Effect of Ionic Strength on the Structure of Polymer−Surfactant Complexes

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We investigate the influence of ionic strength on the interaction between a cationic surfactant, hexadecyltrimethylammonium chloride (HTAC), and a water-soluble nonionic polymer, poly(ethylene oxide) (PEO). The formation of a charged PEO/HTAC complex is manifested by a maximum in the specific viscosity when a PEO solution is titrated with HTAC. The height of the viscosity maximum is diminished in the presence of salt because of the screening of electrostatic repulsions. Conductivity and differential refractometry measurements indicate that added salt (0.1 M KNO_3) stabilizes the binding of HTAC micelles to the polymer. Static light scattering (SLS) studies in the absence of salt reveal the formation of multipolymer PEO−HTAC complexes at the maximum binding point, whereas in 0.1 M KNO_3 predominantly unipolymer complexation occurs. Dynamic light scattering (DLS) analysis indicates, for the complex in water, a broad size distribution that corresponds to a widely polydisperse mixture of multichain clusters. In contrast, in 0.1 M KNO_3 the size distribution of the complex is similar to that of the pure PEO. These changes in the structure of the PEO−HTAC complex appear to be driven through the screening of electrostatic repulsions between surfactant headgroups.

Introduction

Numerous studies[1−6] have established that a strong binding interaction occurs between certain nonionic polymers, notably, poly(ethylene oxide) (PEO) and poly(vinylpyrrolidone) (PVP), and anionic surfactants such as sodium dodecyl sulfate (SDS). Complex formation is manifested by a decrease in the critical aggregation concentration (cac) relative to the critical micelle concentration (cmc) of the free surfactant[1,7−8] and by the fact that the complex exhibits the properties of a polyelectrolyte.[5,6] In particular, as surfactant is added, the specific viscosity increases up to a maximum value at the saturation binding point because of the expansion of the polymer chain due to electrostatic repulsions between the bound micelles and then decreases because of the screening of electrostatic repulsions due to excess added counterions. This behavior has been confirmed through measurements of the radius of gyration (R_g) and hydrodynamic radius (R_h) by static and dynamic light scattering techniques.[1,9−12] Originally, it was thought that such complexes do not form with cationic surfactants because of the bulky headgroups, which lead to a less favorable interaction with the hydration shell of the polymer.[13] However, subsequent studies show that more hydrophobic polymers such as hydroxypropyl cellulose (HPC),[10,14] ethyl(hydroxyethyl) cellulose (EHEC),[9,15] poly(vinyl methyl ether) (PVME), and PPO[16,17] can interact with cationic surfactants, namely, hexadecyltrimethylammonium chloride and bromide (HTAC and HTAB) and tetradecyltrimethylammonium chloride and bromide (TTAC and TTAB). In addition, it was found that PEO will bind with cationic surfactants, when the hydrophobic character of a polymer is increased, by raising the temperature.[11,18] We observe[11,12] that PEO interacts with HTAC above a temperature of 25 °C, as indicated by a decrease in cac

and maxima in the specific viscosity (η_{sp}), hydrodynamic radius (R_h), and radius of gyration (R_g) of the polymer when titrated with surfactant. In addition, we applied multicomponent light-scattering theory[19,20] combined with differential refractometry at dialysis equilibrium to determine the amount of bound surfactant and the molecular weight of the PEO−HTAC complex at $T = 30$ °C. At the maximum binding condition, 0.12 mol of HTAC is bound per mol of PEO repeating unit, representing only 50% of the HTAC present, and on average, two PEO chains are incorporated into the PEO−HTAC complex.

Because of its polyelectrolyte character, an increase in ionic strength should have a significant effect on the structure of the polymer−surfactant complex. Several studies indicate that the binding affinity of anionic surfactant to neutral polymer increases upon the addition of salt.[3,21−24] For example, Cabane and Duplessix[23] observed a small binding affinity (0.25 mol SDS per mol of EO) at zero salt concentration, which increased to 0.85 mol SDS per mol of EO in the presence of salt. Norwood et al.[24] reported that the fraction of sodium dodecyl sulfate (SDS) bound to poly(vinylpyrrolidone) (PVP) in NaCl solution increases from a value of $f = 0.124$ in 0.01 M NaCl to $f = 0.725$ in 0.5 M NaCl.

The issue of whether the complexes formed between neutral polymers and anionic surfactants contain single or multiple polymer chains has received less attention. Gilyani et al.[25] evaluated the molecular weight and binding affinity for complexes formed between SDS and PVP in 0.1 M $NaNO_3$ using multicomponent light-scattering theory and differential refractometry and found that single-chain complexation occurs at the maximum binding point, where essentially all of the surfactant is bound to the polymer. Fundin et al.[26,27] have investigated complexes formed between SDS and the polycation poly(*N,N,N*-trimethylammonio) ethyl acrylate (PCMA)[27] and between the cationic surfactant cetyl-trimethylammonium bromide (CTAB) and the polyanion poly(styrenesulfonate) (PSS).[26] In both

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Structure of Polymer−Surfactant Complexes

J. Phys. Chem. B, Vol. 107, No. 23, 2003 **5461**

systems, multichain structures (clusters) coexist with single-chain complexes, as evidenced by bimodal relaxation functions in dynamic light scattering experiments. The clusters in PCMA/SDS solutions appear to be electrostatically stabilized because they disappear when the salt concentration is increased.[27] In contrast, the clusters formed between PSS and CTAB seem to be hydrophobically stabilized because an increase in salt concentration enhances the formation of clusters.[26]

Here, we investigate the effect of ionic strength on the structure of complexes formed between PEO and the cationic surfactant HTAC near the maximum binding point. Specifically, we compare the molecular weights of PEO−HTAC complexes and the binding affinity of HTAC to PEO in the absence of added salt and in 0.1 M KNO₃. We also examine the effect of salt on the size distribution of species in PEO/HTAC solutions by dynamic light scattering.

