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Polymer/Surfactant Interactions. Sodium Poly(styrenesulfonate) and CTAB Complex Formation. Light Scattering Measurements in Dilute Aqueous Solution

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ABSTRACT: Light scattering measurements (dynamic and total intensity) have been made on the complex formed between the polyelectrolyte sodium poly(styrene sulfonate) (NaPSS) and the ionic surfactant cetyltrimethylammonium bromide (CTAB). The influence on the coil conformation of the weight concentration ratio CTAB/NaPSS, of the total concentration of the formed complex, of added simple salt, and of temperature have been examined. The NaPSS coil contracts strongly with increasing CTAB concentration. It is reasoned that this is due in part to the neutralization of the polyion charge by the oppositely charged surfactant micelles and in part through adaption of the coil conformation to the micellar surface curvature. Inverse Laplace transformation shows that in addition to a faster mode describing the translation of the single chain polyion/surfactant complex, a low weight concentration of multichain clusters is present, and the latter are probably formed by more than one chain being associated with a given surfactant micelle. The clusters may be distinguished from those formed in dilute polyelectrolyte solutions at very low or at zero added NaBr through electrostatic interactions between the polyions.

Introduction

There is extensive interest in polymer/surfactant interactions; see, for example, refs 1–5. Some areas of practical importance include clay flocculation,[6–8] mineral flotation including coal flotation,[9,10] polymer solubilization,[11,12] conformational changes in biopolymers,[13–15] and enhanced oil recovery.[16] Several experimental techniques have been applied, for example, NMR,[17a,18] SANS,[17b] fluorescence decay measurements,[19,20] viscosity,[1] potentiometry,[21] surface tension,[22,23] and fast kinetics measurements.[24] Dynamic and total intensity light scattering techniques have been less frequently employed to elucidate changes in the overall conformation of such complexes. Dubin and co-workers have described light scattering measurements on a negatively charged surfactant in solution with a neutral polymer[25] and also on the complex formed between mixed micelles and an oppositely charged polyelectrolyte.[26,27] With, for example, the now well-studied aqueous PEO/SDS system, small micellar aggregates (having only about one-third of the aggregation number of the free micelles) start to form at the critical aggregation concentration (cac) which is much lower than the critical micelle concentration (cmc) for the free micelles. In this case increasing the concentration of SDS results in association of a substantial amount of micelle-like aggregates with the polymer chain and these grow in size as the surfactant/polymer ratio is increased. The consensus is that the polymer chain is associated with the interface between the hydrocarbon-rich moiety and the aqueous environment. Eventually, a situation is reached where the polymer chain is saturated with surfactant and subsequently free micelles are present in addition to the surfactant/polymer complex. In a polyelectrolyte/ionic surfactant system, micellar aggregates are formed which involve the polyion and the charged surfactant molecules. Abuin and Scaiano,[19] Chu and Thomas,[20] and Almgren et al.[28] have examined the micellar aggregation of alkyltrimethylammonium halide surfactants in the presence of sodium poly(styrene sulfonate) (NaPSS) solutions using fluorescence probing methods which yield the aggregation number of the micellar moiety. In overall respects there are similarities with micelle formation in the presence of neutral polymers. A limited number of micellar aggregates is formed on each polyelectrolyte chain and thereby gathered in clusters of which the surface charge is determined by the polyion and where the polyion contributes to the electrostatic stabilization of the bound surfactant micelles. The aggregation number of the surfactant moiety is determined by the length of its carbon chain; for example, 30–40 for DoTAB (dodecyltrimethylammonium bromide)/PSS and 60–80 for CTAB/PSS;[28] the latter is the system presently examined. With increasing surfactant concentration, the aggregation number does not increase but instead more aggregates are formed per chain and these are more densely packed than normal micelles due to inclusion of the PSS segments. It is highly probable that the polyion is situated at the interfacial region of the micellar aggregate with the phenyl groups suitably oriented toward the micellar core. The strong electrostatic interactions between polyion and surfactant, depending on the micellar surface charge density, may lead to phase separation when part of the polyion charge is neutralized. Thus, reducing the micellar charge by addition of a nonionic surfactant is a possible route to make the system more amenable to study. Dubin and co-workers[26,27] have used this approach. In the system consisting of the polycation poly(dimethyldiallylammonium chloride) (PDMDAAC) and a mixture of the anionic and nonionic surfactants SDS and Triton-X100 they observed that, while at concentrations below 0.1 g/L only intrapolyion complexation occurs, at higher concentrations multichain clusters are also present. Such a trend is also found in the present work. Increasing the concentration of simple salt decreases the electrostatic repulsive forces between the fixed charges on the polyion and leads to a decrease in the interaction energy and eventually phase separation. The strength of the polyanion/surfactant interaction should depend in part on the reduced linear charge density ζ of the chain:

