS}), the polymer–solvent and polymer–ion interaction parameter (χ), the chain length (r), and the lattice parameters Z and d are given in the legend of Figure 1. For all the computations a value of 20 was chosen for the relative dielectric constant of PAA and the solid and a value of 80 was taken for all the other components.

The calculated isotherms are of the high affinity type as is generally found for the adsorption of homodisperse polymers and polyelectrolytes. The effect of the salt concentration on the adsorbed amount in the region 0.001–1 M is rather small. This is not only the case for pH = 4 but is found for the whole pH range. At the high pH end, where the macromolecule is completely charged, the absolute change in the adsorbed amount is about the same as at pH = 4, but since the adsorbed amount at high pH is much lower (as will be illustrated later), the relative effect of the ionic strength at high pH is greater. The computations show that, in the ionic strength range from 0.001–1 M and pH values around the pK_0 of the polyacid, the degree of dissociation is adjusted in such a way that the surface charge is fully compensated and sometimes even overcompensated in the first layer (depending on χ_{pS}), resulting in a slightly negative electrical potential in the first layers. Due to this negative potential, the pH in the layers adjacent to the surface is lower than that in the bulk. As a consequence, the degree of dissociation of the segments in the short loops is very low. Effectively, the particle is virtually neutral with only a very few charged segments in the loops of the adsorbed macromolecule. This explains why salt hardly affects the adsorption at this high surface charge.

From the inset of Figure 1 it can be seen that for very low polyelectrolyte concentrations the adsorbed amount at high salt concentrations is lower than at low c_s, whereas at higher polyelectrolyte concentrations the opposite trend is found. In this example the crossover point for 0.1 and 1 M salt is situated at $\phi_p{}^b \approx 1 \times 10^{-7}$. At all salt concentrations the surface charge has to be compensated, either by salt ions or by charged polyelectrolyte segments as discussed above. At low polyelectrolyte concentrations, an increasing fraction of this compensation will be accomplished by small ions as the ionic strength increases, so that the polyelectrolyte adsorption decreases with increasing c_s. At higher polyelectrolyte concentrations the adsorbed amount is higher and it increases with increasing c_s because the intramolecular electrostatic repulsions are much better screened at high c_s. This explains the crossover as it occurs in Figure 1. Such a crossover has also been found experimentally for the adsorption of surfactants, which adsorb with the charged headgroup onto an oppositely charged surface.[28]

In Figure 2 we have plotted the adsorbed amount as a function of the pH at a bulk volume fraction, $\phi_p{}^b$, of 1×10^{-4}, which is well in the plateau regions of the individual adsorption isotherms. The results in the upper diagram were obtained using the model of Evers et al.[10] (ions are considered as point charges); the bottom figure was calculated with the model of Böhmer et al.[1] (ions occupy the same volume as a polymer segment). Although the parameters in both figures are somewhat different, we can still compare the trends.

Figure 2a gives three curves, one for the adsorption of a neutral polymer ($\alpha = 0$) and two for the adsorption of a weak polyacid ($pK_0 = 4$) onto an uncharged and onto an oppositely charged surface, respectively. If the small ions occupy no volume, the adsorption of a neutral polymer ($\alpha = 0$) is not affected by the surface charge. At low pH all three curves merge to the same adsorbed amount. This is to be expected because in this extreme a weak polyacid is uncharged and should behave like a neutral polymer. When the pH is increased, the adsorption of the weak polyacid onto an uncharged surface becomes lower. When the polyelectrolyte is charged by increas-