Theory

Light Scattering. The scattered-light intensity from a binary polymer solution can be interpreted by the Zimm−Debye equation. In the small-angle limit where interference effects can be neglected, this can be expressed as

$$\frac{Kc_2}{\Delta R_\theta} = \frac{1}{M_w}\left(1 + \frac{\mathbf{q}^2 R_g^2}{3}\right) + 2A_2 c_2 \tag{1}$$

where M_w is the weight-average molecular weight, A_2 is the second virial coefficient, R_g^2 indicates the z average of the mean square radius of gyration, and ΔR_θ is the excess Rayleigh ratio computed by comparing the excess scattering from the solution versus a standard sample whose Rayleigh ratio is known:

$$\Delta R_\theta = \frac{\Delta I_{\theta(solution)}}{I_{\theta(standard)}} \times R_{\theta(standard)} \times \frac{n^2_{(solution)}}{n^2_{(standard)}} \tag{2}$$

$\Delta I_{\theta(solution)}$ is the excess scattered intensity of the solution, and $\Delta I_{\theta(solution)} = i_{(solution)} - i_{(solvent)}$. $n_{(solution)}$ and $n_{(standard)}$ are the refractive indices of the solution and solvent. K is the optical constant, which for vertically polarized incident light is given as

$$K = \frac{4\pi^2 n^2 \left(\frac{dn}{dc_2}\right)^2}{N_A \lambda^4} \tag{3}$$

where n is the refractive index of the solvent, c_2 is the polymer concentration (g/mL), λ is the wavelength of incident light, dn/dc_2 is the refractive index increment (mL/g), and N_A is Avogadro's number. The scattering vector $\mathbf{q}$ is defined as

$$\mathbf{q} = \left(4\pi \frac{n}{\lambda}\right)\sin\left(\frac{\theta}{2}\right) \tag{4}$$

where θ is the scattering angle.

The theory of light scattering for a multicomponent system was first developed by Kirkwood and Goldberg[19] and Stock-mayer.[20] Here, the preferential interaction between the polymer and the mixed-solvent components must be considered. Designating water as component 1, polymer as component 2, and cationic surfactant as component 3, it can be shown that the light-scattering equation for the polymer in the mixed solvent is

$$\left[\frac{K'c_2}{\Delta R_\theta}\left(\frac{\partial n}{\partial c_2}\right)^2_{T,P,c_3}\right] = \frac{1}{(1+D)^2}\left[\frac{1}{M_w}\left\{\left(1 + \frac{\mathbf{q}^2 R_g^2}{3}\right) + 2B^0 c_2\right\}\right] \tag{5}$$

where

$$K' = \frac{4\pi^2 n^2}{N_A \lambda^4} \tag{6}$$

and

$$D = \left[\frac{(dn/dc_3)_{T,P,c_2}}{(dn/dc_2)_{T,P,c_3}}\right]\left(\frac{dc_3}{dc_2}\right)_{T,P,\mu_2,\mu_3} \tag{7}$$

$(dn/dc_3)_{T,P,c_2}$ is the refractive index increment of surfactant at constant polymer concentration, and $(dn/dc_2)_{T,P,c_3}$ is the refractive index increment of polymer at fixed surfactant concentration. We define $D' = (dc_3/dc_2)_{T,P,\mu_1,\mu_3}$ as the amount of surfactant (g) bound per gram of polymer. For such ternary solutions, extrapolating $Kc/\Delta R_\theta$ to zero concentration provides only an apparent molecular weight, $M_{w,app}$, which is a function of the interaction with the solvent components

$$M_{w,app} = M_w(1 + D)^2 \tag{8}$$

Using the above definition of D', eq 5 can be written in the limit of $\mathbf{q} = 0$ and $c_2 = 0$ as

$$\lim_{c_2 \to 0}\left[\frac{K'c_2}{\Delta R_\theta}\left\{\left(\frac{\partial n}{\partial c_2}\right)_{T,P,c_3} + D'\left(\frac{\partial n}{\partial c_3}\right)_{T,P,c_2}\right\}^2\right] = \frac{1}{M_w} \tag{9}$$

Refractive Index Increments. To determine the true molecular weight, M_w, via eq 9 thus requires the measurement of $(\partial n/\partial c_2)_{T,P,c_3}$, $(\partial n/\partial c_3)_{T,P,c_2}$, and D'. A more direct route to M_w was suggested by Casassa and Eisenberg[28] and Overbeek and Vrij,[29] who showed that the measurement of M_w in ternary solutions could be performed via the determination of the refractive index increment of the solution at constant solvent chemical potential. At constant temperature and pressure, the total change in refractive index with a change in solution concentration is given by

$$dn = \left(\frac{\partial n}{\partial c_2}\right)_{T,P,c_3} dc_2 + \left(\frac{\partial n}{\partial c_3}\right)_{T,P,c_2} dc_3 \tag{10}$$

where n is the refractive index, c_i is the mass concentration of component i (g/mL of water), T is the thermodynamic temperature, and P is the pressure. Taking the derivative of eq 10 with respect to c_2 at a constant chemical potential for component 3, μ_3, we obtain

$$\left(\frac{\partial n}{\partial c_2}\right)_{T,P,\mu_1,\mu_3} = \left(\frac{\partial n}{\partial c_2}\right)_{T,P,c_3} + \left(\frac{\partial n}{\partial c_2}\right)_{T,P,c_2}\left(\frac{\partial c_3}{\partial c_2}\right)_{T,P,\mu_1,\mu_3} \tag{11}$$

