Phase Separation Phenomena and Viscosity Enhancements in Aqueous Mixtures of Poly(styrenesulfonate) with Poly(acrylic acid) at Different Degrees of Neutralization

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ABSTRACT: Interactions between poly(styrenesulfonate) (PSS) and poly(acrylic acid) (PA) in aqueous solution have been studied, with and without added salt, and at various degrees of neutralization (α) of PA. Equilibrium phase diagrams have been determined, and the viscosities of monophasic mixtures have been measured. Both types of experiments reveal striking effects of α on the PA–PSS interactions. Salt-free mixtures with fully or partially neutralized poly(acrylic acid) phase separate segregatively, except at very low α where, instead, an association between PA and PSS occurs. The association is evidenced by a dramatically increased viscosity, relative to solutions of PA or PSS alone, in semidilute mixtures. Addition of salt (1 M NaCl) results in an increased two-phase area at all α, and in the appearance of an associative phase separation for non-neutralized PA. The qualitative phase behavior observed in the presence of salt can be generated by calculations using the Flory–Huggins theory, if it is assumed that both the PSS–PA and the PA–solvent interactions change monotonically with α in a specified fashion. All experimental observations, and the theoretical modeling, suggest that the effective PA–PSS interaction changes (over a narrow interval of α) from an attraction at very low α to a repulsion at higher α.

Introduction

Aqueous polymer mixtures exhibit a rich behavior, including synergistic viscosity enhancements and a variety of phase separation phenomena. A quite small repulsive interaction between unlike polymers, or a difference in the polymer–solvent interactions, results in a segregative[1] phase separation. In this type of phase separation, commonly known as “polymer incompatibility”, two liquid phases are formed, where each phase is enriched in one of the polymer components.[2–4] An important application of segregating polymer mixtures, such as the well-known mixtures of poly(ethylene oxide) (PEO) and dextran, is for the partition of biological macromolecules.[3] A preferential attraction between unlike polymers, on the other hand, may give rise to an enhanced viscosity[5,6] or, indeed, to an associative phase separation,[1] where a concentrated liquid phase is formed which is enriched in both polymers. The best studied type of associative phase separation is that occurring in mixtures of two oppositely charged polyelectrolytes,[3,7–9] often referred to as “complex coacervation”.[7] The associative phase behavior is not restricted to oppositely charged polyelectrolytes, however. Indeed, it has been observed for nonionic polymers in nonaqueous solvents.[10]

The phase behavior is particularly complex in polyelectrolyte mixtures, where the entropy of mixing of the small counterions often plays a dominant role.[1,11,12] For instance, on the successive addition of salt, pairs of oppositely charged polyelectrolytes,[3] or of oppositely charged polyelectrolyte and surfactant,[13] have been shown to undergo a transition from an associative phase separation, *via* a complete miscibility, to a segregative phase separation. A strong salt sensitivity is also seen in intrinsically (i.e., in the absence of polyelectrolyte effects) segregating mixtures of a polymer and a polyelectrolyte: The creation of a phase enriched in the polyelectrolyte and its counterions is much facilitated in the presence of salt.[14,15] More complex polymer/polyelectrolyte mixtures, involving partially neutralized poly(acrylic acid) (PA), have been studied by Iliopoulos et al.[5,15] and van Minh et al.[16] They showed that the phase behavior depended strongly on the degree of neutralization of PA. Thus, at low degrees of neutralization, there is a strong attraction between PA and certain nonionic polymers like PEO, poly(vinyl alcohol) and poly(vinylpyrrolidone) (PVP).

Little systematic research has been done on the phase behavior of mixtures of similarly charged polyelectrolytes.[3,17] A previous study[17] has demonstrated that mixtures of the two highly charged polyelectrolytes poly(styrenesulfonate) (PSS) and dextran sulfate give rise to a segregative phase separation, much like a mixed solution of an “incompatible” pair of neutral polymers. It was concluded that, in mixtures of similarly charged polyelectrolytes, the effect on the phase behavior of the dissociated counterions largely disappears, since a segregative phase separation can be achieved without an unfavorable enrichment of counterions in one of the separating phases.

In the present investigation, we have studied interactions in mixtures of the anionic polyelectrolytes PSS and PA. The degree of neutralization, α, of PA has been varied between 1 and 0, so that the transition from a mixture of two roughly equally charged polyelectrolytes to a polymer/polyelectrolyte mixture could be studied in some detail. (Under the conditions of this study, PSS is always fully charged.) As far as we are aware, this particular polymer combination has not been studied in detail before. This is remarkable, in view of the fact that PA and PSS are two of the most common “model polyelectrolytes” encountered in the literature. The studies have been made in salt-free mixtures, as well as in the presence of large amounts of salt (1 M NaCl), to screen out most of the long-range electrostatic interactions. As will become evident below, the PA/PSS mixtures turned out to have a quite rich and partly unexpected behavior, ranging from segregation (for most of the range of neutralization of PA) to association (for uncharged or slightly charged PA). In the absence of

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salt, the association manifested itself as a large increase in viscosity. In the presence of salt, a transition from a segregative phase behavior at high α, to an associative phase behavior at low α, was instead obtained. The latter type of transition is henceforth referred to as an "S–A transition". As will be shown below, all features of the S–A transition of PA/PSS/1 M NaCl mixtures may be reproduced by the Flory–Huggins theory, but only for quite restrictive choices of the pair interaction parameters.

Experimental Section

Materials. Poly(acrylic acid) with a molecular weight (as given by the manufacturer) of 150 000 was purchased from Polysciences as 25% solids in water. The polymer was purified by ultrafiltration and then freeze-dried. Sodium polyacrylate was obtained by addition of an equivalent amount of NaOH to poly(acrylic acid), followed by freeze-drying. Sodium poly(styrenesulfonate) was purchased from MTM Research Polymers and purified by centrifugation (to remove insoluble material) and ultrafiltration, folllowed by freeze-drying. The molecular weight was determined to be 800 000 with an Ubbelohde viscometer in 0.5 M NaCl at 25 °C, using the Mark–Houwink relation $[\eta] = 18.6 \times 10^{-3}M^{0.64}$.[18] No corrections for the water content in the freeze-dried polymers have been made. Samples were obtained by dissolving the freeze-dried polymers in the appropriate solvent (water or 1 M NaCl), adjusting the contents of the acid and sodium salt forms of PA to obtain the desired degree of neutralization. In the following, a sample containing a molar fraction of α of the sodium salt form of PA will be denoted as PA(α). Thus, for instance, PA in the acid form is denoted PA(0), whereas fully neutralized PA is PA(1). All water used was of Millipore quality. Polymer concentrations are given in weight percent (%) throughout.

Methods. Isothermal phase boundaries at 25 °C were obtained from "cloud points" or by determination of the phase compositions of neatly separated samples. For the determination of isothermal cloud points, samples were prepared in the two-phase area, and solvent or polymer solution (as appropriate) was added until the one-phase area was reached. A sample was regarded as monophasic when it was completely clear (without stirring) on inspection or, in some doubtful cases, when no phase boundary could be observed after a few days of storage at constant temperature. For some mixtures, the cloud-point method was also used to obtain phase separation temperatures at fixed compositions.