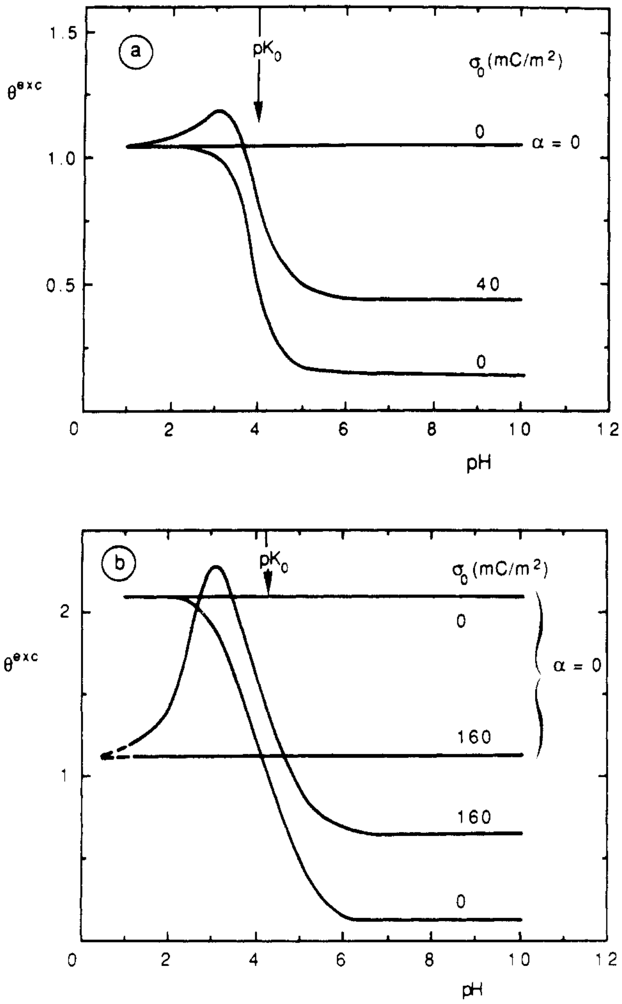

Figure 2. Excess adsorbed amount as a function of the pH for a neutral polymer (α = 0) and a weak polyelectrolyte at different surface charge densities. The top figure (a) has been calculated with the model of Evers et al.[10] (salt ions have no volume; see text). Parameters: $\chi_{pS} = -2.0$, $\chi = 0.5$, $r = 500$ segments, $d = 1.0$ nm, $Z = 12$, $\phi_p{}^b = 1 \times 10^{-4}$, and $c_s = 1.0$ M. The bottom diagram (b) has been computed according to the model of Böhmer et al.[1] (salt ions occupy one lattice site; see text). Parameters: $\chi_{pS} = -8.0$, $\chi = 0.5$, $r = 500$ segments, $d = 0.6$ nm, $Z = 12$, $\phi_p{}^b = 1 \times 10^{-4}$, and $c_s = 0.1$ M.

ing the pH, the inter- and intramolecular electrostatic repulsions oppose the accumulation of polyelectrolyte. Only in the first layer, where segments experience the attractive interaction of the surface does such accumulation occur, resulting in a flat configuration of the adsorbed polyelectrolyte as illustrated by the calculated segment density profiles (profiles not shown). In this manner one molecule will occupy more surface area and the adsorption will be less than when a molecule adsorbs in a conformation with long loops and tails. For the adsorption of a weak polyelectrolyte onto an oppositely charged surface, the behavior is quite different. Starting at low pH, an increase in the pH first leads to an increase in the adsorbed amount, subsequently followed by a decrease, just as for the adsorption onto an uncharged surface. The initial increase is due to the electrostatic attraction between surface and polyelectrolyte, giving an additional electrostatic contribution to the adsorption energy. At the pH values where this increase occurs, the degree of dissociation of the segments not in contact with the surface is very low, so there is hardly any inter- or intramolecular electrostatic repulsion between the segments in the loops or tails. The segments in contact with the surface are, at this pH, dissociated to a much larger extent than the segments in the loops or tails; i.e., some H$^+$ is released upon adsorption. Therefore, there is an extra attraction between surface and polyelectrolyte while there is hardly any extra repulsion. Upon further increase in pH, the electrostatic repulsion increases, and as a result the adsorption will decrease for the same reason as in the case of an uncharged surface. The adsorption of a weak polyacid on an oppositely charged surface is always higher than that on a neutral surface due to the electrostatic contribution to the adsorption energy.

Figure 2b shows similar curves for the model where salt ions have their own volume. In the limit of low pH the curves for weak polyacids merge with the curves for neutral polymers, as is to be expected. An obvious difference between parts a and b of Figure 2 is that in the latter case an increase in the surface charge density reduces the adsorption of an uncharged polymer. The computed segment and ion density profiles show that this reduction is caused by the presence of salt ions at the interface, necessary for shielding the (very high) charge on the surface. The volume occupied by the salt ions is no longer available for the polymer, and as a result the adsorption becomes less (salt exclusion). This salt-exclusion effect occurs only at high surface charge densities, where a considerable fraction of the sites in the first layer are filled with salt ions. To our knowledge such a large effect of the surface charge density on the adsorption of a neutral polymer has never been reported experimentally. It will be difficult to obtain such experimental results because one should then be able to vary the surface charge without affecting the chemical nature of the surface. Nevertheless, Koopal,[29] studying the adsorption of poly(vinyl alcohol) onto AgI, reports a small decrease in the adsorbed amount upon increasing the pAg from 5.6 to 11 (changing the surface charge density from 0 to −35 mC/m^2). He attributes this difference in the adsorbed amount to inaccuracies in the specific surface area of AgI at pAg = 5.6. However, it could also be explained by the salt-exclusion effect.

The pH dependence of the adsorption on an uncharged surface follows similar trends in parts a and b of Figure 2; the lower adsorbed amount at high pH in Figure 2b is mainly due to the lower salt concentration. On the other hand, the adsorption maximum on a highly charged surface is much more pronounced in Figure 2b. This is caused by the fact that charged polyelectrolyte segments and salt ions compete for shielding of the surface charge. Already at low pH this competition is won by the polymer segments because of their adsorption energy. Moreover, the degree of dissociation of the adsorbed segments adjusts itself such as to effectively screen the surface charge.