Inserting this result into eq 9, we derive

$$\lim_{c_2 \to 0}\left[\frac{K'c_2}{\Delta R_\theta}\left(\frac{\partial n}{\partial c_2}\right)^2_{T,P,\mu_1,\mu_3}\right] = \frac{1}{M_w} \tag{12}$$

where M_w is the molecular weight of polymer in the complex. The intercept of the light-scattering plot gives the true molecular weight directly. To determine $(\partial n/\partial c_2)^2_{T,P,\mu_1,\mu_3}$, the differential refractometry measurement is carried out by performing equilibrium dialysis and measuring the refractive index increment between the dialyzed solution and the dialyzate. In addition, from eq 11, we may compute D', the preferential interaction of surfactant with polymer in grams of surfactant per gram of polymer, as

$$D' = \frac{\left[\left(\frac{\partial n}{\partial c_2}\right)_{T,P,\mu_1,\mu_3} - \left(\frac{\partial n}{\partial c_2}\right)_{T,P,c_3}\right]}{\left(\frac{\partial n}{\partial c_3}\right)_{T,P,c_2}} \qquad (13)$$

Finally, combining our knowledge of M_w and D', we find that the molecular weight of the polymer−surfactant complex, $M_{w,com}$ can be calculated from the following equation:

$$M_{w,com} = M_w(1 + D') \qquad (14)$$

It should be realized that the amount of bound surfactant estimated via eq 13 corresponds to the equilibrium condition where the polymer is saturated with the adsorbing species.

Experimental Section

Materials. The poly(ethylene oxide) (PEO) used in this study was purchased from Aldrich Chemical Co. and had a reported molecular weight of 6×10^5. The weight-average molecular weight of PEO in salt solution was determined by light-scattering measurement to be $M_w = 5.99 \times 10^5$, consistent with the manufacturer's specified value. The PEO sample was polydisperse and was determined to have a normalized second cumulant, μ_2/Γ^2, by dynamic light scattering[11] of about 0.5. Commercial-grade hexadecyltrimethylammonium chloride (HTAC) was used as a cationic surfactant, provided by Unilever Holding Inc., and was used as received without further purification. Deionized water was used as a solvent. Reagent-grade potassium nitrate (KNO$_3$), purchased from Ajax Chemicals, was used to prepare the polymer−surfactant solution in the presence of salt. The polymer and the surfactant stock solutions were prepared by % w/v in deionized water and stored at room temperature.

Sample Preparation. The polymer−surfactant solutions were gently stirred for at least 24 h to obtain homogeneous solutions. All measurements were carried out on dilute solutions of PEO with specified amounts of HTAC in 0.1 M KNO$_3$ as the solvent. For comparison, PEO−HTAC complex solutions were also prepared in water. Prior to light-scattering measurements, all solutions were centrifuged at 8000 rpm for 1 h and then filtered directly into the light-scattering cell through 0.45-μm Millipore membranes to remove residual dust particles. All measurements were performed at 30 ± 0.1 °C.

The PEO−HTAC solutions were dialyzed using regenerated cellulose membranes (molecular weight cutoff = 8000), purchased from Spectrum Medical Industries, to determine the refractive index increment at constant chemical potential. The HTAC concentration in the dialysate was the same as that in the PEO−HTAC solution, inserted into the dialysis bag. The duration of dialysis was varied from 1 week to 3 weeks, with two to three exchanges of the external HTAC solution. We found that the refractive index increment became constant after a period of 1 week, indicating that osmotic equilibrium has been reached.

Methods. A conductivity meter, Orion (model 160), was used to determine the critical micelle concentration (cmc) for pure surfactant solutions and the critical aggregation concentration (cac) for polymer−surfactant complex solutions in the absence and in the presence of 0.1 M KNO$_3$.

The refractive index increment (dn/dc) of PEO−HTAC solutions was determined by a Dawn Optilab interferometric refractometer. To avoid confusion, we designate c_2 for PEO concentration (g/100 mL), c_3 for HTAC concentration (g/100 mL), and c_3/c_2 for the HTAC/PEO concentration ratio. Measurements were performed on dialyzed solutions to obtain $(\mathrm{d}n/\mathrm{d}c_2)_{\mu_3}$, where μ_3 refers to the concentration of all solvent components at constant chemical potential at a fixed HTAC/PEO concentration ratio of $c_3/c_2 = 1.75$. This ratio lies at or slightly above the value where maximum binding of HTAC occurs at each PEO concentration in both water and 0.1 M KNO$_3$. The change in the refractive index of the ternary solution by varying the PEO concentration at fixed HTAC concentration $[(\mathrm{d}n/\mathrm{d}c_2)_{c_3}]$ and the binary solvent refractive index increment at a constant polymer concentration $[(\mathrm{d}n/\mathrm{d}c_3)_{c_2}]$ were also determined as described in our previous report.[12] Following Gilyani et al.,[25] PEO/HTAC solutions dissolved in 0.1 M KNO$_3$ were treated as pseudo-ternary systems (i.e., we assume that KNO$_3$ is a neutral salt).