$$\zeta = e^2/4\pi\epsilon bkT \qquad (1)$$

where ϵ is the dielectric constant of the solvent and b is

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the distance between adjacent charges along the polymer backbone. The principal consequence of an increase in the linear charge density is a stronger surfactant/polyion interaction, as was observed by Thalberg and Lindman[29] in their work on the interaction between Na hyaluronate and cationic surfactants. However, in a comparison between poly(styrenesulfonate) (PSS), dextran sulfate (DXS), and polyacrylate (PA) dealing with the interaction tendency with oppositely charged surfactants, it was found that PSS interacts more strongly than DXS which in turn interacts more strongly than PA, although the reduced linear charge densities for these polyions are similar.[30] Other factors thus contribute to the interaction between polyions and surfactants: for example, the relative hydrophobicities of the components, the nature of the charged groups, and the flexibility of the chain play a part. In such systems it has become clear that the interaction is in part hydrophobically driven, in addition to the reduction of the overall charge on the complex as binding of surfactant increases.

This article describes the results of light scattering experiments on a high molecular weight polyelectrolyte NaPSS in the presence of the oppositely charged surfactant CTAB in the dilute concentration range. Such an approach yields complementary information to the fluorescence studies listed above on PSS/surfactant complexes since the overall conformation of the surfactant/polyion complex is probed rather than the aggregation numbers of the surfactant micelles involved. The role of the concentration of NaBr (from the limit of zero added salt up to 100 mM) on the size/shape of the complex has also been examined.

Experimental Section

Sodium poly(styrenesulfonate), molecular weight $M_w = 6 \times 10^5$, was synthesized using the method for preparing fully sulfonated polystyrene described by Vink[32a] from a polystyrene fraction with $M_w = 2.9 \times 10^5$ ($M_w/M_n = 1.06$) supplied by Pressure Chemicals, Pittsburgh, PA. The polyelectrolyte when 100% ionized has a linear charge density characterized by one charge per segment length of 0.27 nm. Surfactants CTAB (Merck) and DeTAB (decyltrimethylammonium bromide) (Tokyo Casei Inc.) were used without further purification. The water used was Milli-Q grade from a Millipore apparatus. All solutions were filtered into 15-mm-diameter cylindrical glass cells through 0.2-μm Sartorius Minisart N filters.

Sample Preparation. Stock solutions were prepared. When the surfactant/polyion solutions were prepared, a solution containing NaPSS (0.2% w/w) and NaBr was slowly titrated from a buret with an equal volume of CTAB solution (0.12; 0.18 or 0.24% w/w) also containing NaBr under constant stirring. Stirring was thereafter continued for 48 h to attain equilibrium. The mixture was diluted appropriately and filtered as above. Solutions were dialyzed against aqueous solutions of NaBr. The membrane (dialysis membrane from Union Carbide Corp.) only allowed passage of the small ions (pore diameter ≈2.5 nm) and retained the polyions. Dialysis was carried out for 28 days. The slow approach to equilibrium presumably reflects the limiting diffusion rate of the surfactant through the membrane.

