Complexation of Ionomers and Surfactant Molecules of the Same Charge in a Nonpolar Solvent

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ABSTRACT: Complexation between sulfonated polystyrene ionomers and bis(2-ethylhexyl) sulfosuccinate sodium salt (aerosol OT, AOT) surfactant molecules in *m*-xylene was studied by ultracentrifugation, vapor pressure osmometry, viscometry, and dynamic light scattering. When the dilute ionomer solution is mixed with the AOT solution, complexation takes place for both the slightly aggregated state of AOT and reversed micelles of AOT containing water. In the presence of excess AOT molecules, some of the AOT are free from the ionomers, and there are well-defined limiting compositions for complexes of the ionomer and AOT and for those of the ionomer and AOT micelles. The limiting composition depends on the species of the salt or acid group of the ionomer and on the state of AOT before mixing. The composition was estimated to be 0.21–0.66 reversed AOT micelles per salt/acid group for the ionomer–AOT micelle complexes and 14–23 AOT molecules per salt/acid group for the ionomer–AOT complexes. AOT molecules were found to disrupt efficiently the cluster-forming contacts among salt/acid groups, each of them encapsulating a single salt/acid group. The AOT micelles, however, do not completely disrupt the intrachain aggregation.

Introduction

Polymer–surfactant complexes (PSC) composed of surfactant molecules and various polymers have been a subject of growing interest in recent years. PSC combine properties inherent to the surfactant molecules and those of the macromolecular component. The resultant characteristics can lead to some unexpected areas of practical application.[1-3]

The best investigated PSC are the complexes between a linear synthetic polyelectrolyte and oppositely charged low molar mass surfactant molecules.[4-10] The polyelectrolyte–surfactant complexes are formed by Coulombic interaction between the micellar-forming surfactant molecules and the polyelectrolyte chain units in aqueous solution. Hydrophobic interactions between nonpolar fragments of the surfactant molecules further stabilize these complexes. The formation of polyelectrolyte–surfactant complexes proceeds cooperatively in dilute solution at surfactant concentrations mostly below the critical micelle concentration.

When the polymeric component is amphiphilic, one can also expect formation of PSC via nonspecific amphiphilic interactions. Water-soluble complexes of this kind consisting of poly(ethylene oxide) or poly(vinylpyrrolidone) and sodium dodecyl sulfate, an anionic surfactant, have been most intensively studied.[11] Complexation of surfactant with water-soluble amphiphilic copolymers containing a small amount, 0.5–3.0 mol %, of hydrophobic segments has been reported recently.[12-14] It was concluded,[13,14] on the basis of fluorescence data, that the association of the hydrophobic side groups and surfactant molecules may be cooperative in nature.

In contrast to water-soluble PSC, little is known about the possibility of formation of amphiphilic PSC of ionomers in nonpolar solvents. Ionomers are copolymers with a nonpolar backbone containing a small amount (1–5 mol %) of salt groups present either as side groups or at the ends of the chain. The influence of additives, such as aliphatic alcohols, acids of various molar masses, and amines, on the solubility of the ionomer and on the solution viscosity has been studied.[15-17] The low molar mass additives were considered as cosolvents for salt groups and act to disrupt aggregates of the salt groups.[15-17]

Our recent data[18] indicate a PSC formation for the ionomer–(bis(2-ethylhexyl) sulfosuccinate sodium salt (commonly called aerosol OT or AOT)) system in a nonpolar solvent (*m*-xylene). We ascribed the complexation to the interaction between AOT polar head groups and ionomer salt groups. It was suggested that the ionomer salt groups play the role of molecular "anchors" that bind AOT molecules to the ionomer chain, while the hydrophobic ionomer backbone stabilizes the PSC in the nonpolar solvent.[18]

The present work is devoted to the further study of an amphiphilic PSC consisting of sulfonated polystyrene ionomer and AOT, an oil-soluble surfactant, of the same charge in *m*-xylene. We prepared the ionomer–AOT system by mixing the ionomer solution and the AOT solution for various initial aggregation states of AOT molecules in *m*-xylene including reversed micelles encapsulating water molecules. The techniques we employed are ultracentrifugation, vapor pressure osmometry (VPO), viscometry, and dynamic light scattering (DLS). We estimate the stoichiometric compositions of the PSC, especially the limiting compositions in the presence of excess AOT, and discuss their structures. There is a light scattering study[19] on a mixture of unmodified polystyrene and AOT micelles. It was shown that, in an excess of AOT reversed micelles, they are preferentially adsorbed onto polystyrene chains at a constant mass/mass ratio. To our knowledge, the present contribution is the first to report the compositions of ionomer–AOT complexes.