Static and dynamic light scattering (SLS and DLS) measurements were carried out with a Malvern (model series 4700) light-scattering instrument. The light source was an argon laser emitting vertically polarized light at a wavelength of 514.5 nm. Toluene was used as a standard solution with a value of 3.2×10^{-5} cm^{-1} for the Rayleigh ratio.[30] The PEO−HTAC complex in 0.1 M KNO$_3$ was characterized at a HTAC/PEO mass ratio of 1.75 for comparison with earlier studies[12] near the location where maximum binding occurs between PEO and HTAC.

The intensity autocorrelation function $g^2(\tau)$ obtained by DLS is related to the electric-field correlation function $g^1(\tau)$ by

$$g^2(\tau) = A[1 + B\{g^1(\tau)\}^2] \qquad (15)$$

where A is the experimental baseline and B is a constant determined by the collection efficiency of the detection apparatus. $g^1(\tau)$ can be expressed as the Laplace transform of the distribution function of the relaxation rate $G(\Gamma)$:

$$g^2(\tau) = \int G(\Gamma) \exp(-\Gamma\tau) \, \mathrm{d}\Gamma \qquad (16)$$

The relaxation rate Γ is related to the apparent diffusion coefficient, D_{app}, as

$$\Gamma = D_{app}\mathbf{q}^2 \qquad (17)$$

Here, $\mathbf{q}$ is the scattering vector that depends on the scattering angle θ ($\mathbf{q} = 4\pi(^n/_\lambda) \sin\,^\theta/_2$). The Malvern software calculates $G(\Gamma)$, which is equivalent to $G(D_{app})$, the apparent diffusion coefficient distribution. The mean value of D_{app} (i.e., $\langle D_{app}\rangle$) is then computed as

$$\langle D_{app}\rangle = \int D_{app}\, G(D_{app})\, \mathrm{d}D_{app} \qquad (18)$$

$\langle D_{app}\rangle$ values are then plotted versus $\mathbf{q}^2$, and the zero intercept gives the center of mass diffusion D_{cm} of the polymer chain:

$$D_{app} = D_{cm}(1 + C\mathbf{q}^2 R_g^2 + \cdots) \qquad (19)$$

C is a coefficient determined by the slowest internal motion of the particle and the polydispersity of the polymer.[31] The mean

Structure of Polymer−Surfactant Complexes

J. Phys. Chem. B, Vol. 107, No. 23, 2003 **5463**
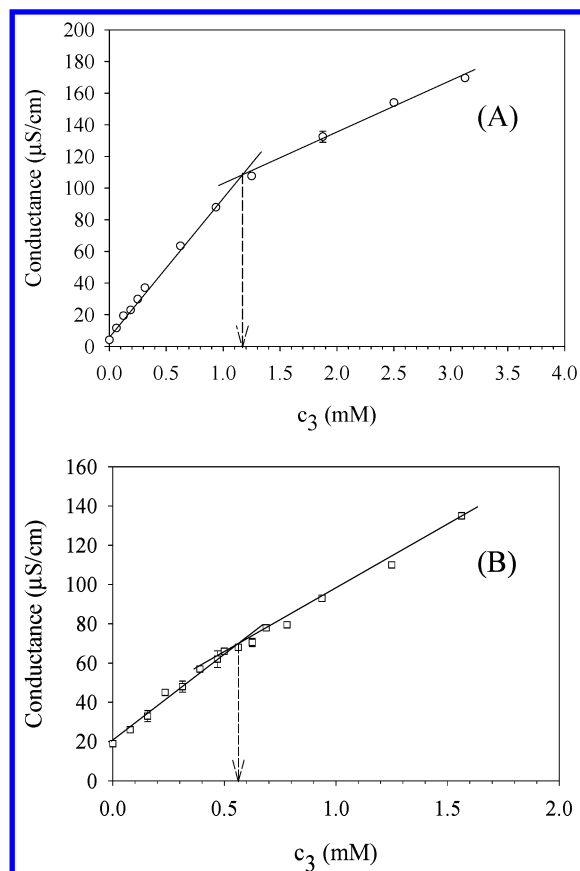
Figure 1. Variation of the conductivity with the surfactant concentration at 30 °C in water: (A) pure HTAC solution and (B) HTAC in the presence of PEO.

hydrodynamic radius (R_h) is calculated via the Stokes−Einstein equation

$$R_h = \frac{k_B T}{6\pi \eta_s D_{cm}} \qquad (20)$$

Here, k_B is the Boltzmann constant, T is the absolute temperature, and η_s is the viscosity of the solvent.

Viscosity measurements were performed with a Cannon-Ubbelohde viscometer. The size of the viscometer was chosen to suit the efflux time for each solution. The PEO concentration (0.1 g/100 mL) used in this study was well below the overlap concentration c^* evaluated from $c^* = 1/[\eta]$, where $[\eta]$ is the intrinsic viscosity.

Results and Discussion

(a) Conductivity Measurements. Figures 1 and 2 show the variation in the conductivity of HTAC alone and the PEO−HTAC complex dissolved, respectively, in water and in 0.1 M KNO$_3$ as the surfactant concentration is increased. The break points in pure surfactant solutions identify the critical micelle concentration (cmc), and those in PEO−HTAC solutions correspond to the onset of polymer-bound micelles, denoted as the critical aggregation concentration (cac). In both Figures, we see that the cac values are lower than the cmc values, characteristic of a binding interaction between polymer and surfactant. Values of the cmc and cac, determined by this procedure, are shown in Table 1.