Dynamic Light Scattering. The apparatus and technique used were essentially those summarized in ref 33. An ALV 5000 wide band multi-τ, digital autocorrelator was employed, making it possible to determine relaxation times over up to nine decades in delay time. The measured time correlation function is related to the field correlation function by the Siegert relation:

$$g_2(t) = 1 + \beta|g_1(t)|^2 \qquad (2)$$

where β takes into account deviations from the ideal correlation. For an infinite range of particle sizes, in a continuous distribution, the inverse Laplace transform (ILT) may be used:

$$g_1(t) = \int_0^\infty A(\tau)\exp(-t/\tau)\,d\tau \qquad (3)$$

Here τ is the relaxation time which is obtained together with the corresponding relative amplitude using the inversion algorithm REPES.[34] The latter is similar in many respects to CONTIN[35] but directly minimizes the sum of the squared differences between experimental and calculated $g_2(t)$ functions. Relaxation time distributions are given in the form $\tau A(\tau)$ versus log τ, providing an equal area representation. Diffusion coefficients are calculated from the ILT moments as $D = (\Gamma/q^2)_{q\to 0}$, where q is the magnitude of the scattering vector.

Static light scattering measurements were made using a Hamamatsu photon-counting device, together with a 3-mW He–Ne laser. Benzene was used for calibration (Rayleigh ratio = 8.51×10^6 cm^{-1}).[36] The concentration C in (KC/R_θ) and (dn/dC) is the sum of the weight concentrations of polymer and surfactant in the predialyzed solutions. (dn/dC) was measured on the complex with weight concentration ratio (CTAB/NaPSS) = 0.6 in 50 mM NaBr dialyzed solutions at the same wavelength as the measured intensity (632 nm) in a differential refractometer using Rayleigh interference optics.

The value is $(dn/dC) = 0.152 \pm 0.002$ mL/g. This value was used throughout. For comparison, a value of $(dn/dC) = 0.178$ mL/g exists for NaPSS in 0.2 M NaCl,[32b] and for CTAB in 50 mM NaBr $(dn/dC) = 0.142$ mL/g at 30 °C.

Results and Discussion

Polymer/Surfactant Complex Diffusion. The two curves in Figure 1 show the change in the diffusion coefficient (evaluated from the peak moments by inverse Laplace transformation (ILT)) ($C_{\mathrm{NaPSS}} = 0.1\%$) for the polyelectrolyte chain on addition of two surfactants differing in hydrocarbon chain lengths. The value of D at finite concentration decreases with increasing surfactant concentration. This trend is anticipated owing in part to the progressive decrease of charge–charge interactions on the polyion as the net charge is decreased by complexation with surfactant and in part to the simultaneous screening of charge–charge interactions by surfactant co-ions. At a given concentration of surfactant, the diffusion coefficient of the chain with CTAB is lower than with DeTAB. This may reflect the stronger surfactant/polyion interaction for CTAB vs DeTAB over the concentration range up to about 2.5 mM surfactant. Micelles are formed in aqueous solutions of CTAB without added salt at very low concentration (cmc ≈ 0.93 mM). However, it is well-known that the cac of a surfactant in the presence of polymer is much lower than the cmc (by about 2 powers of 10), and thus at the concentrations used here we are concerned with the interaction between the polyanion and the micellar surfactant species. The difference between the cac and the cmc has also been shown to increase with increasing surfactant chain length.[31] The trend in Figure 1 agrees qualitatively with the results of Almgren et al.[28] for the respective micellar aggregation numbers of CTAB and the similar compound DoTAB per interaction site using a time-resolved fluorescence technique. The convergence of the diffusion coefficients as the concentration of surfactant approaches saturation is also expected. Almost all surfactant will be associated in the form of micellar aggregates with the polyanion up to about 65% neutralization of the latter. The value of 65% charge neutralization has been estimated for DoTAB in NaPSS solutions by Almgren et al.[28] using a surfactant-selective electrode when determining the binding isotherm. The present observations confirm a very similar value for CTAB in NaPSS solutions. The 65% neutralization level of the polyion is consistent with a surfactant concentration of ≈3.3 mM. It can thus be assumed that the concentration of free micelles can be neglected. Further increase of the