Experimental Section

Materials. Zinc-neutralized, sodium-neutralized, and as-prepared sulfonated polystyrene ionomers, abbreviated as SPZn,

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Table 1. Molar Content *m* of Salt or Acid Groups of Ionomer Samples

ionomer	counterion	m/(mol %)	ionomer	counterion	m/(mol %)
SPZn	Zn^{2+}	1.3	SPNa	Na^+	1.4
SPZn	Zn^{2+}	2.6	SPNa	Na^+	2.7
SPZn	Zn^{2+}	4.3	SPH	H^+	4.5

SPNa, and SPH, respectively, were kindly supplied by Dr. R. D. Lundberg. They were obtained from anionically polymerized polystyrene (PS) with $M_w/M_n \cong 1.05$ and $M_w = 115000$ (M_w and M_n are the weight-average and number-average molecular masses, respectively) as described elsewhere.[20] Table 1 lists the ionomer samples with various degrees of sulfonation used in our experiments. The molar content m of $SO_3(Zn)_{1/2}$, SO_3Na, and SO_3H groups was determined by elemental analysis. Aerosol OT (AOT) oil-soluble surfactant (Fluka) was purified as described elsewhere.[21] The content of water traces in AOT was controlled by near-infrared spectroscopy.[22] We used 1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt (PTSNa) (Eastman Kodak) as a probe for detectng AOT reversed micelles in the scan mode of ultracentrifugation experiments. PTSNa has a high molar extinction coefficient. It is known that there is little interaction between PTSNa and AOT polar head groups.[23] m-Xylene (99%, dielectric constant $\epsilon \cong 2.2$) was used without further purification to dissolve the polymers. Twice-distilled water, after being additionally purified by a Millipore ion-exchange system, was used as a solvent for PTSNa and to prepare AOT reversed micelles.

Sample Preparation. Polymer solutions were prepared volumetrically. All ionomer stock solutions were stirred by a magnetic stirrer for about 5 days to ensure complete dissolution. The reversed AOT micelles (hereafter referred to also as mic.AOT) were prepared from a m-xylene solution of AOT with added water in the molar ratio of $[H_2O]/[AOT] = 5.0$ by intensive agitation for 5–10 min at room temperature until the mixture became transparent.[24] Then the solutions of AOT micelles were preserved at room temperature for at least 2–3 h. At least 24 h was allowed to pass after mixing the ionomer solution with the AOT solution or the mic.AOT solution before the measurements.

Ultracentrifugation Measurements. The ultracentrifugation measurements in the schlieren mode and the scan mode were carried out using Beckman-E analytical ultracentrifuges at 48 000 rpm and 20 °C. Sedimentation patterns were detected by a change in the optical absorption, Abs, of the solution at 358 nm (one of the maxima in the PTSNa absorption spectrum) in the scan mode and by a change in the refractive index n of the solution, dn/dx, in the schlieren mode, where x is the radial distance in the sedimentation cell. The sedimentation coefficient S can be evaluated in both modes from the velocity of the sedimentation that is obtained as a change in the location of the sedimentation boundary in the cell per unit time. In svedbergs, S is calculated as $S = (\omega^2 x)^{-1}(dx/dt) \times 10^{13}$, where ω is the angular velocity of the rotor in hertz and t is time in seconds. For a polymer solution, S is related to the molecular mass M and the friction coefficient Ξ of translational motion by $S = M(1 - \bar{\nu}\rho_s)/N_A\Xi$, where $\bar{\nu}$ is the partial specific volume of the polymer, ρ_s is the solvent density, and N_A is Avogadro's number. Because $\Xi \propto M^\nu$ with $\nu < 1$, a distribution in the molecular mass causes a distribution in S and in the sedimentation boundary. The concentration of polymers was held constant at 5.0×10^{-2} M, and the probe concentration was at $[PTSNa] \cong 1 \times 10^{-5}$ M. The molar concentration of polymer is expressed in terms of monomer molar concentration, unless otherwise specified.

Vapor Pressure Osmometry Measurements. VPO measurements were carried out with a Wescan Model 233 vapor pressure osmometer at 40 °C, the lowest temperature available for m-xylene. For temperature equilibration, each sample was kept in the syringe for 10 min before the measurement. All the measurements were repeated 3–5 times. VPO gives the apparent number-average molar mass, M_{app}, by $\Delta R/c = k/M_{app}$,[25] where ΔR is the difference in the resistance between the solution thermistor and the solvent thermistor, c is the solute concentration, and k is a constant. The value of k was calibrated for solutions of oligo(propylene glycol) of molar mass 425 and azobenzene of molar mass 182 as standards. The M_{app} of AOT aggregates was estimated as a function of the AOT concentration in the dilute solution regime.

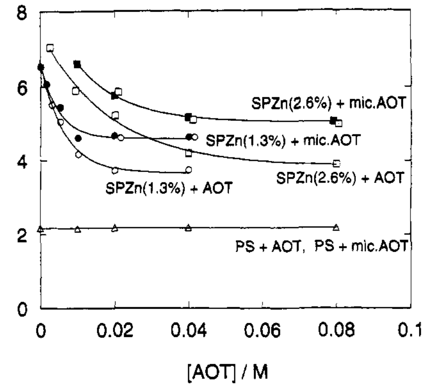


Figure 1. Sedimentation coefficient S versus AOT concentration in m-xylene solution of SPZn ionomer (m = 1.3 and 2.6 mol %) and AOT or AOT micelles. Open symbols with a dot and other symbols were obtained in the scan mode and schlieren mode, respectively. The data for a mixture solution of polystyrene–AOT and polystyrene–mic.AOT are also shown. [SPZn] = [PS] = 0.05 M.