We also find that the cmc value for HTAC in salt solution (0.94 mM) is lower than in water (1.19 mM), indicating that the surfactant micelles are stabilized in salt solution. A similar
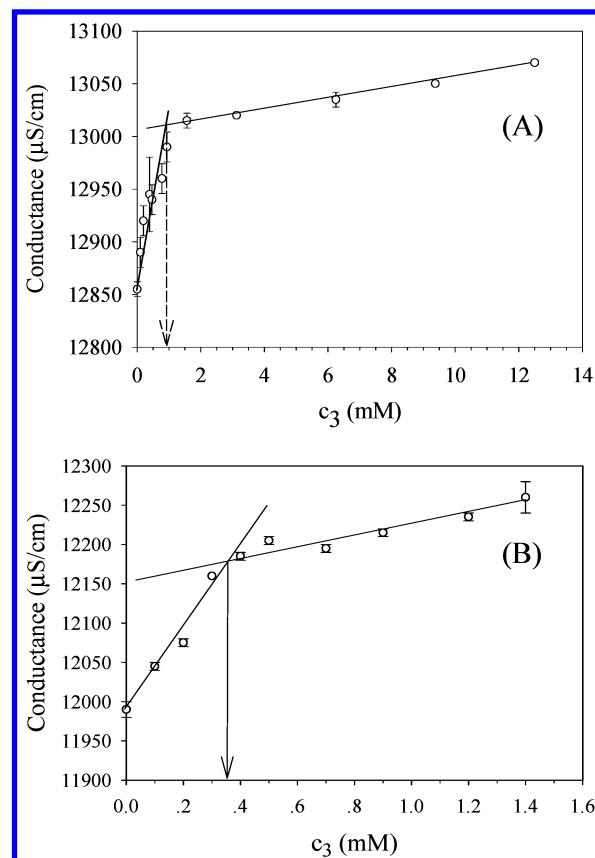
Figure 2. Variation of the conductivity with the surfactant concentration at 30 °C in the presence of 0.1 M KNO$_3$ salt solution: (A) pure HTAC solution and (B) HTAC in the presence of PEO.

TABLE 1: Data from Conductivity Measurements for PEO−HTAC in 0.1 M KNO$_3$ and in Salt-Free Solutions

parameters	PEO−HTAC complex in aqueous solution	PEO−HTAC complex in 0.1 M KNO$_3$ solution
cmc^a (mM)	1.19	0.94
cac (mM)	0.56	0.35
ΔG (kJ/mol)	1.88	2.53

^{a} The cmc values are the critical micelle concentrations of HTAC in the absence of polymer.

decrease was observed in the cac in 0.1 M KNO$_3$. The addition of salt leads to a reduction of electrostatic repulsions between the charged surfactant headgroups on micelles and between bound micelles on the polymer. Quantitatively, we can express the reduction in the Gibbs free energy of micelles when bound to a polymer as

$$\Delta G = RT \ln\left[\frac{cac}{cmc}\right] \qquad (21)$$

We calculate that the reduction in the free energy of polymer-bound micelles is 1.88 kJ/mol of surfactant in water and increases to 2.53 kJ/mol of surfactant in 0.1 M KNO$_3$, which confirms that salt-induced electrostatic screening increases the stability of polymer-bound surfactant.

(b) Viscosity Measurements. Next, we investigate the variation in the viscosity of ternary PEO−HTAC solutions in 0.1 M KNO$_3$ when titrated with HTAC and compare the results with our earlier experiments in the absence of added salt.[12] Figure 3 shows the variation in the specific viscosity (η_{sp}) with an increasing mass concentration ratio of HTAC to PEO (c_3/c_2). In this experiment, the PEO concentration was fixed at
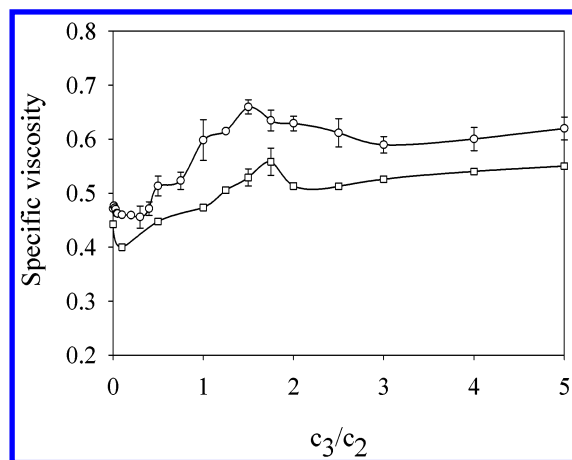
Figure 3. Dependence of the specific viscosity on the surfactant/polymer concentration ratio in water (O) and in the presence of a 0.1 M KNO$_3$ solution (□). The PEO concentration is 0.1 g/100 mL.

0.1 g/100 mL, and the HTAC concentration was varied. The viscosity of the PEO solution in 0.1 M KNO$_3$ is slightly lower than that of the PEO in water, an effect attributed to the contraction of the PEO chain because the added salt competes with the polymer for the water of hydration due to the breaking of intermolecular hydrogen bonding between the polymer and water, as reported by Lance-Gomez and Ward.[32]

As evident in Figure 3, when PEO is titrated with HTAC 0.1 M KNO$_3$, after the initial dip, η_{sp} increases up to a maximum value and then decreases slightly, essentially mirroring the behavior seen earlier in the absence of salt,[12] which is also shown for comparison in Figure 3. Two differences that are evident in 0.1 M KNO$_3$ are that the magnitude of the viscosity maximum is smaller and that the location of the peak is at a slightly higher concentration ratio. The first observation is qualitatively consistent with the interpretation of the viscosity maximum as an increase in the hydrodynamic radius (R_h) because of electrostatic repulsions between the bound micelles. The chain expansion is substantially reduced in 0.1 M KNO$_3$ because of the screening of electrostatic repulsions. This result is also in agreement with previous studies of the binding of anionic surfactants,[1-2,10,33] which found that the strongest coil expansion is observed at the lowest concentration of added salt. The second observation is in agreement with reports by Cabane and Duplessix[23] and Francois et al.[33] that the binding ratio of SDS to PEO increases with increasing ionic strength.