In Figure 3 we illustrate the effect of the chain length on the excess adsorbed amount. This figure has been computed with the model of Böhmer et al.[1] We have plotted θ^{exc} as a function of chain length for three pH values and for a neutral and a highly oppositely charged surface, respectively. At pH = 6.5 the polyacid is almost completely dissociated and the adsorbed amount does not depend on the molecular weight, as has been found for strong polyelectrolytes by Van der Schee et al.[26] and Papenhuijzen et al.[27] Increasing the surface charge density at this pH leads to an increase in the adsorbed amount due to the extra electrostatic attraction between surface and polyelectrolyte. For the other extreme (pH = 1.01), the polyacid is virtually uncharged and behaves like a neutral polymer. The adsorbed amount depends now linearly on the logarithm of the molecular weight, as dem-

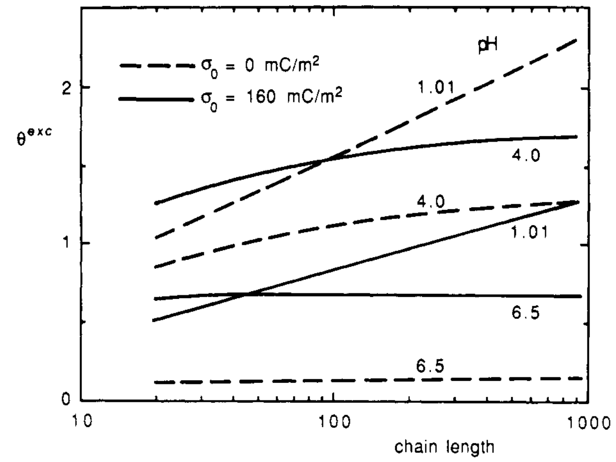

Figure 3. Dependence of the excess adsorbed amount on the chain length, at three pH values and two surface charge densities, respectively, as predicted by the model of Böhmer et al. Parameters: $\chi_{pS} = -8.0$, $\chi = 0.5$, $d = 0.6$ nm, $Z = 12$, $\phi_p{}^b = 1 \times 10^{-4}$, p$K_0$ = 4.25, and c_s = 0.1 M.

Table I
Properties of the Latices That Have Been Used in the Adsorption Studies[a]

latex no.	particle diameter, nm	std deviatn, nm	d_{32}/d_{10}	σ_0, mC/m^2
1	834	23.3	1.0015	100
2	771	7.5	1.0002	160

[a] The variables d_{32} and d_{10} are the volume–surface average diameter and the number-average diameter, respectively, and σ_0 is the surface charge density.

Table II
Characteristics of the PAA Samples Used in the Adsorption Experiments[a]

PAA sample	M_w	M_n	M_w/M_n
1	18 100	12 800	1.41
2	70 900	39 400	1.80

[a] M_w and M_n are the weight- and number-average molecular weights, respectively.

onstrated by Scheutjens and Fleer[11] for the adsorption of a neutral polymer from a Θ solvent. At this pH an increase in the surface charge density results in a decrease in the adsorbed amount due to the salt-exclusion effect. At pH = 4 an intermediate situation is found, with a weaker chain-length dependence than at pH = 1.01 and a higher adsorption when the surface carries an opposite charge.

Experimental Section

Latex. We used polystyrene latex with a positive pH-independent surface charge as the adsorbent. The preparation of this latex has been described elsewhere.[30] The properties of the latices used are given in Table I.

Poly(acrylic acid). Poly(acrylic acid) (PAA) in the sodium form was purchased from Polysciences Inc. (Warrington, PA). The molecular weight distributions of the samples are rather broad, as can be seen from Table II. The molecular weights reported in Table II are as given by the manufacturer and were determined by gel permeation chromatography.

Conductometric titrations of PAA revealed that the samples as obtained from the manufacturer contained some excess of NaOH, because the initial part of the first titration curve with HCl showed a rather steep decay of the conductivity on adding HCl. Successive titrations showed the normal behavior of a weak polyacid with a strong base. From the back titration curve the concentration of PAA is obtained in meq/L. This concentration can be converted to ppm using a monomer molecular weight of 73. The concentration of PAA determined in this way was less than that based on dry sample weight, even after correction for the excess amount of NaOH. The discrepancy could be reduced by drying the PAA in an oven at 80 °C. So we concluded that Na–PAA is hygroscopic, and we decided to use the conductometric titration method for the determination of PAA in the stock solutions. All PAA concentrations in this paper are expressed in ppm (mg/L) based on PAA in the acidic form.

Adsorption Isotherms. The adsorption experiments were performed in 10-mL polycarbonate centrifuge tubes. Before the solutions were pipetted into the centrifuge tube, they were adjusted to the required ionic strength and pH. Measurements with the single-particle optical sizer as described by Pelssers[31] revealed that it was necessary to sonicate the latex suspension for 20 min to get a suspension with only singlet particles.