Dynamic Light Scattering Measurements. DLS measurements were carried out in the same way as described before using an Ar ion laser operated at wavelength λ = 514.5 nm and a digital correlator (Langley-Ford Instruments Model 1096).[26] All the measurements were performed at 20 °C (refractive index $n^{20}{}_\lambda \sim 1.496$ and viscosity $\eta_0 \sim 0.6165$ cP for m-xylene). The scattering angle θ was 25°. Prior to DLS measurements, the polymer–surfactant mixture was repeatedly filtered (about 3 times) into a test tube through a Millipore PTFE membrane filter with 0.2-μm pore size.

A baseline-subtracted, normalized homodyne autocorrelation function $g_2(t)$ for a delay time t was first converted to an absolute value of a normalized electric-field autocorrelation function $g_1(t)$. The two autocorrelation functions are related by $g_2(t) = [g_1(t)]^2$. The $g_1(t)$ was analyzed by the CONTIN program originally provided by Provencher[27] as $g_1(t) \sim \int_{-\infty}^{\infty}\Gamma G(\Gamma) \times \exp(-\Gamma t)\, d \ln \Gamma$ to obtain the spectrum $G(\Gamma)$ of the decay rate Γ. When the polymer solution is dilute and the scattering angle θ is low, average decay rate $\langle\Gamma\rangle$ is related to the center of mass diffusion coefficient D_z by $\langle\Gamma\rangle = D_z q^2$, where $q = (4\pi n/\lambda) \sin(\theta/2)$ is the magnitude of the scattering vector.

Results and Discussion

(1) Ultracentrifugation and Vapor Pressure Osmometry.

Our recent ultracentifugation data suggest[18] that the interaction between sulfonated polystyrene ionomers and AOT surfactant molecules leads to the formation of PSC in m-xylene solution. We applied here the ultracentrifugation technique to study systematically the ionomer–AOT interaction in mixtures of ionomers and AOT molecules and in those of ionomers and AOT micelles in a wide range of mixture compositions in the solution.

The sedimentation coefficient S was obtained in the schlieren mode and the scan mode. To explore the dependence of S on the ionomer–AOT and ionomer–mic.AOT mixture compositions, the AOT concentration was changed in the dilute solution regime. The ionomer concentration was fixed at 0.05 M. SPZn ionomers with m = 1.3 and 2.6 mol % were used here. It is known[26] that some of SPZn (m = 1.3 mol %) molecules aggregate at this concentration without added surfactant. The tendency to aggregate is expected to be larger for the other ionomer SPZn (m = 2.6 mol %).

Figure 1 shows S as a function of [AOT]. The value of S for the SPZn (m = 1.3 mol %) dilute solution without added surfactant is about 3 times as large as that of PS solution of the same concentration and molecular mass. This difference can be attributed mainly to interchain aggregation of ionomer coils and partly to a more compact conformation of isolated ionomer coils due to association of $SO_3(Zn)_{1/2}$ groups on a single chain. An addition of AOT into the ionomer solution initially decreases S. With a further increase in [AOT], S approaches an asymptote. The approach is slower for the ionomer with a higher content of salt groups. The asymptotic value of S appears to be independent of m for the SPZn–AOT system. For a mixture of SPZn and mic.AOT, however, the asymptote for m = 2.6 mol % appears to be larger than that for m = 1.3 mol %. In contrast to the ionomers, S of polystyrene does not depend on [AOT] for a mixture of PS and AOT or for a mixture of PS and AOT micelles, a result indicating that there is no interaction between PS and AOT surfactants. The decrease in S of the ionomer solution as [AOT] increases indicates a disruption of intrachain and interchain aggregates of the salt groups by AOT molecules. The existence of asymptotes of S at high [AOT] suggests the formation of well-defined {ionomer–AOT} and {ionomer–mic.AOT} complexes of invariant dimensions in the presence of excess AOT and AOT micelles. The differences in S among PS, {ionomer–AOT} complex, and {ionomer–mic.AOT} complex at their respective limiting compositions may also indicate structural differences. These differences in S will be discussed subsequently.