(c) Differential Refractometry Measurements. The refractive index increments $(dn/dc_2)_{T,P,\mu_3}$, $(dn/dc_2)_{T,P,c_3}$, and $(dn/dc_3)_{T,P,c_2}$ were determined, and the preferential binding of HTAC to PEO (D') was calculated via eq 13. All of these results are listed in Table 2 and compared with the corresponding values obtained in our previous study[12] in the absence of added salt. As seen in Table 2, D' increases from 0.87 to 1.64 (g of HTAC/g of PEO) on adding salt (i.e., from 0.12 mol HTAC/mol EO to 0.23 mol HTAC/mol EO). We also list in Table 2 the number of bound HTAC molecules per PEO chain ($N_{3,b}/N_2$) calculated from $N_{3,b}/N_2 = D'M_{w,PEO}/M_{HTAC}$, where $M_{w,PEO}$ is the molecular weight of PEO (599 000 g/mol) and M_{HTAC} is the molecular weight of HTAC (319 g/mol). Comparing $N_{3,b}/N_2$ versus the total number of HTAC molecules per PEO chain ($N_3/N_2 = 3290$ in 0.1 M KNO$_3$ at $c_3/c_2 = 1.75$), it is apparent that, in the presence of salt, the number of bound HTAC molecules per chain increases from 50 to 94% of the total HTAC present. The increased binding affinity of HTAC to PEO when salt is added is likely due to the reduced electrostatic repulsions between the surfactant headgroups.

TABLE 2: Comparative Study of the PEO−HTAC Complex in Aqueous Solution and in the Presence of a 0.1 M KNO$_3$ Solution at the Maximum Binding Point

| physical parameters	PEO−HTAC complex in H$_2$O[a]	PEO−HTAC complex in 0.1 M KNO$_3$ solution
$(dn/dc_2)_{T,P,\mu_3}$ (mL/g)	0.1880 ± 0.004	0.2706 ± 0.002
$(dn/dc_2)_{T,P,c_3}$ (mL/g)	0.1002 ± 0.001	0.1012 ± 0.004
$(dn/dc_3)_{T,P,c_2}$ (mL/g)	0.1005 ± 0.001	0.1035 ± 0.001
D'	0.87	1.64
$M_w \times 10^{-5}$ (g/mol)	12.07 ± 1.39	7.04 ± 0.13
$M_{w,com} \times 10^{-5}$ (g/mol)	22.62 ± 1.68	18.89 ± 1.06
R_g (nm)	169.8 ± 6.4	75.4 ± 4.4
R_h (nm)	82.5 ± 5.2	38.0 ± 2.4
no. of PEO chain	2.0 ± 0.3	1.18 ± 0.02
N_3/N_2	3335	3290
$N_{3,b}/N_2$	1670	3080

[a] Results for the PEO−HTAC complex in water were reprinted from our previous paper.[12]

Our results may be compared with those of Cabane and Duplessix,[23] who reported a binding ratio of 0.25 mol SDS per mol EO without added salt, which increases to 0.85 mol SDS per mol EO at an ionic strength of 0.4. Shirahama[21] and Cabane[22] also observed in the PEO−SDS system a higher binding ratio in salt solution than in salt-free systems, viz., ∼ 0.2 mol SDS per mol EO in salt-free water to 0.4 in 0.1 M NaCl, determined by the surface tension method. In the PVP−SDS system,[34] the addition of salt was observed to increase the binding ratio from 0.3 mol SDS per mol of vinyl pyrrolidone in water to 0.9 mol SDS in 0.1 M NaCl. Another study of complex formation between PVP and SDS in 0.1 M NaNO$_3$[24] indicates that essentially all available surfactant is bound to the polymer (0.39 mol SDS per mol vinyl pyrrolidone). Thus, our results indicate that the effect of neutral salt on the binding of cationic surfactants to nonionic polymers is similar to its effect on the binding of anionic surfactants, with the difference being that the binding levels are smaller (i.e., that nonionic polymers interact weakly with cationic surfactants relative to their interaction with anionic surfactants). This is consistent with previous studies[13,17,35] indicating that cationic surfactants interact weakly because of their more bulky headgroups, which cause a less favorable interaction with the hydration shell of the polymer.

(d) Light-Scattering Measurements. To avoid any change in the structure of the complex upon varying the polymer and surfactant concentration, static light scattering measurements were performed at a constant concentration ratio of PEO and HTAC. Figure 4 shows a Zimm plot for the ternary PEO−HTAC solution in 0.1 M KNO$_3$ solution at a constant ratio of $c_3/c_2 = 1.75$, which is close to the maximum binding ratio of the PEO−HTAC system based on viscosity measurements reported above.