Phase compositions were obtained by the following procedure. After mixing, the samples were stored at 25 °C for a few days to achieve macroscopic phase separation. The two phases were then collected separately and diluted as appropriate for concentration determinations. The PSS content was determined by UV absorbance at 262 nm. In samples containing salt, the salt concentration in each of the separating phases was determined by chloride titration with mercury(II) nitrate.[19] Chloride forms a complex with mercury(II) ions and an excess of mercury(II) is indicated with diphenylcarbazone. The PA content was obtained from measurements of the refractive index, using calibration curves determined separately for all added species [NaCl, PSS, PA(0) and PA(1)]. Prior to these measurements, the samples were diluted to a total solute concentration of ≤0.1%, where measurements had shown that the contributions to the refractive index from the different solutes were additive. After subtracting the contributions from the species determined independently (PSS and NaCl), the PA content was calculated using the approximation that the degree of neutralization of PA was the same in both of the separating phases. [The latter approximation is not serious, since the refractive index increments of PA(0) and PA(1) are not very different.]

Viscosity measurements were performed at room temperature in an Ostwald viscometer with a capillary tube dimension of 0.6 mm for 0.1% solutions or 1.0 mm for 0.6–2.0% solutions.

Results

Phase Diagrams in Pure Water. Figure 1 shows ternary phase diagrams for aqueous mixtures of PSS with PA at different degrees of neutralization. A nearly symmetrical segregative phase separation is seen over most of the range of α, from PA(1) to PA(0.25) (Figures 1a–c). In this region, the tie lines (i.e., the lines connecting two phases in equilibrium) are nearly horizontal, signifying that the water content of equilibrium phases is nearly equal. The slight slopes seen in most of the diagrams change progressively with decreasing α so as to make the PSS-rich phase more dilute. A peculiar observation, not evident in the phase diagrams, was a shift in the relative densities of the PSS-rich and the PA-rich phases when the degree of neutralization was lowered. For PA(1), the PA-rich phase was the bottom phase, but for PA(0.43) and PA(0.25), it formed the top phase. Presumably, this trend is caused by an increase in the specific volume of PA with decreasing α.

At low degrees of neutralization (Figures 1d,e), the phase diagrams look rather different. The two-phase area, which now shrinks with decreasing α, is displaced toward the PSS–water axis, and the tie lines are quite tilted. PA is again enriched in the bottom phase, whereas the PSS content is almost the same in the two phases. To obtain a neat phase separation and an accurate determination of the phase compositions in this region proved to be difficult. Slightly turbid bottom phases indicated that the samples were not in equilibrium. Although the slopes of the tie-lines were all practically the same, the positions of the end points varied in an erratic manner. Therefore, the phase boundaries were here determined entirely by the cloud-point method, and the tie lines shown in Figure 1d,e only indicate the slopes of the experimental tie lines. A marked sensitivity to temperature was noted at low α. Thus, the phase boundary to the right in Figure 1e (α = 0) moves toward the PA axis at increased temperature. A similar growth of the two-phase area with increasing temperature was seen for PA(0.08) (Figure 1d), where a clear mixture of 5% PA and 5% PSS became turbid on heating.

Mixtures of equal amounts of PA(0) and PSS were always monophasic (Figure 1e) and were found to have a much enhanced viscosity, in the semidilute region, compared to pure PA or PSS solutions. This feature will be explored in more detail below.

Phase Diagrams in 1 M NaCl. Although a mixture of two polymers, salt, and water is strictly a four-component system, we will here treat it as a pseudo-three-component system, using the ordinary three-component representation. The salt is thus included in the solvent, even though the salt/water ratio may be different in two separating phases. Figure 2 shows such pseudo-ternary phase diagrams for PSS and PA in 1 M NaCl, at different degrees of neutralization of PA. As when water is the solvent, there is a segregative phase separation for fully neutralized PA, and there are only small changes in the phase diagram on going from PA(1) to PA(0.43). In this high-α region, the chloride concentrations are almost the same in the separating phases. The major difference from the salt-free case (Figure 1a,b) is that the two-phase area is larger in 1 M NaCl and the tie lines are more horizontal. As expected, the viscosities of the phases are also lower in the presence of salt, owing to the contraction of the polyions. A further subtle difference is that in 1 M