In the presence of the ionomers, AOT molecules and AOT micelles either are bound to the salt groups of the ionomers to form complexes or are free from the ionomers. To estimate the fraction of bound AOT molecules in the ionomer–AOT and ionomer–mic.AOT mixtures, we employed the ultracentrifugation and vapor pressure osmometry techniques. The composition of {ionomer–mic.AOT} complexes was evaluated by the ultracentrifugation technique in the scan mode. An introduction of a small amount of PTSNa ([PTSNa]/[AOT] $\leq 5 \times 10^{-4}$, molar ratio) into the AOT reversed micelles allowed us to estimate the fraction of the surfactant that exists in micelles in {ionomer–mic.AOT}. We expect that PTSNa is uniformly distributed among AOT micelles. Scan sedimentation patterns of the reversed AOT micelles (solid lines) and of the SPZn (m = 1.3 mol %)-mic.AOT mixtures (dashed lines) at constant ionomer concentration [SPZn] = 0.05M and various AOT concentrations in m-xylene are shown in Figure 2 against x, the distance from the meniscus in the sedimentation cell. The sensitivity limit for the detection of AOT micelles is as low as [AOT] = 2.5×10^{-3} M; AOT micelles could not be detected below this concentration. The sedimentation pattern for AOT micelles (solid lines) shows little dependence on [AOT] and reaches a plateau in one step at a similar location of x. The pattern implies a uniform micelle size independent of micellar concentration. The introduction of the ionomers causes the pattern (dashed lines) to depend on [AOT]. At [AOT] $\cong 1 \times 10^{-2}$ M, the pattern has only one step located at a larger value of x than the one given by the solid lines. This result indicates that all AOT micelles are in {ionomer–mic.AOT} complexes. A further increase in [AOT] leads to the appearance of a secondary step at similar locations as in the curves for reversed AOT micelles without ionomers. The secondary step is ascribed to unbound micelles. The fractional content of the unbound micelles increases as [AOT] increases. Here we assume that the heights of the two steps in the curves in Figure 2 are proportional to the quantities of bound and unbound micelles. Then we find that the percentage of bound AOT micelles is about 80 and 52% at [AOT] = 0.02 and 0.04 M, respectively. From these percentages, we estimate the limiting composition of the {ionomer–mic.AOT} complex to be 5.0 and 6.0 AOT micelles per SPZn (m = 1.3 mol %) chain at [AOT] = 0.02 and 0.04 M, respectively, or 28 AOT molecules per salt group, on the average. Here it was presumed that an AOT reversed micelle comprises 70 AOT molecules[24] as evidenced by our DLS data. We measured by DLS the diffusion coefficient D of micelles in m-xylene at a concentration [AOT] = 0.02 M. The hydrodynamic radius R_H was estimated to be 21 Å using $R_H = k_B T/(6\pi\eta_0 D)$, where k_BT is the thermal energy. The value of R_H is equal that obtained for the same AOT–water mixture in toluene.[24] The ultracentrifugation measurements were conducted also at higher AOT concentrations. The number of bound micelles per ionomer chain remained the same within experimental error.

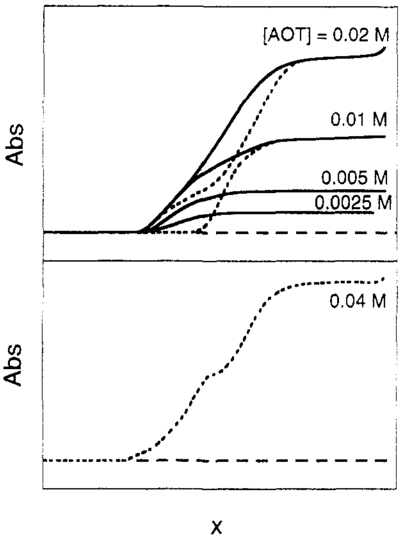


Figure 2. Scan sedimentation profiles of AOT micelles in m-xylene without ionomers (solid lines) and with added SPZn of m = 1.3 mol % (dashed lines) at [SPZn] = 0.05 M plotted against x, the distance from the center of the sedimentation cell. The AOT concentrations are indicated adjacent to the curves.

Table 2. Number of AOT Micelles φ per Salt or Acid Group

ionomer	m/(mol %)	φ	ionomer	m/(mol %)	φ
SPZn	1.3	0.40	SPNa	1.4	0.66
SPZn	2.6	0.34	SPNa	2.7	0.48
SPZn	4.3	0.27	SPH	4.5	0.21

The scan mode measurements were also performed for the ionomers with SO_3Na and SO_3H groups. The calculated limiting compositions of {ionomer–mic.AOT} complexes saturated with mic.AOT are summarized in Table 2 in terms of φ, the average number of AOT micelles per salt or acid group. We find that, as the molar content m of salt groups increases, φ decreases, although the total number of AOT micelles bound to an ionomer chain increases. We also find that, compared at a similar content of salt/acid groups, φ tends to increase in the order $SO_3H < SO_3(Zn)_{1/2} < SO_3Na$. This trend correlates well with the solubility of the ionomers in m-xylene in the absence of mic.AOT, which decreases in the order $SO_3H > SO_3(Zn)_{1/2} > SO_3Na$. As the solubility decreases, the number of salt/acid groups contained in an aggregate increases, as was suggested in the literature.[28] Then, in the presence of mic.AOT, a micelle will contain more salt/acid groups.