The weight-average molecular weight of polymer in the complex, M_w, is determined via eq 12 using $(dn/dc_2)_{T,P,\mu_1\mu_3} = 0.271 ± 0.004$ mL/g. Knowing M_w and the preferential binding of HTAC to PEO (D') computed via eq 13, we can calculate the molecular weight of the complex via eq 14. Table 2 compares the values of M_w and $M_{w,com}$ for PEO−HTAC complexes in a 0.1 M KNO$_3$ solution versus corresponding values in water at the same c_3/c_2 ratio, which were reported in a previous paper.[12]

From Table 2, we see that the addition of salt leads to a reduction in the formation of multichain aggregates because the average number of PEO chains in the complex is reduced from 2.0 to essentially 1.18. This result appears to be consistent with the conductivity measurements, which show that the cac of the

Structure of Polymer−Surfactant Complexes

J. Phys. Chem. B, Vol. 107, No. 23, 2003 **5465**
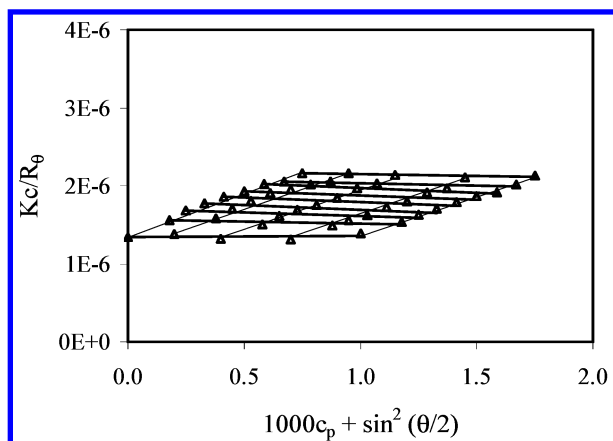
Figure 4. Zimm plot for the PEO−HTAC complex solution in a 0.1 M KNO$_3$ solution at 30 °C at the maximum binding point ($c_3/c_2 =$ 1.75). The lines were drawn by a least-squares fitting method.

Figure 5. Particle-size distributions for PEO ($M_w = 5.99 \times 10^5$ g/mol) in water (—) and in a 0.1 M KNO$_3$ solution (···).

Figure 6. Particle-size distributions for PEO + HTAC at $c_3/c_2 = 1.75$ in water (—) and in a 0.1 M KNO$_3$ solution (···). The PEO molecular weight is 5.99×10^5 g/mol, and the PEO concentration is 0.1 g/ 100 mL.

PEO−HTAC complex in a 0.1 M KNO$_3$ solution (0.35 mM) is smaller than that in water (0.56 mM), indicating that the polymer-bound micelles are more stable in salt solution than without salt. Therefore, we deduce that the driving force for PEO chains to share HTAC micelles is that this reduces electrostatic repulsions between surfactant headgroups and increases the stability of bound micelles at low ionic strength. Another promoting factor may be the decrease in the hydrophilicity of PEO with added salt. Thus, as evident in Table 2, R_g for the free PEO chain in the presence of salt is 68.0 ± 2.0 nm, which is substantially smaller than that observed in water[12] (86.8 ± 3.2 nm). The shrinkage of R_g is consistent with the observed decrease of η_{sp} and indicates a change in chain conformation due to the disruption of the structure of water solvation by adding salt.

Another interesting feature in Table 2 is that R_g of the PEO−HTAC complex in salt solution is much smaller than that of the complex in water, although the molecular weights, $M_{w,com}$, are comparable because the dissociation of multichain complexes is counteracted by an increase in the binding ratio of HTAC to PEO. Moreover, R_g of the complex in salt is only slightly larger than that of the free PEO chain in salt solution, although the molecular weight of the complex is 3 times larger. The large decrease in R_g of the PEO−HTAC complex in 0.1 M KNO$_3$ reflects both the screening of electrostatic repulsions and the disentanglement of the polymer chains in the complex. The fact that the R_g value of the complex in salt is comparable to that of the free PEO further suggests that the binding of micelles in unipolymer complexes may be accompanied by a contraction of the PEO chain.

We note that the large decrease in the hydrodynamic volume of the chain on adding salt (ca. ×8), relative to the fact that the number of polymer particles in solution increases by only a factor of ~2, has to be reconciled with the observation (Figure 3) that the viscosity of the solution near maximum binding decreases by only about 20%. This suggests that very large clusters may be present, which contribute little to the viscosity because they dramatically reduce the number of particles but have a large effect on the hydrodynamic size, as indeed observed in the experiments on oppositely charged polymers and surfactants.[26,27]

This was confirmed by investigating the particle-size distribution (PSD) by dynamic light scattering analysis (DLS). Figure 5 compares the PSD for a solution containing 0.1 g/100 mL of PEO in water and in the presence of salt. A single peak is observed, with the characteristic of a diffusion mode (i.e., the
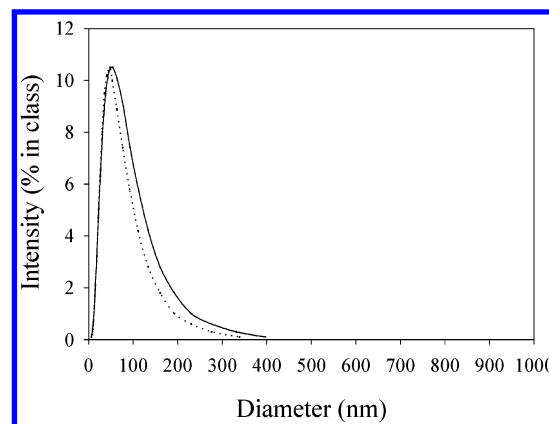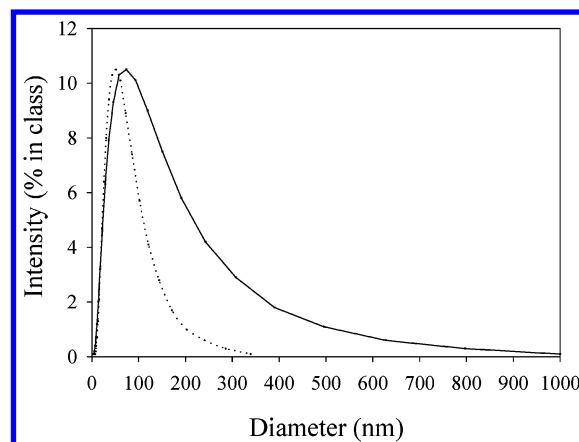
measured hydrodynamic diameter is independent of the scattering angle). In water, the PSD has a mean hydrodynamic radius of $R_h = 42$ nm, which is reduced to $R_h = 35$ nm in 0.1 M KNO$_3$. This result agrees well with the shrinkage of R_g in the presence of salt.