A total of 2 mL of the latex suspension (ca. 0.6 m^2) was pipetted into a tube, followed by the desired volume of a KNO_3 solution and the required amount of the PAA stock solution. The total volume in the centrifuge tubes was 8 mL. Then the tubes were capped, vigorously shaken, and slowly rotated end-over-end for 24 h. Preliminary experiments had shown that after rotating for 24 h the adsorbed amount did not increase any more. An almost clear supernatant was obtained by centrifuging for 20 min at 20 000 rpm (Beckman centrifuge, JA21 rotor). Then the pH of the supernatant was measured, and a latex-free solution was obtained by filtering the supernatant through an acrodisc filter assembly (Gelman Sciences, 0.2 μm). The concentration of PAA in the latex-free solution was determined, and the adsorbed amount, Γ (in mg/m^2), was calculated from the mass balance.

Determination of Residual PAA Concentrations. During our experiments we had to change our method for determining the equilibrium concentrations PAA twice. At low ionic strength (0.001 M) we used a colorimetric colloid titration procedure, which is based upon a stoichiometric complex formation between a polyanion and a polycation. This did not work satisfactorily at an intermediate ionic strength (≈0.01 M). Here we used a total organic carbon analyzer (TOC). At high ionic strength (≥0.1 M) the TOC determination was not reliable so we used here a simple acid–base titration procedure.

a. Colorimetric Titration. Colloid titrations can be a suitable tool for determining concentrations of positively or negatively charged polyions as long as they combine stoichiometrically with an oppositely charged polyelectrolyte.[32,33] The method as outlined by Terayama[32] was used for measuring unknown concentrations PAA in low ionic strength (0.001 M) media. To a PAA solution was added an excess of positively charged poly(diallyldimethylammonium chloride). The excess of this polycation was titrated back with potassium poly(vinyl sulfate) to a colorimetric end point with toluidine blue as the indicator. When a calibration curve was used, concentrations of PAA could be determined with an accuracy of 2% down to a concentration of a few ppm. For media with a higher ionic strength than 0.001 M it was difficult to determine the equivalence point in the back-titration step because the color change was not distinct. Probably the complexes formed between PAA and poly(diallyldimethylammonium chloride) are not sufficiently stable at higher salt concentrations.

b. Total Organic Carbon Analyzer. For the determination of PAA in media of higher ionic strength we used an automatic total organic carbon (TOC) analyzer (TOC Sin II, phase separation, Queensferry, U.K.). This apparatus measures the total organic carbon content after combustion of the sample to CO_2 and H_2O in a furnace at 1100 °C, followed by drying of the gas stream and subsequent reduction of CO_2 to CH_4 by H_2 in the presence of a catalyst at 200 °C. The amount of CH_4 is determined by a flame ionisator. Before the sample is combusted, any CO_2 from the atmosphere is removed by acidifying the sample, followed by deaerating. When a calibration procedure was used, PAA could be accurately determined in media of medium ionic strength (≤0.01 M). However, at higher ionic strength (≈0.1 M) the apparatus was not reliable. The malfunctioning of the analyzer was due to plugging of the tubing by salt, especially of the pipe that entered the furnace, and to contamination of the catalyst.

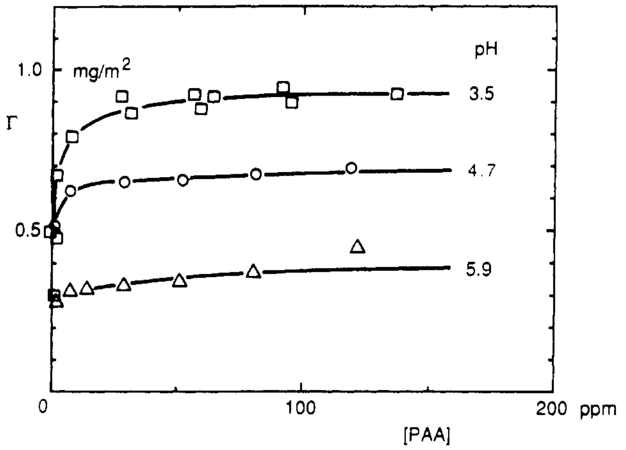

Figure 4. Experimental adsorption isotherms of PAA (M_w = 18 100) onto a cationic latex with σ_0 = 100 mC/m² in 0.001 M KNO_3, at three pH values. The equilibrium concentrations PAA are expressed in ppm (w/w).

c. Potentiometric Titration. For the measurements at 0.1 M KNO_3 we developed a simple titration procedure. The pH of a 5-mL aliquot of the solution to be analyzed was adjusted to just below pH = 4. Then the amount of titrant (5×10^{-3} N NaOH) necessary to raise the pH from 4 to 7 was measured. With a calibration procedure PAA could be determined. The calibration curve (amount of titrant needed to raise the pH from 4 to 7 versus [PAA]) showed that approximately 70% of the carboxylic groups are titrated in the pH range 4-7. We chose to start at pH = 4 because otherwise the blank titration required too much titrant and stopped at pH = 7 to prevent interference of CO_2.

Results and Discussion

The experiments were designed to check the major trends discussed in the Theory section. Special attention was paid to the pH dependence of the adsorbed amount (where the theory predicts a maximum at pH < pK_0 at high opposite surface charge density) and the effects of salt concentration, chain length, and surface charge.