As for {ionomer–AOT} complexes, we cannot estimate φ in the scan mode, because PTSNa molecules are not encapsulated in slightly aggregated AOT without added water. The schlieren mode of the ultracentrifugation

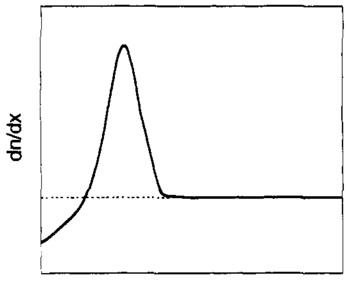


Figure 3. Schlieren sedimentation profile of SPZn (m = 1.3 mol %)–AOT mixture in m-xylene. [SPZn] = 0.05 M; [AOT] = 0.02 M.

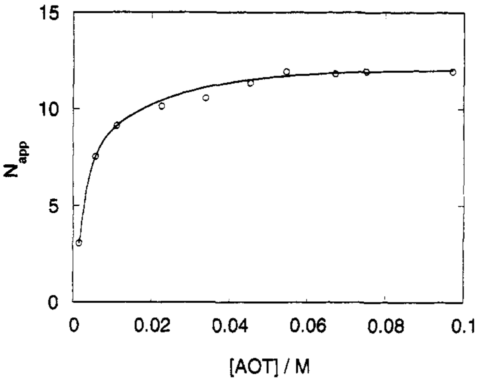


Figure 4. Apparent aggregation number N_{app} of AOT molecules in m-xylene solution plotted as a function of AOT concentration.

technique does not provide quantitative information on φ either. The schlieren sedimentation pattern for a mixture of SPZn (m = 1.3 mol %) and AOT is shown in Figure 3. In addition to the peak of {SPZn–AOT} complex (the "fast", positive peak in Figure 3), one can observe a "slow", negative peak located at the meniscus of the sedimentation cell. The latter corresponds to AOT aggregates free from ionomers.[28] These peaks are unfortunately overlapped, which precludes the estimation of φ in the schlieren mode of the ultracentrifugation technique. The situation is aggravated by the difficulties in the measurements of differential refractive indices dn/dc for AOT molecules and the complexes.

We used instead vapor pressure osmometry to estimate the limiting composition of {ionomer–AOT} complex in the presence of excess AOT molecules. First, the technique was applied to a solution of AOT molecules in m-xylene to obtain the number of AOT molecules N_{app} per aggregate as a function of the AOT concentration. Note that AOT molecules tend to aggregate in a nonpolar solvent such as m-xylene even without added water. The dependence of N_{app} on [AOT] is given in Figure 4. At [AOT] $\lesssim 4.5 \times 10^{-3}$ M an increase in [AOT] leads to a sharp increase in N_{app} up to 7, followed by a gradual increase in N_{app} up to 12 at [AOT] = (4.5–5.0) × 10^{-2} M. Then N_{app} levels off. The observed characteristics of the AOT aggregation in m-xylene is in good agreement with the VPO data on the counterpart in benzene.[29]

Then VPO was applied to a mixture of the ionomers and AOT in m-xylene. In the mixture, the depression in m-xylene vapor pressure is solely due to AOT aggregates free from ionomers, because the contribution by the complexes or the ionomers is negligibly small: the concentration of the ionomer (4.5×10^{-5} M; polymer concentration) is much lower than the operational AOT concentration, [AOT] $\geq 2 \times 10^{-2}$ M. The quantity f of AOT molecules bound to ionomers in 1 L of the solution was calculated using $f/[\mathrm{AOT}] = 1 - \Delta R_{\mathrm{ionomer\text{-}AOT}}/\Delta R_{\mathrm{AOT}}$, where $\Delta R_{\mathrm{ionomer\text{-}AOT}}$ and ΔR_{AOT} are ΔR values for the ionomer–AOT mixture and for the pure AOT solution, respectively, at the same AOT concentration. The AOT concentration was changed while the ionomer concentration was fixed at 0.05 M. The values of f for SPZn (m = 1.3 mol %) and SPNa (m = 1.4 mol %) ionomers are given in Table 3 for various [AOT]. The quantity of bound AOT molecules depends little on the composition of the ionomer–AOT mixture for [AOT] ≥ 0.02–0.03 M. This behavior is in good agreement with the independence of S for the ionomer–AOT mixture in the same range of [AOT] (see Figure 1). Thus VPO data also prove the formation of limiting {ionomer–AOT} complexes in the presence of excess AOT. The value of f corresponds to about 14 and 23 AOT molecules per ionomer salt group for the SPZn and SPNa ionomers, respectively. This difference is parallel to the difference in φ between the two ionomers in ionomer–mic.AOT complexes.

Table 3. Molar Quantity of Bound AOT Molecules, *f*, in 1 L of the Ionomer–AOT Mixtures[a]

SPZn (1.3 mol %)		SPNa (1.4 mol %)	
[AOT]/M	f/mol[b]	[AOT]/M	f/mol[b]
0.020	0.0082	0.034	0.0142
0.034	0.0085	0.073	0.0152
0.066	0.0095	0.091	0.0149
0.073	0.0090	0.113	0.0157
0.113	0.0092		

[a] [SPZn] = 0.05 M. [b] Calculated.