In Figure 6, we present the PSD for the ternary PEO−HTAC solution at a constant concentration ratio, $c_3/c_2 = 1.75$, in the presence and absence of salt. The PSD in 0.1 M KNO$_3$ is, in fact, very similar to that of the PEO itself (Figure 5), whereas in the absence of salt the PSD has a very broad distribution, with a prominent high molecular weight "tail" ascribed to the presence of large multichain aggregates. The addition of salt leads to a reduction in the mean size of the complex from $R_h =$ 82.5 to 38 nm, in good agreement with the R_g values, which also decrease by a factor of 2 on adding salt (Table 2). Moreover, R_h of the complex (38 nm) in the KNO$_3$ solution is comparable to that of the free PEO chain (35 nm), again consistent with the R_g measurements (Table 2).

It is possible to rationalize the decrease in specific viscosity η_{sp} to the change in hydrodynamic radius, R_h, using a theoretical model for polyelectrolyte viscosity developed by Cohen et al.[36]

$$\eta_{sp} \approx \frac{R_h l_B^2 c_{po}^2 Z_p^2}{\kappa^3} \tag{22}$$

These authors derived the following result, neglecting numerical prefactors, where l_B is the Bjerrum length, Z_p is the net charge on the PEO−HTAC complex, c_{po} is the molar concentration of

the complex, and κ^{-1} is the Debye length. Inserting $c_{po} = c_2/M$ and $Z_p = \alpha_p D' M_2/M_3$, where c_2 and M_2 are the PEO concentration and molecular weight, respectively, M_3 is the molecular weight of HTAC, and α_p is the fraction of bound counterions on the micelles, eq 22 can be rewritten as

$$\eta_{sp} \approx \frac{R_h c_2^{1/2}(D')^2\alpha_p^2}{M_3^{1/2}\kappa^3} \tag{23}$$

In comparing the viscosity decrease in 0.1 M KNO$_3$ versus that in the salt-free solution (decrease of 20%) via eq 23, we note (see Table 2) that R_h decreases by a factor of 2, D' increases by a factor of 2, and κ increases by a factor of $(0.1/0.005)^{1/2} = 4.5$, whereas c_2 and M_3 remain unchanged. Thus, to bring about a 20% decrease in viscosity, there must be a 56% decrease in the fraction of bound counterions at the higher ionic strength, which seems to be a reasonable number.

Finally, our results suggest that a weak binding affinity of surfactant to polymer enhances the tendency of polymer chains to share micelles when forming complexes between nonionic polymers and charged surfactants in salt-free aqueous solution. Although we are not aware of any previous study of the multichain association of nonionic polymers with surfactant, two previous studies of complex formation between oppositely charged polymers and surfactants exist. One,[26] involving PSS and CTAB, found that multichain complexation was enhanced by salt, and the other,[27] involving SDS and poly(*N,N,N*-trimethylammonio) ethyl acrylate (PCMA), found that addition of salt diminished the formation of multichain complexes. The difference was attributed to the existence of a hydrophobic driving force for complex formation in the former, whereas electrostatic interactions are the driving force in the latter. In the latter system, it was further observed[27] that the stability of the bound micelles is increased in the presence of salt, as evidenced by a decrease in the cac. Thus, a similarity to our present results exists in that the formation of multichain complexes is associated with a decrease in the stability of bound micelles.

Conclusions

We investigated the structure of complexes formed between PEO and HTAC in 0.1 M KNO$_3$ near the maximum binding point and compared the results with earlier data in the absence of salt. Light-scattering measurements of molecular weight, coupled with the refractometric determination of the amount of bound HTAC, indicate that on average 1.18 ± 0.06 PEO chains are incorporated into the complex in 0.1 M KNO$_3$ salt solution compared to 2.0 ± 0.3 in the absence of salt. Moreover, 0.23 mol of HTAC are bound per mol of EO in the presence of salt compared to 0.12 mol of HTAC per mol of EO in salt-free aqueous solution, corresponding to a salt-induced increase in the number of HTAC molecules bound per PEO chain from 50 to 94% of the total HTAC available in the solution. These differences are attributed primarily to the fact that, in the presence of salt, the stability of bound micelles is enhanced

because of the screening of electrostatic repulsions between the surfactant headgroups, as evidenced by a decrease in the cac. The tendency of PEO chains to share micelles at low ionic strength is driven by the resulting reduction in electrostatic repulsions. Moreover, R_g and R_h values of the PEO−HTAC complex in 0.1 M KNO$_3$ are significantly smaller than in water because of the twin effects of chain contraction via electrostatic screening and dissociation of multichain complexes.

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