In Figure 4 we give some experimental adsorption isotherms for the PAA sample of M_w = 18 100 onto latex with σ_0 = 100 mC/m² in 0.001 M KNO_3, at three different pH values. The adsorbed amount, expressed in milligrams per square meter, is plotted as a function of the equilibrium concentration PAA in ppm, measured by means of the colorimetric colloid titration procedure. It is obvious from this figure that in the region around pK_0 (4.5 for PAA) the pH has a large effect on the adsorbed amount, just like theories predict (see Figure 2). The adsorption isotherms are of the high-affinity type, but they are not quite as sharp as in the theory. This is probably due to the polydispersity of the polyelectrolyte sample, as suggested by Cohen Stuart et al.[34] It appears from Figure 4 that the isotherms become less sharp when the pH decreases. This can be attributed to the fact that the adsorption depends more strongly on the molecular weight at a low pH (see Figure 3), which gives rise to more pronounced polydispersity effects.

Our adsorption data may be compared with trends reported in the literature. The adsorption of PAA onto rutile (TiO_2) and hematite (αFe_2O_3) has been studied by Gebhardt and Fuerstenau.[35] They found also a large decrease in the adsorbed amount upon increasing the pH from 4 to 8. They explained this solely from the decrease in surface charge density on increasing the pH, thereby neglecting the increase of the charge on the polyelectrolyte chain. Our results, applying to a constant σ_0, show how important the effect of the polyelectrolyte charge is on the adsorbed amount. Foissy et al.[36] studied the adsorption of PAA onto anatase (TiO_2) and reported a high adsorbed amount at pH = 2.8 and a very low adsorbed amount at pH = 9.8. There is a big difference between the results of Gebhardt and Fuerstenau[35] and Foissy et al.[36] The latter authors found an adsorption density that was about 7 times higher, although the molecular weight of their samples was much lower. Another difference is that Foissy et al.[36] still found adsorption at pH = 9.8, whereas Gebhardt and Fuerstenau[35] did not measure any adsorption above pH = 7. The plateau region of the adsorption isotherms as measured by Gebhardt and Fuerstenau[35] is reached at the same equilibrium concentration PAA as in our case, whereas in the experiments of Foissy et al.[36] the plateau region is reached at equilibrium concentrations that are 10 times higher. If these large differences in the adsorption of PAA onto rutile anatase are real, they must be mainly due to a different chemical affinity (different χ_{pS}) of PAA for the two crystal forms of TiO_2 because the electrokinetics of rutile and anatase are virtually the same.[37,38]

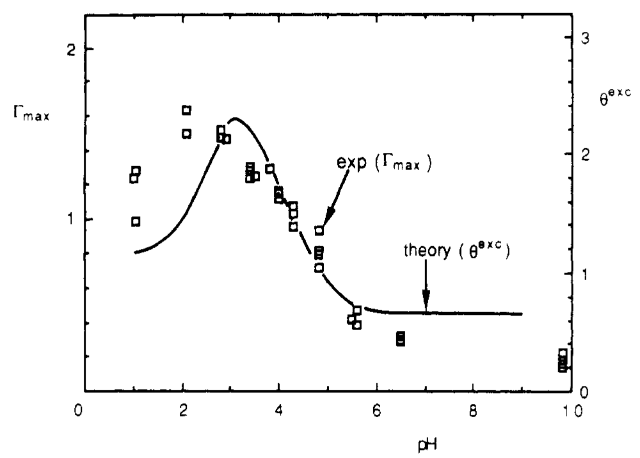

Figure 5. Adsorbed amount, Γ, as a function of the pH for the adsorption of PAA (M_w = 70 900) onto a cationic latex with σ_0 = 160 mC/m² in 0.1 N KNO_3. The experimental points (corresponding to the left-hand scale in milligrams per square meter) were measured at an equilibrium concentration of 100 ppm (w/w). The drawn curve is the theoretical excess adsorbed amount, θ^{exc} (right-hand scale, in equivalent monolayers). This curve was computed according to the model of Böhmer et al.,[1] using $\chi_{pS} = -8.0$, $\chi = 0.5$, $r = 500$ segments, $d = 0.6$ nm, $Z = 12$, $\phi_p^b = 1 \times 10^{-4}$, $pK_0 = 4.25$, $\sigma_0 = 160$ mC/m², and $c_s = 0.1$ M.

The experimental pH dependence of the adsorption of PAA on positively charge latex is shown in Figure 5 and compared with the theoretical predictions. The adsorbed amount was measured at an equilibrium concentration PAA of 100 ppm, which is in the (semi)plateau of the adsorption isotherms. The points in this graph are the experimentally determined adsorbed amounts for the adsorption of the M_w = 70 900 PAA sample onto latex with a surface charge density of 160 mC/m² in 0.1 M KNO_3; for these points the left-hand scale (Γ in milligrams per square meter) applies. The final concentrations PAA were measured by means of the potentiometric titration procedure. The drawn curve gives the theoretical excess adsorbed amount, θ^{exc} (right-hand scale, in equivalent monolayers), as predicted by the model of Böhmer et al.,[1] with values for the variables as given in the legend.