From ultracentrifugation and VPO data we conclude that the interaction between sulfonated polystyrene ionomers and AOT surfactants of the same charge in a nonpolar solvent leads to the formation of {polymer–surfactant} complexes in a well-defined limiting composition in the presence of excessive surfactant. The complexation is driven by a gain in the conformational entropy of the ionomer coil, as the contacts between the salt or acid groups are replaced by their respective contacts with amphiphilic AOT molecules and subsequently the chain acquires the ability to access more conformations. In the dilute ionomer solution, the complexation expands the dimension of an individual coil. One can also anticipate a screening of AOT polar head groups by the ionomer hydrocarbons in the resultant complexes. The screening will result in a decrease in the electrostatic free energy of the whole system. The limiting composition of the {ionomer–AOT} complex is 14–23 AOT molecules per salt group, whereas the AOT aggregation number without added ionomer does not exceed 10–12 in the same range of AOT concentration. The difference in the aggregation number means that salt groups promote an additional aggregation of AOT molecules in the course of the complexation. There is also a difference in complexation between ionomer–AOT and ionomer–mic.AOT. The number of AOT molecules per salt group for {ionomer–mic.AOT} is about twice as high as that for {ionomer–AOT}.

As deduced from VPO data, there exists a considerable number of free AOT molecules in equilibrium with the {ionomer–AOT} complexes. Compared at [AOT] = 0.02 M and for SPZn (m = 1.3 mol %), the fractions of AOT molecules bound to the ionomers are 0.41 and 0.91 in the mixtures of SPZn–AOT and SPZn–mic.AOT, respectively. The difference means that the equilibrium constant of the ionomer–mic.AOT complexation reaction is larger than that of the ionomer–AOT complexation.

(2) Viscometry. To elucidate differences in the structure of the complexes, we carried out viscosity

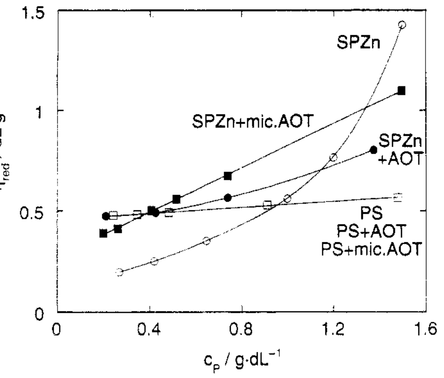


Figure 5. Reduced viscosity $\eta_{\rm red}$ versus polymer concentration $c_{\rm P}$ for PS (with or without AOT or mic.AOT), SPZn (m = 1.3 mol %), SPZn with AOT, and SPZn with AOT micelles. [SPZn]/[AOT] = 2.5 (in monomer moles).

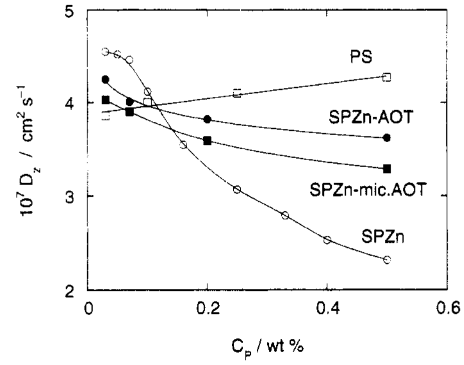


Figure 6. Diffusion coefficients D_z plotted as a function of the polymer concentration $c_{\rm P}$ for PS, SPZn (m = 1.3 mol %), SPZn with AOT, and SPZn with AOT micelles. [SPZn]/[AOT] = 2.5 (in monomer moles).

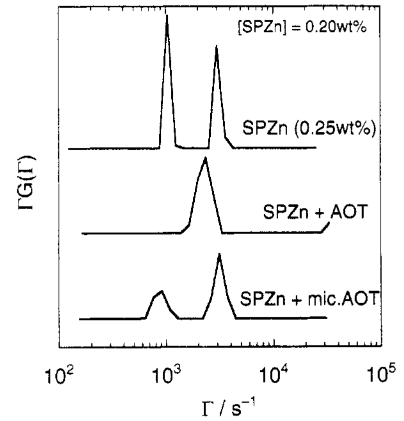


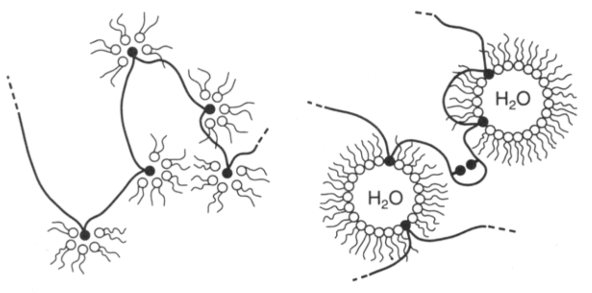
Figure 7. Spectra of the decay rate Γ in $g_1(t)$ for a solution of SPZn (m = 1.3 mol %), SPZn with AOT, and SPZn with AOT micelles. [SPZn]/[AOT] = 2.5 (in monomer moles).