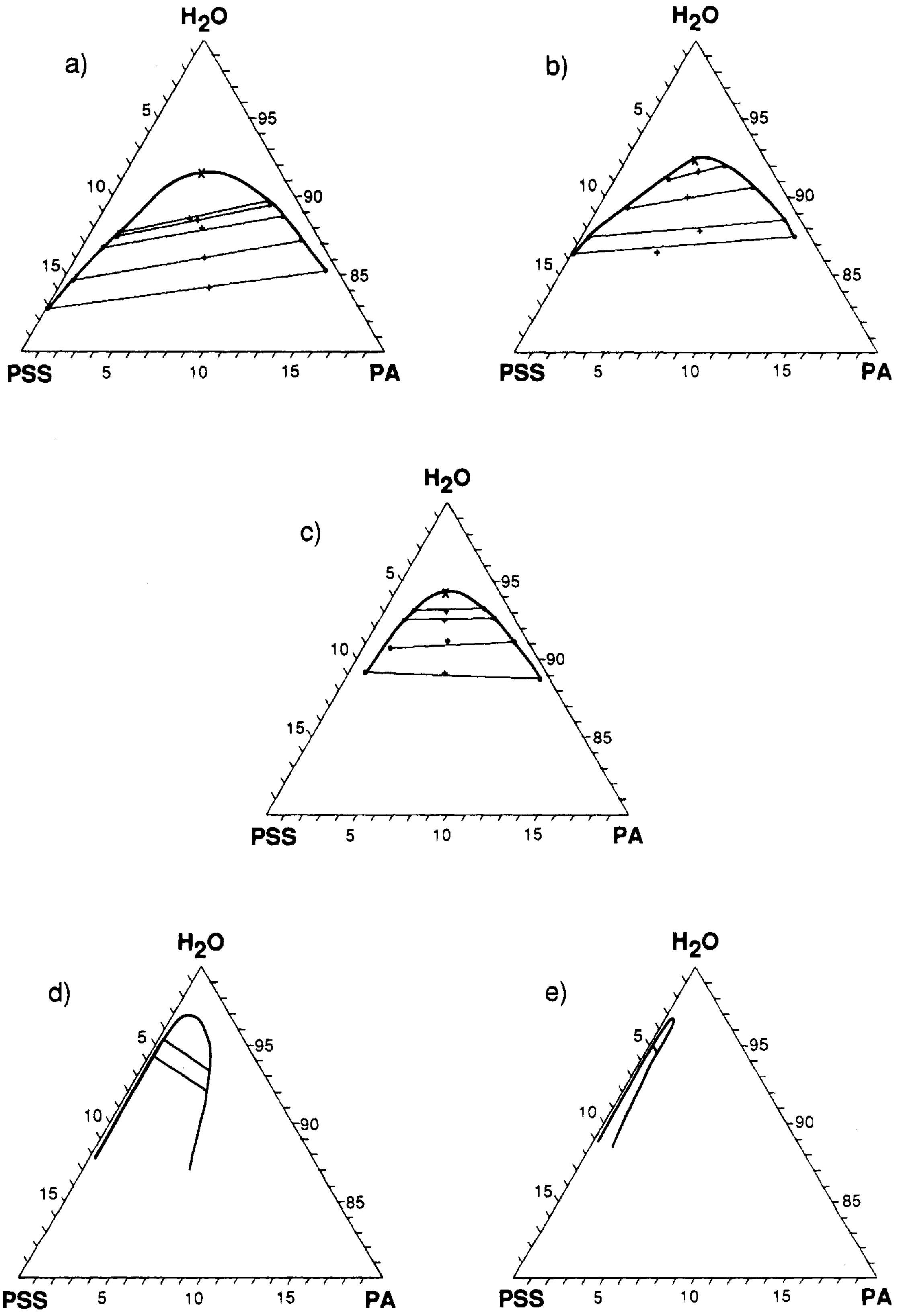

Figure 1. Ternary phase diagrams (compositions in weight %) of aqueous mixtures of PSS and PA(α) for α = 1.0 (a), 0.43 (b), 0.25 (c), 0.08 (d), and 0 (e). Diagrams a−c are based on equilibrium compositions of separating phases (●), obtained from samples with varying total compositions (+), and on cloud points (×) of mixtures of equal amounts (by weight) of PSS and PA. Tie lines connect equilibrium phases. Diagrams d and e are obtained from cloud-point measurements; tie lines indicate the slopes of experimental tie lines.

NaCl, the PSS-rich phase is the top phase at all values of α.

On reducing α to 0.29 (Figure 2c), however, a development is seen which has no correspondence in the salt-free case. Although the phase separation is still segregative, the two-phase area has increased considerably and the tie lines have a pronounced slope. A phase-separated sample of equal amounts of PSS and PA(0.29) contains a small (about one-fifth of the total volume) concentrated PA-rich bottom phase and a larger, less

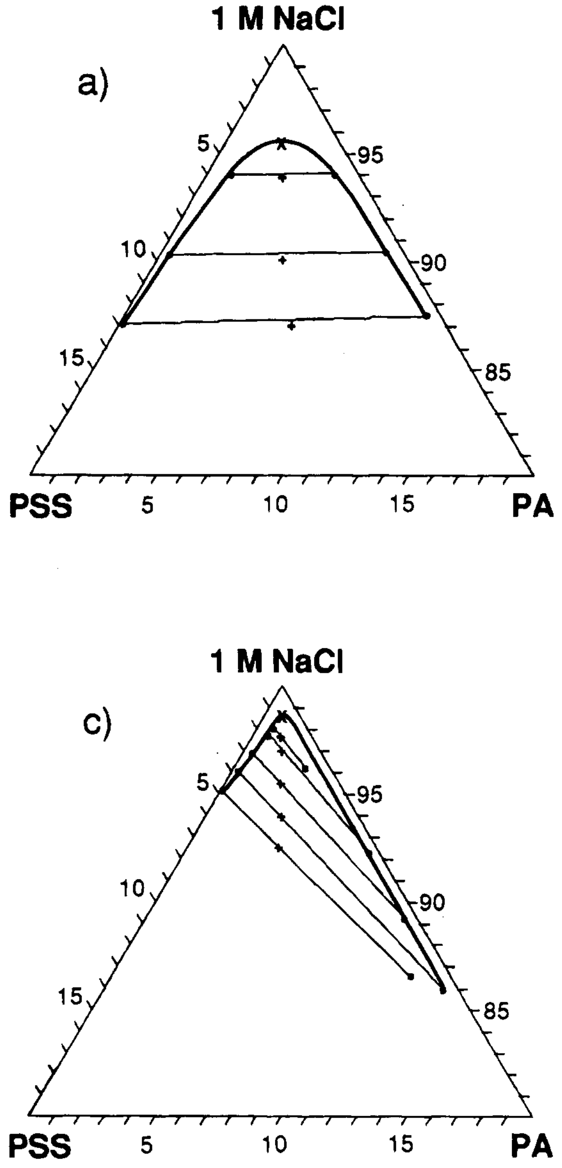

Figure 2. Pseudo-ternary phase diagrams (compositions in weight %) of mixtures of PSS and PA(α) in 1 M NaCl for α = 1.0 (a), 0.43 (b), 0.29 (c), and 0 (d), based on equilibrium compositions of separating phases (●), obtained from samples with varying total compositions (+), and on cloud points (×) of mixtures of equal amounts (by weight) of PSS and PA. Tie lines connect equilibrium phases. Pseudo-binary mixtures of PA/1M NaCl were found to phase separate for PA(0.29) above 4% and for PA(0) above 0.01%. Arrows in (d) indicate top phases which become cloudy on heating. The phase boundary in (d) is only schematic (cf. text).

concentrated top phase enriched in PSS. In this case, the salt/water ratio (i.e., the effective solvent composition) was significantly different in the two separating phases. This tendency was more pronounced at higher polymer concentrations. For instance, for the sample with a total of 6% polymer, the PA-rich phase contained about 14% less NaCl (counted as moles of NaCl per mole of H_2O) than the PSS-rich phase. Evidently, the interaction between NaCl and PA(0.29) is unfavorable. This is also reflected in the well-known limited solubility of PA at low α in salt solutions. According to the literature, a miscibility gap in 1 M NaCl should appear approximately for $\alpha < 0.3$ (depending on the temperature).[20,21] Our studies confirmed the appearance of a miscibility gap in the quasi-binary mixture of PA(0.29) in 1 M NaCl. [Note that, as a consequence of the uneven salt distribution, the treatment of 1 M NaCl as a pseudocomponent is here a poor approximation, and the triangular phase diagram (Figure 2c) is correspondingly inadequate to represent the full phase behavior. Thus, the PA-rich phases indicated in the diagram are only monophasic by virtue of the fact that the salt concentration in the solvent is actually lower than 1 M.] It was further noted that the phase separation for PA(0.29) in 1 M NaCl exhibits a large sensitivity to temperature, as a temperature decrease of a few degrees immediately resulted in turbid top and bottom phases.

For mixtures of PA(0) and PSS (Figure 2d), the phase separation in 1 M NaCl was clearly associative, rather than segregative, cf. the almost vertical tie lines in the phase diagram. A phase-separated sample formed one small, very viscous, polymer-rich bottom phase in equilibrium with a large, very dilute top phase. In Figure 2d, there is considerable scatter in the points representing the compositions of the bottom phases. This is because these concentrated phases were quite difficult to handle and analyze. The phase volumes were small, and the phases were very "sticky". This is also the reason why a more complete phase diagram was not obtained for this system. We did, however, confirm the existence of a one-phase region at high concentrations by preparing (by mixing at elevated temperatures) a concentrated mixture of 15% PSS and 14% PA(0) in 1 M NaCl. This mixture remained monophasic after