The qualitative agreement between theory and experiment is excellent: the overall shape of the theoretical and experimental curves is identical: both showing a maximum at a pH somewhat below pK_0. Their is a difference, of the order of 0.5 unit in the pH, in the exact position of the maximum, but the main trends are fully accounted for in the theoretical model.

The theoretical curve predicts a slightly sharper maximum than was obtained experimentally. A reason for this might be the way in which water is accounted for in the model. For calculation of the degree of dissociation of the polyelectrolyte segments the local water concentration is taken into account. Because both segments and salt ions occupy one lattice site, the volume fraction water in the first layer becomes very low at high surface charge densities, resulting in a rather low degree of dissociation. As a consequence, more salt ions are needed for screening the surface charge, leading to a lower adsorbed amount at low pH than is found experimentally.

For a more quantitative comparison one should relate the experimental scale (milligrams per square meter) to the theoretical one (equivalent monolayers). For such a comparison one needs an estimate for the conversion of monolayers to milligrams per square meter, and it is very difficult to find an exact conversion factor. Assuming that one polymer segment is identical with one monomer and using a reasonable molecular model, one finds that a fully packed monolayer would correspond to about 0.4 mg/m^2, whereas Figure 5 suggests a value of 0.7 mg/m^2. The agreement is reasonable, especially considering the fact that we did not try to optimize the theoretical parameters (lattice spacing, chain length, interaction parameters χ and χ_{pS}). At present, there is not enough information to make such a best fit. However, already now we may conclude that the correlation between the SCF theory in which the electrostatic interactions are incorporated and experiment is semiquantitative. The available experimental data cannot, at present, distinguish between the model with[1] and without[10] a volume for the ions. For such a comparison, more detailed information would be needed.

There are only a very few examples in the literature where a maximum in Γ(pH), as in Figure 5, is obtained. Tanaka et al.[13] report for the adsorption of cationic polymers (modified starch) onto bleached kraft pulp such a maximum in the adsorbed amount. For different cationic polymers, it is found at a pH where approximately 3% of the active groups in the bulk solution are ionized. The cationic groups on the polymer are a result of a chemical modification of the macromolecule, and the degree of substitution is always lower than 0.8. Since the chemically modified groups will have different interaction energies, it is not yet possible to give a theoretical interpretation for these experiments. Also the characteristics for their adsorbent are not known. Nevertheless, it is noteworthy that the maximum appears at low degrees of ionization, well below pK_0.

Wang et al.[39] and Durand-Piana et al.[40] have studied the adsorption of a cationic copolymer as a function of the fraction τ of cationic monomeric groups in an otherwise uncharged polymer. Wang et al.[39] adsorbed this polymer onto silica, whereas the latter authors used a sodium montmorillonite clay as the adsorbent. At τ = 1% these authors found a maximum in the adsorbed amount. For these copolymers it is very likely that the different monomers have different interaction energies with the surface and with the solvent, and therefore the present theoretical models cannot be applied to these experiments. An additional problem is that the mean-field approach might break down for a polymer chain with only 1% strong cationic groups that behave as discrete charges. Notwithstanding the uncertainties in the detailed theoretical interpretation, the fact that a maximum is found at a low fractional polymer charge is an interesting feature.

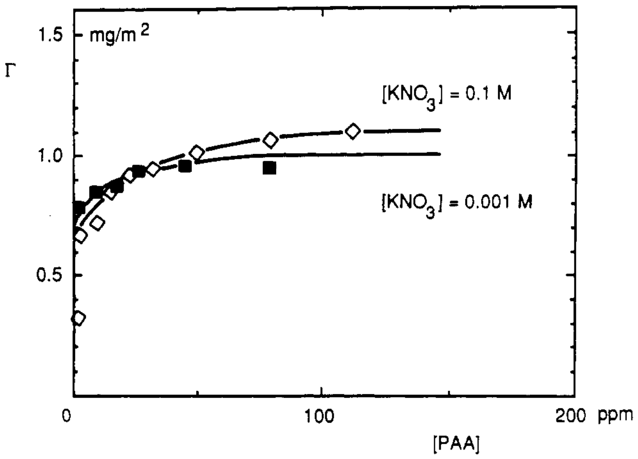

Figure 6. Effect of the ionic strength on the adsorption isotherms of PAA (M_w = 18 100) onto latex (σ_0 = 160 mC/m^2) at pH = 4.0.