measurements for solutions containing the complexes. The dependence of the reduced viscosity $\eta_{\rm red}$ on the polymer concentration $c_{\rm P}$ is shown in Figure 5 for the {SPZn–AOT} and {SPZn–mic.AOT} complexes. The solutions contained excess surfactant ([SPZn]/[AOT] = 2.5, in monomer moles).[30] The concentration dependences of $\eta_{\rm red}$ for PS and SPZn are shown for reference. The concentration dependence of $\eta_{\rm red}$ for SPZn suggests an intrachain aggregation of the salt groups in the dilute regime and a progressive interchain aggregation as $c_{\rm P}$ increases, as discussed before.[26] This behavior is typical of ionomers in nonpolar solvents.[31] An addition of AOT or AOT micelles increases $\eta_{\rm red}$ in the dilute solution regime but decreases it in the semidilute solution regime. The effect of the addition of the surfactant is well explained by the formation of PSC that substitutes contacts among salt groups for those between salt groups and AOT molecules. There is a small difference in $\eta_{\rm red}$ between {SPZn–AOT} and {SPZn–mic.AOT}. Below 0.4 g/dL, $\eta_{\rm red}$ for {SPZn–mic.AOT} is smaller than that of $\eta_{\rm red}$ for {SPZn–AOT} but is larger above 0.4 g/dL. With an increase in $c_{\rm P}$, $\eta_{\rm red}$ for {SPZn–mic.AOT} increases linearly. In contrast, $\eta_{\rm red}$ for {SPZn–AOT} exhibits different characteristics in the two ranges of $c_{\rm P}$: Below 0.5 g/dL, $\eta_{\rm red}$ coincides with that of PS, and above 0.5 g/dL, $\eta_{\rm red}$ changes linearly with $c_{\rm P}$ but with a concentration coefficient smaller than that for {SPZn–mic.AOT}. AOT molecules are thus found to be more efficient than AOT micelles in the solvation of the salt groups that disrupts interchain aggregation in the semidilute regime. The coincidence of $\eta_{\rm red}$ of {SPZn–AOT} and that of PS below 0.4 g/dL may be ascribed to the complete disruption of the salt group aggregates by AOT molecules.

(3) Dynamic Light Scattering. The difference in the structure between {SPZn–AOT} and {SPZn–mic.AOT} is also evidenced by DLS measurements. Concentrations of the ionomers were $c_{\rm P}$ = 0.03, 0.07, 0.20, and 0.50 wt % for both complexes, and the surfactant was supplied in excess ([SPZn]/[AOT] = 2.5, in monomer moles). We note that, for SPZn in m-xylene, the autocorrelation function $g_1(t)$ was nearly a single exponential below 0.1 wt % but, above 0.1 wt %, had a slowly decaying component ascribed to aggregates of the ionomers.[26] The $g_1(t)$ was nearly a single exponential in the whole concentration range measured for {SpZn–AOT}. For {SPZn–mic.AOT}, however, $g_1(t)$ was close to a single exponential at $c_{\rm P}$ = 0.03 and 0.07 wt % but had a slowly decaying component at 0.20 and 0.50 wt %. The z-average diffusion coefficients D_z, calculated from the initial decay rate in $g_1(t)$, are plotted in Figure 6 for PS, SPZn (m = 1.3 mol %), {SPZn–AOT}, and {SPZn–mic.AOT}. The data for PS and SPZn are reproduced from our preceding contribution.[26] At concentrations that yield a single-exponential decay, both AOT and AOT micelles make the diffusion slower. The expansion of the ionomer chain by disruption of the intrachain association of salt groups and the attachment of bulky units to the chain, especially, AOT micelles, lead to a reduced D_z. Unlike PS, D_z of SPZn–AOT decreases as $c_{\rm P}$ increases, a result indicating that the solution condition is still not good even with added AOT.

In the range $c_{\rm P} < 0.4$ g/dL, the diffusion of SPZn–AOT is faster than that of SPZn–mic.AOT, although the reduced viscosity of the former is larger. This apparent contradiction is considered to derive from the aggregation of SPZn–mic.AOT that reduces the effective number of diffusants.