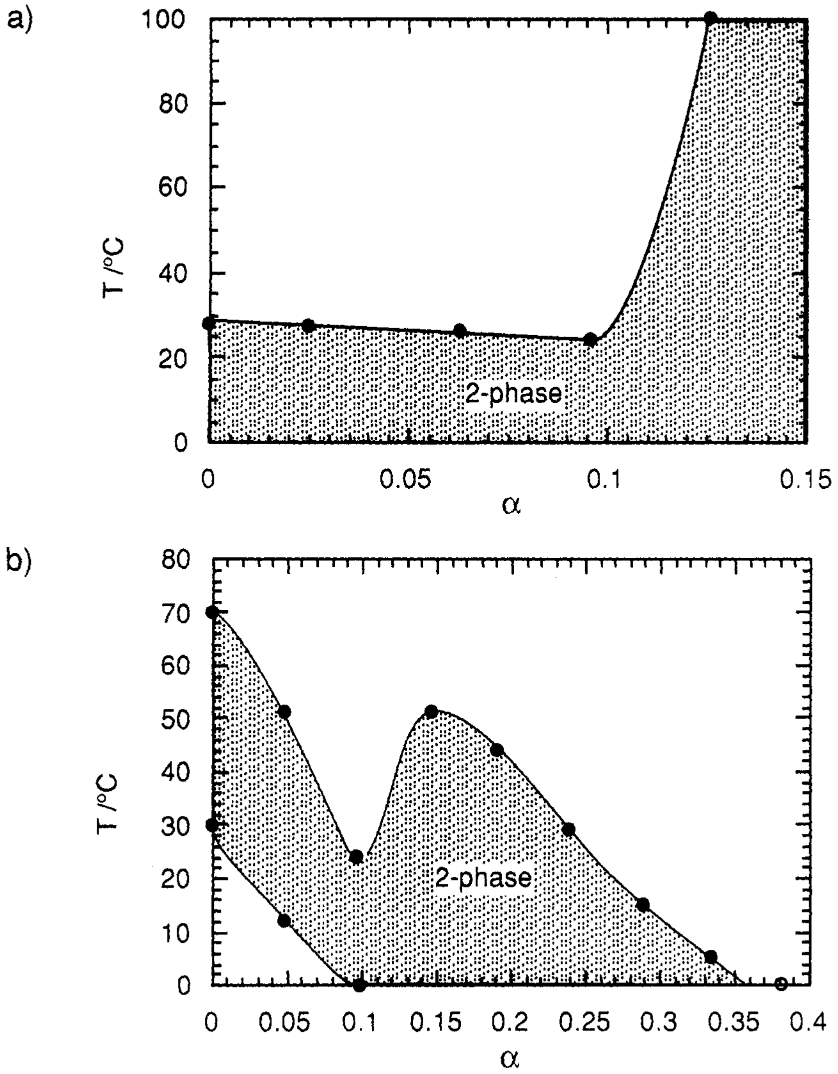

Figure 3. Variation of phase behavior with temperature and with the degree of neutralization of PA for mixtures of 10% PA/10% PSS (a) or 0.6% PA/2.0% PSS (b) in 1 M NaCl.

cooling to 25 °C. However, upon dilution with 1 M NaCl to a total concentration of 19%, a milky biphasic system was obtained at 25 °C.

For the phase-separated samples shown in Figure 2d, the salt content of the solvent was lower by approximately 15% in the polymer-rich phase. This again indicates that an unfavorable salt–polymer interaction plays an important role in the phase behavior. PA(0) alone phase-separated at very low polymer concentrations in 1 M NaCl.

Interestingly, the effect of temperature was different in different parts of the phase diagram in Figure 2d. The separating top phases found on the right-hand side of the diagram (i.e., those phases containing an excess mass fraction of PA) became turbid on cooling. In contrast, the two top phases containing an excess of PSS (indicated by arrows in the phase diagram) showed an inverse temperature dependence and became turbid on heating. The latter top phases were slightly more viscous than the other top phases, which were more water-like. All bottom phases reacted similarly on temperature and became turbid when cooled.

Owing to the experimental difficulties mentioned in connection with Figure 2d, no attempts were made to determine isothermal phase equilibria in the region $0 < \alpha < 0.29$. Rather, in an attempt to gain more information on the S–A transition occurring between the segregative (Figure 2c) and the associative (Figure 2d) phase behavior, we chose to investigate the temperature and α dependences of the phase behavior for two strategic compositions of the system. These compositions were chosen close to the phase boundary of the PSS/PA(0)/1 M NaCl mixture, where phase transition could be accomplished by small changes in temperature (cf. above). The results are given in Figure 3.

Figure 3a shows results for a concentrated mixture of 10% PSS and 10% PA(0), to which dry PA(1) or NaOH was added in small portions, to progressively change the degree of neutralization. After each addition, the phase separation temperature was determined. The original mixture was monophasic (and very viscous) above 28 °C, and the transition temperature remained nearly constant until $\alpha = 0.1$. We take the overall constancy of the behavior to indicate that the nature of phase separation was similar (i.e., associative) up to this point. At $\alpha = 0.13$, however, the phase behavior was dramatically different, and the system was now found to be biphasic up to the highest temperature investigated (100 °C). This indicates that the selected composition was no longer close to a phase boundary, but deep inside a two-phase region extending to much higher total concentrations. This is expected if the phase separation was now segregative, rather than associative.

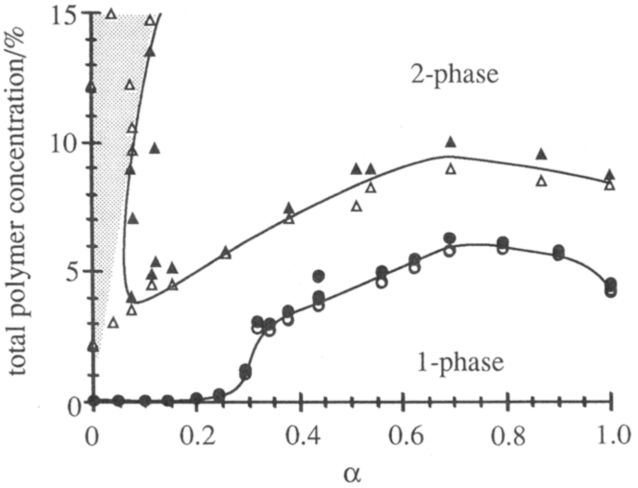

Figure 4. Biphasic (filled symbols) and monophasic (empty symbols) mixtures containing equal amounts (by weight) of PSS and PA, at varying degrees of neutralization of PA, in water (triangles) and in 1 M NaCl (circles). Shadowed area indicates region of increased viscosity in water.

The other sample investigated (Figure 3b) was a mixture of 2% PSS and 0.6% PA(0), situated in the region close to those top phases indicated in Figure 2d, where an inverse temperature dependence was found. The sample was monophasic (and highly viscous) at room temperature, but phase separated on heating to roughly 30 °C. On further heating, the sample became monophasic again roughly at 70 °C. On a change in α (by adding NaOH), this biphasic temperature interval shifted in a complicated fashion. Initially, it moved progressively to lower temperatures, until, at $\alpha = 0.1$, the system was biphasic below 24 °C and monophasic above this temperature. At $\alpha = 0.15$, however, the biphasic region was suddenly greatly expanded and extended all the way from 0 to 51 °C. A further increase in α beyond this point resulted in a monotonic decrease of the biphasic temperature region, until the sample was monophasic in the entire temperature interval 0−100 °C at $\alpha = 0.38$.

The above tests clearly indicate that a transition in the phase behavior occurs in a very narrow region of charge neutralization, just above $\alpha = 0.1$. Presumably, this transition is nothing but the S−A transition. As might be expected, the transition region is characterized by a comparatively large miscibility (a small extension of the two-phase area), but the transition is nevertheless continuous: The segregative and associative two-phase areas are connected, without an intervening region of total miscibility.