In Figure 6 we show two adsorption isotherms at pH = 4.0 for the adsorption of PAA (M_w = 18 100) onto a highly charged surface at two salt concentrations. In agreement with theory (see Figure 1) there is only a small effect of the ionic strength on the adsorption. At low equilibrium concentrations the adsorption from the low ionic strength medium is slightly higher, whereas at higher concentrations the reverse is observed. Such a crossover point is also predicted by theory. The theoretical crossover appears at a much lower concentration than the experimental one. This is probably related to the shape of the isotherm, which for the experimental, polydisperse system is much more rounded than for a monodisperse polyelectrolyte. It is noteworthy that the theoretically predicted and the experimentally determined crossover points appear at the same relative adsorption, i.e., at the same fraction of the plateau in the isotherm. Anyhow, the most important conclusion is the weak ionic strength dependence for the adsorption of weak polyelectrolytes, both theoretically and experimentally, in strong contrast with the behavior of a polyelectrolyte with strong groups. As explained in the Theory section, the reason is the high degree of dissociation of groups close to the surface (leading to charge compensation) and the low charge of groups in loops and tails.

When the ionic strength is increased from 0.001 to 0.1 M KNO_3, the plateau values of the adsorption isotherms increase with approximately 9%. The calculations for these experimental conditions (Figure 1) predict also a small increase. The agreement is within experimental error. The computations also show that the absolute amount by which the adsorption increases on increasing the ionic strength is almost independent of the pH. This implies that at a high pH, where the adsorbed amount is low, the relative increase in the adsorbed amount is much larger.

We are not aware of any paper dealing with the adsorption of a weak polyelectrolyte onto a highly oppositely charged surface as a function of the ionic strength. Meadows et al.[41] report for the adsorption of 90% hydrolyzed polyacrylamide (weak polyacid) onto a latex with weak cationic groups a strong dependence of the adsorbed amount on the ionic strength. Cafe et al.,[42] studying the adsorption of radio-labeled PAA onto $BaSO_4$ crystals at pH values where the crystals are slightly negatively charged, found a small increase in the adsorbed amount upon increasing the ionic strength. Wright et al.[43] investigated the adsorption of spin-labeled PAA onto $BaSO_4$

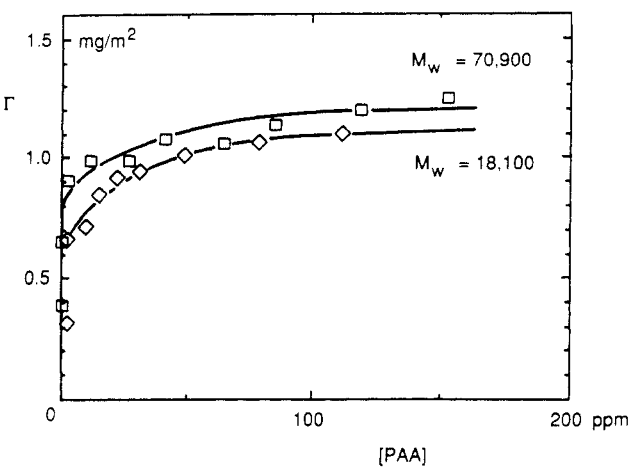

Figure 7. Effect of molecular weight on the adsorption isotherms of PAA onto latex (σ_0 = 160 mC/m²) in 0.1 N KNO_3 at pH = 4.0.

crystals prepared in a slightly different manner. They report a large increase in the adsorbed amount with increasing ionic strength. The usual assumption in studies of the adsorption of spin- or radio-labeled macromolecules is that the label does not affect the behavior of the polymer. This assumption may not be valid because it has been shown[39,40] that for a polymer that has a very low affinity for a negatively charged surface, the introduction of only 1% strong cationic groups is enough to get a large adsorbed amount. This might be a reason why Cafe et al.[42] report different adsorption results for spin- and radio-labeled PAA.

The molecular weight dependence of the adsorbed amount in 0.1 M KNO_3 at pH = 4 is illustrated in Figure 7. In this figure we have plotted two adsorption isotherms for M_w = 70 900 and M_w = 18 100, respectively, onto latex with σ_0 = 160 mC/m². The adsorption at this pH increases only slightly upon increasing the molecular weight. In the plateau region the increase is about 10% from M_w = 18 100 to M_w = 70 900. Theoretically (Figure 3), approximately the same increase is predicted. Foissy et al.[36] report for the adsorption of low molecular weight PAA samples (M_w = 700, 2000, and 4000, respectively) onto anatase at pH = 2.8 a much larger dependence of the adsorbed amount on molecular weight. This is clearly understood because at this pH PAA behaves more like a neutral polymer. Moreover, at low molecular weights the dependence of the adsorption on chain length is most pronounced. These two effects are demonstrated in Figure 3.

Our last experimental result deals with the effect of the surface charge. The dependence of the adsorption of PAA on the surface charge density of the latex is shown in Figure 8, for M_w = 18 100 in 0.001 M KNO_3 at pH = 4. Two latices were used, with surface charge densities of 100 and 160 mC/m², respectively. It is evident that by increasing the surface charge density the adsorption increases, in this case by about 12%. The computations for this situation with the model of Böhmer et al.[1] predict an increase that is of the same order of magnitude. Again the agreement is satisfactory.