To better represent the polydispersity in the diffusion coefficient observed for [SPZn–mic.AOT} as $c_{\rm P}$ = 0.20 and 0.50 wt %, $g_1(t)$ was analyzed by CONTIN. An example of the decay rate spectrum $G(\Gamma)$ is shown in Figure 7 for $c_{\rm P}$ = 0.20 wt %.[32] The spectra of Γ for SPZn ($c_{\rm P}$ = 0.25 wt %) and {SPZn–AOT} ($c_{\rm P}$ = 0.20 wt %) are shown for comparison. The spectrum patterns are nearly the same at $c_{\rm P}$ = 0.50 wt %. The spectrum for SPZn is composed of two peaks, the one at a higher frequency being ascribed to isolated ionomers and the other to interchain aggregates of ionomers.[26] The peak at a lower frequency disappears when AOT is added excessively, indicating a complete disruption of interchain aggregates by the surfactant molecules. The peak in the spectrum of {SPZn–AOT} is located at a lower frequency than that for the high-frequency peak for SPZn, which shows that the chain dimension of the complex is larger than that for the isolated ionomers with intrachain aggregation of salt groups. In contrast, the spectrum for {SPZn–mic.AOT} shares two



{ionomer-AOT} complex {ionomer-mic.AOT} complex

Figure 8. Structures of the ionomer complexes. Thick lines and filled circles represent ionomer backbones and salt/acid groups on them. Shaded circles and wavy lines represent the polar heads and aliphatic tails of AOT surfactants, respectively.

peaks with that for SPZn around the same locations, although the area under the low-frequency peak is smaller than that of the counterpart in the SPZn spectrum. We therefore find that mic.AOT can disrupt the interchain aggregation to some extent, but it is incomplete. The high-frequency peak is located at nearly the same location as the counterpart in the SPZn spectrum. Apparently, chain expansion does not occur in the complexation of the ionomers with micelles.

We also carried out DLS measurements for a mixture of PS and AOT in *m*-xylene and a mixture of PS and mic.AOT in the solvent. The ACF from the PS–AOT mixture was the same as that for a pure PS solution of the same polymer concentration. In the ACF for a mixture of PS and mic.AOT, CONTIN separated an additional peak at a higher frequency that is ascribed to isolated micelles. The main peak in the spectrum was the same as that in the pure PS solution. This finding demonstrates that there is no interaction between PS molecules and AOT micelles.

(4) Structure of the Complexes. The experimental data of ultracentrifugation, VPO, viscometry, and DLS suggest that there is a difference in the structure between {ionomer–AOT} and {ionomer–mic.AOT} complexes in the presence of excess surfactant. In {ionomer–AOT} complexes, almost each salt or acid group participates independently in complexation with AOT molecules, as illustrated in Figure 8. The small size of an AOT cluster consisting of a salt/acid group and a few AOT molecules facilitates the complexation without steric hindrance between the clusters. In the cluster, all AOT polar heads are directed toward the salt/acid group, thereby being screened from the nonpolar solvent.

In contrast, conjecture on the structure of the {ionomer–mic.AOT} is not straightforward. We consider that an individual AOT reversed micelle does not change its structure in the course of complexation. Any rearrangement of micelles would involve release of water molecules into the nonpolar solvent, which is not likely to occur. The limiting composition of {ionomer–mic.AOT} complex was found to be about 0.21–0.66 AOT micelles per salt/acid group. The number smaller than one indicates that some AOT micelles contain two or more salt/acid groups. Moreover, the number of bound AOT micelles per salt/acid group decreases with an increase in the number of such groups on the ionomer chain. Such behavior is partly ascribed to the large size of the micelles (the radius is estimated at 21 Å). When the micelle is bound to a salt/acid group, another group in the vicinity on the same chain is either enclosed in the micelle or forced to make a short loop that preserves the contact between salt groups existing in the absence of the micelles. An increase in the density of salt/acid groups will increase the average number of the groups encapsulated in a micelle. A possible structure is depicted in Figure 8.

We consider that the difference in the structure between {ionomer–AOT} and {ionomer–mic.AOT} complexes results in a more compact conformation of the {ionomer–mic.AOT} complexes when they exist isolated from neighboring complexes. This difference in size was supported in the viscosity and DLS measurements in the range of $c_P < 0.5$ wt %. As c_P increases, {ionomer–mic.AOT} complexes exhibit a more pronounced tendency to interchain aggregation. Encapsulation of salt/acid groups on different chains by a single micelle, as shown in Figure 8, is expected to be the mechanism for the aggregation.

Concluding Remarks

The interaction of ionomers and low molar mass surfactant molecules of the same charge in a nonpolar solvent leads to the formation of polymer–surfactant complexes. The complexation in the dilute solution regime is ascribed to the entropy gain of amphiphilic ionomer coils by substitution of self-contacts among ionomer salt/acid groups for their respective contacts with surfactant molecules and also to a screening of polar groups by the hydrocarbon backbones of the ionomers. The ionomer salt/acid groups play the role of molecular "anchors" that bind efficiently surfactant molecules and facilitate surfactant aggregation onto the ionomer chain.

It was found there is a difference in the structure between {ionomer–AOT} and {ionomer–mic.AOT} complexes. The difference is considered to derive from the large size of the reversed micelles. Further study of the size distribution in the ionomer complexes in wide ranges of AOT and ionomer concentrations, in particular, at low AOT concentrations, is necessary to elucidate further the structure of {ionomer–mic.AOT} complexes.

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