Phase Boundaries for Mixtures of Equal Concentrations. Figure 4 shows the variation with α of the isothermal phase boundaries for mixtures containing equal masses of PSS and PA, in water and in 1 M NaCl, and at total polymer concentrations below 16%. This representation of the phase behavior is complementary to the information given in Figures 1 and 2, in that the degree of neutralization is now varied in small steps for a fixed PSS/PA ratio. One new feature that becomes evident in Figure 4 is that the miscibility of the polymers, both with and without salt, passes through a maximum in the high-α region. Otherwise, the picture given earlier is confirmed by Figure 4: A rather weak dependence of the phase behavior on the degree of neutralization of PA is seen over a large range of α, from fully neutralized PA down to a degree of neutralization around 0.3. The effect of salt in this region is essentially only to lower the miscibility of the two polymers. At lower degrees of neutralization, however, the effects of varying α or of adding salt both become more pronounced. In the salt-free case, a minimum in the miscibility is seen around $\alpha = 0.10$; here also a one-phase region appears at high polymer concentrations. Compared to the single polymer solutions, a mixed solution in the latter one-phase region has an increased viscosity. On dilution, such a mixture first becomes turbid, but on further addition of water, it becomes clear again. For PA(0), mixtures of equal concentrations of the two polymers are always monophasic (cf. Figure 1e), and the viscosity is quite high in the semidilute concentration range.

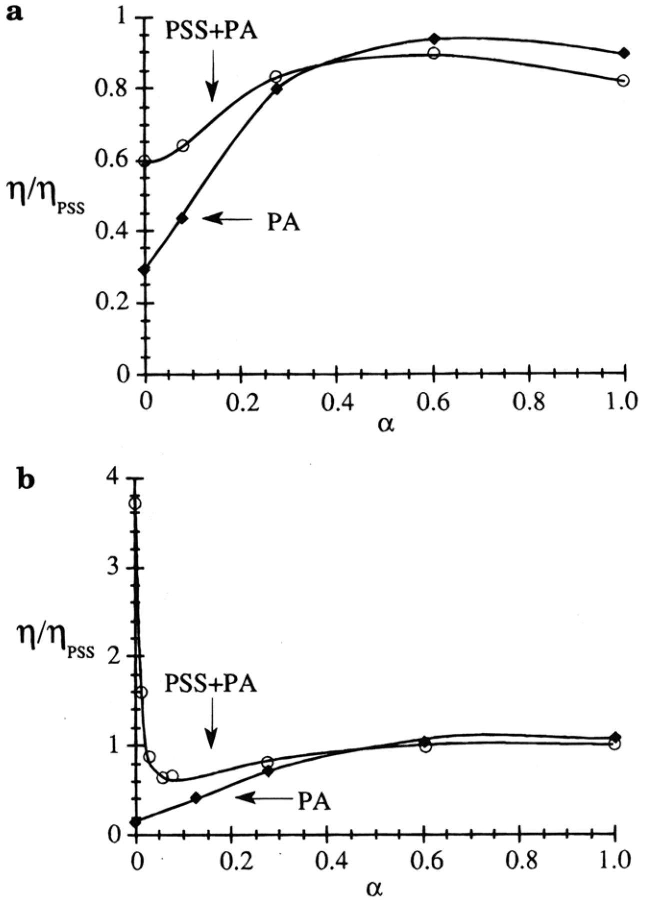

Figure 5. Normalized (relative to the viscosity of aqueous PSS) viscosities of aqueous PA (♦) and aqueous mixtures of equal concentrations (by weight) of PSS and PA (○) at different degrees of neutralization of PA. Total polymer concentrations were constant at 0.1% (a) or 2.0% (b).

In 1 M NaCl, on the other hand, phase separation occurs below $\alpha = 0.3$ even if the total polymer concentration is extremely low. Note, in Figure 4, that the two-phase area in 1 M NaCl is continuous over the whole range of α and, in particular, in the region $0 < \alpha < 0.29$, where the S−A transition occurs. As stated in the previous section, a one-phase area appears again at quite high total polymer concentrations (above 20%), in the range $0 < \alpha < 0.1$.

Viscosity. One of the most striking properties of PSS/PA mixtures is the highly enhanced viscosity that appears in salt-free, semidilute mixtures of PSS and PA(0). This feature was investigated more closely by capillary viscometry. Figure 5 shows the viscosities, normalized with respect to the viscosity of aqueous PSS, of aqueous mixtures of equal concentrations of PSS and PA, at different degrees of neutralization of PA and at

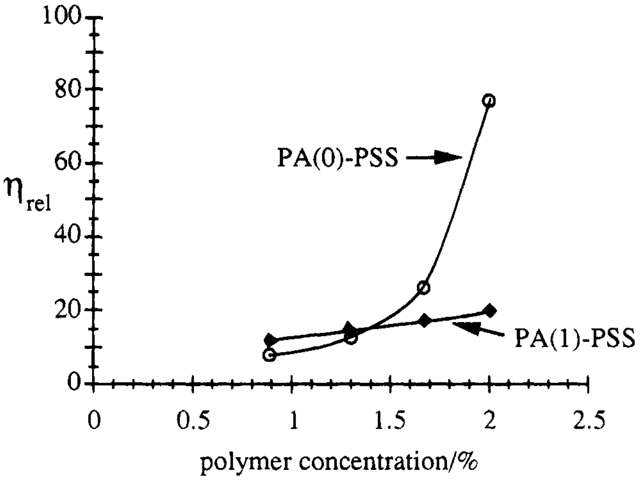

Figure 6. Relative viscosities for aqueous mixtures of equal concentrations (by weight) of PSS and PA(1) (♦) or PA(0) (○) as a function of the total polymer concentration.

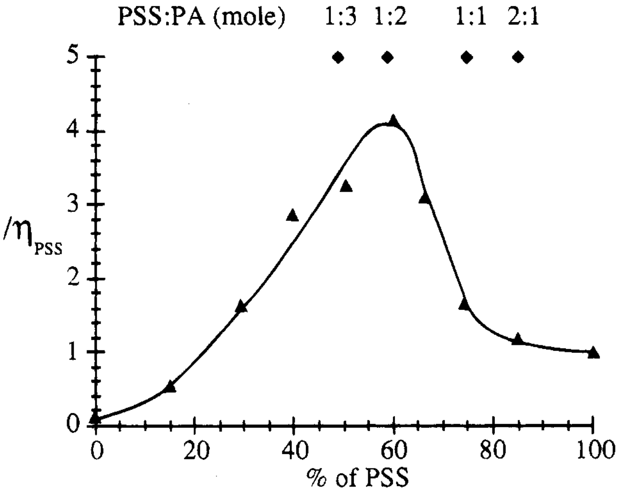

Figure 7. Normalized viscosities of 2.0% (total polymer) aqueous mixtures of PSS and PA(0) with varying PSS content. Monomer molar ratios of PSS to PA are indicated on the top horizontal axis (♦).

two different total polymer concentrations. All mixtures were well within the one-phase area, according to Figure 4. For comparison, the normalized viscosity of aqueous PA alone is also shown. At the lower total concentration (Figure 5a), no particular effect is seen in the mixtures, and the viscosity is always close to the average of the viscosities of the pure PSS and PA solutions. The only discernible effect of varying α is due to the well-known extension of the PA chain on increasing its charge density.[22] In contrast, at the higher polymer concentration (Figure 5b), a steep increase in the viscosity appears on lowering α below 0.05.