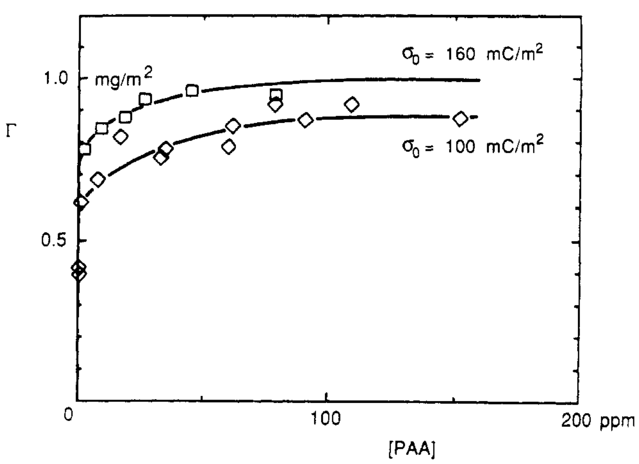

Figure 8. Effect of the surface charge density on the adsorption isotherms of PAA (M_w = 18 100) onto latex in 0.001 M KNO_3 at pH = 4.0.

In the theoretical section we stated that the surface charge is already compensated in the first layer. On the basis of this statement, one would expect the adsorption to increase roughly proportional to the increase in the surface charge density. However, one has to bear in mind that at the same pH in the bulk solution the degree of dissociation of segments in contact with a highly charged surface is higher than that of segments in contact with a less charged surface. Therefore, when the surface charge density is increased, only a small increase in the number of train segments is needed to compensate the surface charge in the first layer.

Conclusions

The adsorption of poly(acrylic acid) (PAA) onto a highly charged polystyrene latex with strong cationic groups depends strongly on the pH. When the plateau values of the adsorption isotherms are plotted as a function of the pH, a maximum is obtained at a pH that is about 1 unit below the pK_0 of the polyacid. The measurements were used to test a theoretical model[1] that describes the adsorption of weak polyelectrolytes. The experimental maximum in the adsorbed amount is found close to the pH where the theory predicts the maximum. The maximum arises because of two opposing trends. With increasing pH there is a higher electrostatic contribution to the segmental adsorption energy, but as the polyelectrolyte groups become progressively dissociated the increasing repulsion between these groups opposes the accumulation of polyelectrolyte near the surface.

The effect of the salt concentration on the adsorbed amount at pH = 4 is very low. This is also predicted by the computations, which show that the polymer segments in contact with the surface are dissociated to such a degree that already in the first layer the surface charge is compensated, or even slightly overcompensated. The segments in the loops and tails are dissociated to a much lower degree. So effectively, looking from the bulk solution, one sees a nearly neutral particle. Therefore, salt will hardly affect the adsorption. It is interesting to note that adsorption isotherms at two different ionic strengths intersect each other at a low polyelectrolyte concentration, both experimentally and theoretically.

Not only the dependences of the adsorption on the pH and on the ionic strength but also the effects of the molecular weight of the macromolecule and the surface charge density of the adsorbent are well predicted by theory. We can conclude that the adsorption of PAA onto a positively charged latex is described semiquantitatively by recent SCF theories, in which the electrostatics are incorporated.

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Viscoelastic Properties of Blends of Poly(acrylonitrile-*co*-styrene) and Poly[styrene-*co*-(*N*-phenylmaleimide)]

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ABSTRACT: Dynamic viscoelastic properties for miscible polymer blends of poly[styrene-*co*-(*N*-phenylmaleimide)] (SMI) and three kinds of poly(acrylonitrile-*co*-styrene)s (AS) with the same composition but different molecular weights (AS-2, AS-3, and AS-4, in increasing molecular weight) are measured by using a concentric cylinder-type rheometer. It is found that the time–temperature superposition principle can be applied over the entire temperature range for the blends. The temperature dependence of the shift factors can be expressed by the WLF equation $\log a_T = -8.86(T - T_s)/(101.6 + T - T_s)$. The T_s and, in other words, the glass transition temperature of the blends increase linearly with an increase in the mole fraction of SMI. The zero-shear viscosities at constant temperatures increase concavely with the SMI content for SMI/AS-2, have a minimum at 20 wt % SMI for SMI/AS-3, and hardly depend on the SMI content for SMI/AS-4. When compared at the same free volume fractions, the zero-shear viscosities decrease convexly with SMI content for all blends. Such compositional dependences of the zero-shear viscosities can be interpreted by the change in the number of entanglement couplings, without any change in each entanglement molecular weight in the component copolymers. It means that the relaxation behavior of the miscible SMI/AS blends is similar to that of a blend consisting of homologous polymers with different molecular weights. It is emphasized that the viscoelastic functions of miscible blends should be compared at the isofree volume condition.

Introduction

Recently, it has been demonstrated that systems consisting of a homopolymer and a copolymer or two different copolymers are miscible for a certain range of copolymer composition, even though the combinations of their corresponding homopolymers are immiscible. It has been proposed that the miscibility of the copolymers is due to a repulsion between the two different monomer units comprising the copolymers,[1–3] and in a mean-field approach

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