The concentration dependence of the viscosity in mixtures of PSS with equal concentrations (by weight) of PA(0) or PA(1) is shown in Figure 6. For PA(0), a rapid increase in viscosity begins at a critical polymer concentration near 1.5%. In contrast, the viscosity in a mixture with PA(1) rises quite gradually, again demonstrating the difference in interactions with PSS displayed by neutralized and non-neutralized PA. Figure 7, finally, shows the viscosity as a function of the PSS content in mixtures of PA(0) and PSS at a constant total polymer concentration of 2%. Already, a minor replacement of PA(0) with PSS leads to an enhanced viscosity, and with increasing content of PSS, the viscosity rises to a maximum at 60% (by weight) of PSS. The monomer molar ratio of PSS to PA(0) is also indicated in the figure, and at the maximum viscosity this ratio is about 1:2. The significance of the latter stoichiometry is not clear, since the maximum refers to a single overall concentration. Nevertheless, the data in Figures 5–7 strongly suggest that an effective attraction between PA and PSS sets in at very low degrees of neutralization of PA, leading to a molecular association between the two types of polymer.

Discussion and Interpretations

The results presented above reveal a very complex behavior of PA/PSS mixtures. The most interesting effect is certainly the association between unlike polymers that appear at low α. This association and the low solubility of PA in salt solutions at low α seem to be key factors responsible for the transition from a segregative phase separation at high α to an associative phase separation at very low α in 1 M NaCl. A similar S–A transition has previously been reported for mixtures of PA with PVP.[15] The latter case is similar to ours in that the association does not involve oppositely charged polyelectrolytes. An important difference, however, is that a region of complete miscibility was found in PA/PVP mixtures between the segregative and the associative regions. Such a discontinuity in the S–A transition seems to be the rule rather than the exception.[3,10,13] To the best of our knowledge, our study represents the first observation of a continuous S–A transition for two polymers in a common solvent.

To unravel the variation in the phase behavior of PA/PSS mixtures in detail is obviously complex. Below, we will first give a qualitative discussion of the phase behavior at high and low α, with and without salt. We will then use model calculations using the Flory–Huggins theory[2] to gain more insight into the possible role of the PA–PSS and PA–solvent interactions for the complex phase behavior in 1 M NaCl. Lastly, we will briefly discuss the nature of the PA(0)/PSS association. Although the inverse temperature dependence of the phase separation for certain compositions is notable and interesting, its origin is unclear to us, and it will therefore not be discussed further.

Segregation at High α. At high degrees of neutralization of PA, the PSS/PA mixture is a mixture of two similarly charged polyelectrolytes with comparable charge densities. For such a mixture, just as for an ordinary mixture of nonionic polymers,[2,3] a segregative phase separation is generally expected even in the absence of salt.[12,17] The segregation found at high α is therefore not surprising. Still, two features in this segregative region deserve to be discussed further, i.e., the nonmonotonic variation of the two-phase area with α and the salt sensitivity of the segregation. Both these features are readily apparent in Figure 4.

In the absence of polyelectrolyte effects (and for fixed molecular weights), the extension of a segregative two-phase area is essentially determined by two factors, i.e., the effective repulsion between unlike polymers and the possible difference in their affinity for the solvent.[4,23,24] These two factors may be expected to dominate the segregation of PA/PSS in 1 M salt, where polyelectrolyte effects should be of minor importance. The existence of a minimum in the extension of the two-phase area around α = 0.8 (cf. Figure 4) is then interesting, since both the PA/PSS and the PA/solvent interactions are expected to change in a monotonic fashion with decreasing α. Since the PA/PSS interaction changes in the direction of an increasing *attraction* with decreasing α, this factor alone cannot give rise to an increasing segregation below $\alpha = 0.8$. The only remaining explanation is then that the difference in the polymer–solvent interactions increases as α is moved away from 0.8 to either higher or lower values. As the PA/solvent interaction should change monotonically in the direction of increasingly bad solvent conditions with lower degrees of neutralization, this would imply that the polymer–solvent interactions are actually very similar at $\alpha = 0.8$ and that 1 M NaCl is a better solvent for fully neutralized PA(1) than for PSS. We will return to this point in connection with the model calculations presented below.

In the absence of salt, the two-phase area is smaller, compared to the situation in 1 M NaCl, all across the high-α region. Two factors may account for this trend. First, the polymer–solvent interactions are changed to the better (recall that PA(0) is completely miscible with water but not with 1 M NaCl). Second, in the absence of salt, the entropy of mixing of the counterions becomes an important factor. Generally, the dissociating counterions of two similarly charged polyelectrolytes will always affect the phase separation in such a way as to create a more even concentration of counterions in the two separating phases. This leads to a shrinking of the two-phase area, relative to an otherwise equivalent mixture of uncharged polymers, except in the case when the charge densities of the two polyelectrolytes are "matched" in the sense that the concentrations of the counterions happen to be equal in the separating phases that would be produced by the nonelectrostatic interactions alone.[12]

Phase Behavior at Low α. Again, it is instructive to first consider the behavior in 1 M NaCl (Figure 2c,d). For PA(0.29), a strongly asymmetrical phase diagram is found, at a degree of charge neutralization of PA where the salt-free system is still quite symmetrical [cf. Figure 1c, for PA(0.25)]. The reason for this asymmetry is primarily the bad solvency conditions for PA in 1 M NaCl at low α. We recall that a miscibility gap in mixtures of PA with 1 M NaCl appears for $\alpha < 0.3$. The tilted tie lines for PA(0.29) and the increase of the two-phase area are both expected from an increasing PA–solvent repulsion. Thus, no changes in the polymer–polymer interaction are required to explain the qualitative changes from PA(0.43) to PA(0.29); the phase behavior is still segregative.

On going from PA(0.29) to PA(0), however, the phase behavior of PA and PSS in 1 M NaCl changes abruptly from a segregation to an association. The abrupt change at low α is in agreement with the association revealed by the viscosity measurements in water (Figure 5). In addition, the associative phase separation is aided by the limited solubility of PA(0) in 1 M NaCl, and by the fact that the counterion contribution to the solubility of PSS has been effectively removed by the large salt concentration. The net result is that associated PA and PSS are salted out, and one polymer-rich and one polymer-poor phase are created. As expected, the polymer-rich phase contains less NaCl.

Turning now to the salt-free case, we note that the phase behavior of the PA(0.08)/PSS/water system (Figure 1d) resembles that of the PA/salt/water system at low α, with PSS taking the role of the neutral salt: The solubility of PSS in the PA phase is large, whereas only a very small amount of PA is soluble in PSS. The PSS content is larger in the PA-poor phase, just as for a salting-out process. It appears therefore that the dominating effect of PSS in this system, which should be close to the borderline between segregation and association, is to salt out PA. At very low α, finally, the miscibility of PA and PSS increases considerably (Figure 1e), as expected, in view of the transition to an attractive PA/PSS interaction. A narrow two-phase area is still obtained, however, at large PSS/PA ratios and above a total polymer concentration of a few percent. The nature of this phase separation is not clear to us at the moment. It is possible, however, that it may be viewed as a salting-out of a PSS/PA "complex" at large excesses of PSS.

Model Calculations. To gain further insight into the interactions in PA/PSS mixtures, we made attempts to model, qualitatively, the phase behavior in terms of the pair interactions in the system, using the Flory–Huggins lattice theory for a mixture of two flexible polymers in a common solvent.[2] The modeling was restricted to the behavior in 1 M NaCl (Figure 2), where the long-range electrostatic interactions are effectively screened, and it may be assumed that no important features are lost by treating all interactions as short-range (nearest neighbor). We also treated the salt solution as a single (quasi)component, the solvent ($=S_1$) of the system. The interaction of the solvent with PSS ($=P_2$) was described by a single Flory–Huggins interaction parameter,[2] χ_{12}, which, naturally, was kept constant, independent of the degree of neutralization of PA. The interactions of PA ($=P_3$) with the other two components were described by two mean pair interaction parameters, $\chi_{13}(\alpha)$ and $\chi_{23}(\alpha)$, which were varied in some fashion as α was varied. The abbreviations $P_3(1)$ and $P_3(0)$ represent the sodium salt and the acid form of PA, respectively. For both polymers, the relative length, r, was arbitrarily set to 1000 in the modeling. A binary polymer–solvent mixture becomes partly immiscible if the interaction parameter $\chi_{\text{solvent-polymer}}$ exceeds the critical value $\chi_c = [1 + (r)^{-1/2}]^2/2$. With $r = 1000$, we thus obtain $\chi_c = 0.532$ for the binary systems S_1/P_2 or S_1/P_3.

Figure 8 shows examples of theoretical phase diagrams, calculated with the interaction parameters given in Figure 9. A comparison with Figures 2 and 4 shows that the Flory–Huggins model can indeed reproduce all the features observed for the phase behavior of PA/PSS mixtures in 1 M NaCl: The continuous S–A transition, the continuous change in the slopes of the tie lines, and the occurrence of a minimum in the extension of the two-phase area in the high-α region (Figure 8b). This agreement required, however, all those qualitative features of the α-dependence of the interaction parameters shown in Figure 9. This we infer from systematic model calculations, covering a large part of the parameter space.[25] In particular, these calculations showed that changes in *both* χ_{13} and χ_{23} with changing α were essential to yield a qualitatively correct description. A change in χ_{23} alone, under good ($\chi_{\text{polymer-solvent}}$ well below χ_c) or marginal ($\chi_{\text{polymer-solvent}}$ just below χ_c) solvent conditions for both polymers, was found to inevitably yield a region of complete miscibility (contrary to the observations) between the segregative and the associative regions. Thus, the poor solubility of $P_3(0)$ ($\chi_{13} > \chi_c$) was found to be an essential ingredient for the observed continuity of the S–A transition. An S–A transition driven *only* by the deterioration of the solvency of P_3 (changes in χ_{13} at constant χ_{23}), on the other hand, was found to be possible, but only for very

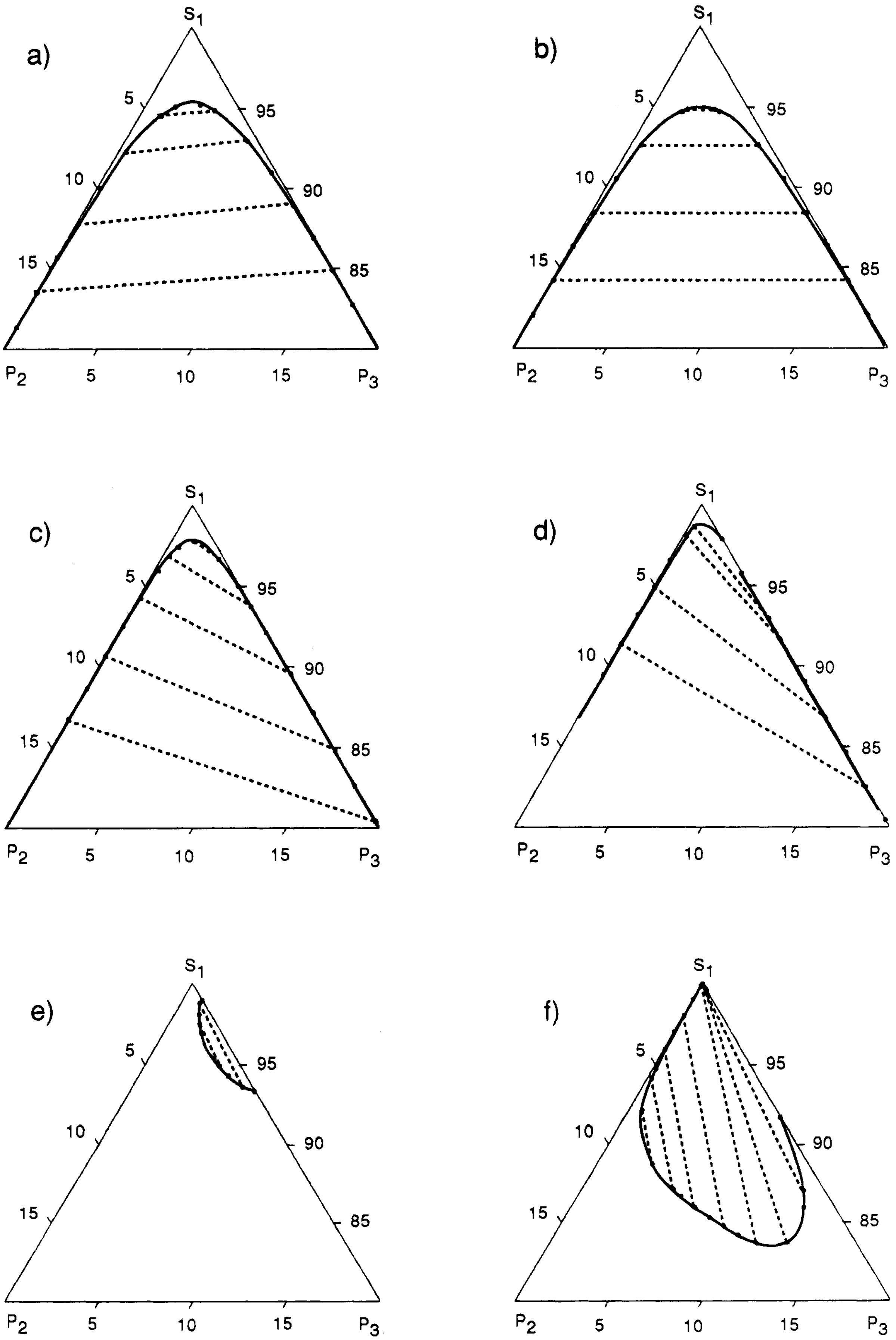

Figure 8. Calculated continuous transition from segregation to association for fixed χ_{12} with χ_{13} and χ_{23} varying according to Figure 9, at $\alpha = 1$ (a), 0.8 (b), 0.2 (c), 0.04 (d), 0.02 (e), and 0 (f). $r = 1000$ in all cases. Compositions in volume %.

restrictive choices of the other interaction parameters: χ_{23} had to be close to zero and χ_{12} had to be close to χ_c.

These choices, furthermore, either led to a discontinuous transition, or required a limited solubility of P_2 at all

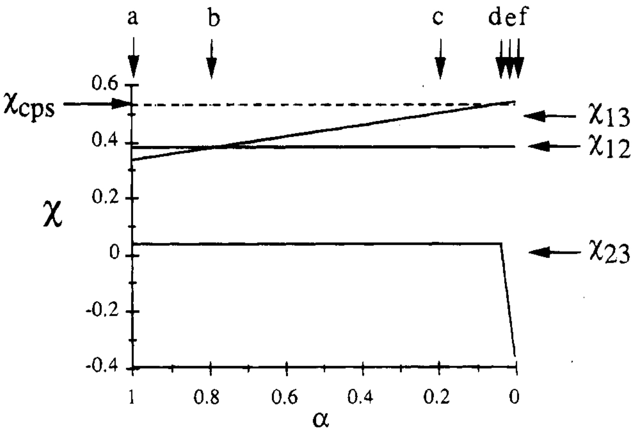

Figure 9. Variation of interaction parameters with α, chosen to qualitatively reproduce the experimental phase behavior of PA(α)/PSS/1 M NaCl mixtures. Dotted line indicates χ_{cps}. Vertical arrows refer to the parameter sets in the various diagrams of Figure 8.

values of α. Both of these features were clearly different from the experimental behavior that we wished to mimick.

Next, we considered the details of the variations in χ_{13} and χ_{23}. Since the composition of P_3 changes linearly with α, it would be natural to also let the interaction parameters vary linearly between some values chosen to represent the system at $\alpha = 1$ and 0, respectively. However, with such a variation of χ_{23}, we were unable to find a model description that could capture all features of the system. Over most of the high-α range, where the phase behavior was found to be quite insensitive to changes in α, the χ_{23} parameter had to be repulsive and to change rather slowly. Close to $\alpha = 0$, however, χ_{23} had to change abruptly to become quite attractive, in order to reproduce the dramatic changeover to associative phase behavior.

The continuous changes in the slopes of the tie lines could be reproduced by letting χ_{13} increase monotonically with decreasing α. A detail in the phase behavior, the rather shallow minimum in the extensive in the two-phase area around $\alpha = 0.8$, could be mimicked by letting $\chi_{13} = \chi_{12}$ at this particular point, assuming that χ_{13} change from a value below χ_{12} at $\alpha = 1$, to a value above χ_c at $\alpha = 0$. The increasing difference between χ_{13} and χ_{12} as the degree of neutralization is moved away from $\alpha = 0.8$ then explains the increase in the two-phase area, as well as the increasingly sloping tie lines, for phase diagrams away from this value.

The interaction parameters given in Figure 9 conform to the above prescriptions. The solubility parameter χ_{13} increases linearly from a value below χ_c at $\alpha = 1$ and crosses χ_c at $\alpha = 0.044$. (The fact that this point is different from the experimental value of $\alpha \approx 0.3$ should not concern us; our ambitions are not to quantitatively reproduce the phase behavior.) In contrast, we have let χ_{23} be constant over the interval $1 > \alpha > 0.04$. A slow decrease of χ_{23} in this region could also have been allowed; an essential feature is, however, the sharp drop when $\alpha = 0$ is approached, representing a strong attraction. Moreover, this drop, or more precisely, the change in sign of χ_{23}, must not occur until χ_{13} has increased above χ_c; otherwise, the S–A transition would not be continuous. We have here arbitrarily chosen a linear decrease between $\alpha = 0.04$ and $\alpha = 0$.

We thus find that the Flory–Huggins theory is indeed able to produce a phase behavior similar to that of PSS and PA in 1 M NaCl, with interaction parameters that vary monotonically with the degree of neutralization of PA. Still, this success occurs at the cost of introducing a sharp onset of a strongly attractive PA–PSS interaction in a narrow α range. The latter artifice indicates that the nature of the association in the real system is such that the concentrated phase is not well described by the assumptions (a random mixture of flexible polymers) made in the Flory–Huggins model.

Nature of Association. The appearance of an association between PA(0) and PSS was quite unexpected, and the nature of the attractive interaction is unclear. The polymer pair is not mentioned in reviews on interpolymer complexes,[26,27] nor does a PA/PSS complex readily fall into any of the four classes recognized by Tsuchida and Abe,[27] based on the type of interaction involved (polyelectrolyte complexes, hydrogen-bonding complexes, stereocomplexes, or charge-transfer complexes). We found a similar association between PA(0) and poly(4-vinylbenzyl)trimethylammonium chloride)—a polymer which may be regarded as a cationic polystyrene derivative—i.e., a very viscous solution was formed on mixing 13% solutions of the two polymers, and a concentrated phase separated out on increasing the ionic strength. A phase separation was also found on mixing 10% solutions of polystyrene and PA(0) in dioxane, with the formation of one more concentrated, viscous phase and one more dilute, less viscous phase. More studies are needed, however, in order to elucidate whether the latter phase separation is associative or segregative.

A conspicuous property of the association is that it disappears quite abruptly when only a small fraction of the polymer units are neutralized. This feature was found in all experiments and was confirmed in the Flory–Huggins analysis above. Evidently, the association is quite cooperative, and sensitive to only a small proportion of heterounits on the chain. We note that a similar cooperative association has previously been found for the complexation of PA with PEO.[28,29] The detailed nature of the latter complexation does not seem to be well understood, but the similarity of the two association phenomena suggests that they are closely related.

Conclusions

Aqueous mixtures of PSS and PA display a complex phase behavior, where both segregation and association may be found, depending on the degree of neutralization of PA, α, and on the content of added salt. In salt-free solutions at high α, this polyelectrolyte/polyelectrolyte/solvent mixture behaves as an ordinary polymer/polymer/solvent mixture, where a segregative phase separation is the rule rather than the exception. When α approaches zero, the phase behavior becomes different. For PSS and PA(0), an effective attraction, together with the high solubility of PSS in salt-free solutions, results in an increased miscibility, and only a small two-phase area, displaced toward the PSS–water axis, remains. Viscosity measurements confirm the attraction between PSS and PA(0), and semidilute mixtures are found to be highly viscous.

The two-phase area is generally increased upon addition of salt. As in pure water, a segregation occurs at high α. At lower α, in the interval $0.1 < \alpha < 0.3$, the phase-separation tendency is very strong, and unfavorable interactions between PA and the solvent (1 M NaCl) result in a very asymmetric phase diagram, where the PA-rich phases are much more concentrated.

A consequence of the unfavorable PA-salt interaction is that the salt is unevenly distributed between the phases. When α is further reduced, the phase behavior of PA and PSS in 1 M NaCl changes abruptly from a segregative to an associative phase separation. At $\alpha = 0$, both polymers associate into one phase, in equilibrium with a salt solution almost free of polymer. Three factors contribute to making the associative phase separation possible: the attraction between PA(0) and PSS (which was found also in salt-free solution), the low solubility of PA(0) in 1 M NaCl, and lastly, the fact that it is possible in high salt to form a phase concentrated in PSS without too large a loss in the entropy of mixing of the counterions.

All evidence (experiments and model calculations) suggests that the change in the PA–PSS interaction (from being repulsive over most of the α range to being attractive at low α) is quite sharp; i.e., it occurs over a narrow interval of α. This suggests a cooperative association phenomenon. Clearly, further studies are needed to yield more information on molecular structures and on the nature of the attractive interaction(s) in the associating mixtures.

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