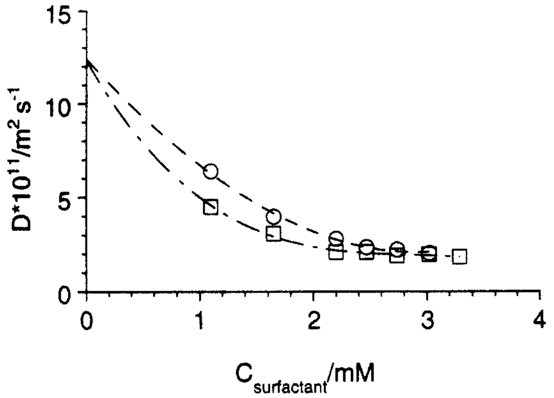

Figure 1. Effective diffusion coefficient for the single chain complex (fast mode as for example in Figure 2) as a function of surfactant concentration: DeTAB (circles); CTAB (squares). Conditions: NaPSS concentration 0.1%; no added salt.

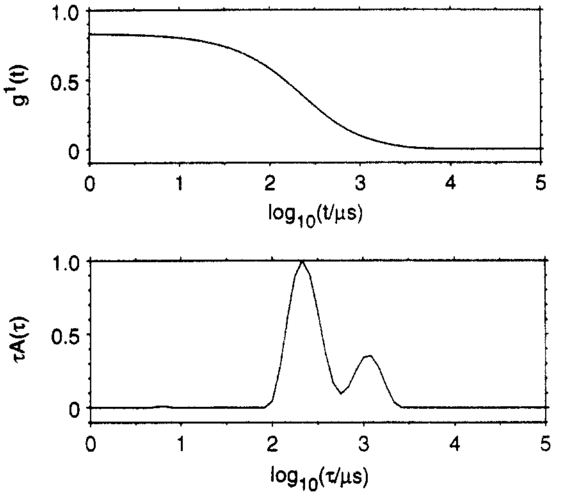

Figure 2. Field correlation function (upper) and inverse Laplace transformation (lower) for CTAB/NaPSS (ratio 1.2) in 10 mM NaBr. Conditions: C_{NaPSS} = 0.08%; measurements at 25 °C and angle 90°.

surfactant/polyion ratio brings one to the solubility limit, and phase separation occurs.

Multichain Cluster Formation. Figure 2 (upper) shows the field autocorrelation function for the CTAB/NaPSS system (C_{NaPSS} = 0.08%) where the weight ratio between surfactant and polymer is 1.2 in 10 mM NaBr. The correlation function is bimodal as is shown by the result of inverse Laplace transformation (ILT) in the lower part of the figure.

Figure 3a shows relaxation time distributions at different values of the scattering vector (q): the relaxation rates for both modes are linearly dependent on q^2 (Figure 3b), demonstrating their diffusive character.

Diffusion coefficients are summarized in Table 1 for the different systems. The interpretation made here is that the fast mode is due to the translational motions of the single chain complex while the slow mode derives from the diffusion of multichain clusters. The origin of the latter is not yet clearly established. The phenomenon of cluster formation in dilute polyelectrolyte solutions without or with a low concentration of simple electrolyte has been extensively discussed; see for example refs 29, 37, 38, and 39–41. The term "cluster" is used here to express *multichain association* (in distinction to the micellar aggregates referred to for the surfactant). The concentration above which multichain clustering occurs in the case of polyion/surfactant complexes in solution depends on the concentration of added salt and the surfactant concentration. When either the ionic strength is increased or the surfactant/polyion ratio is increased, the concentration at which clusters are formed is reduced.

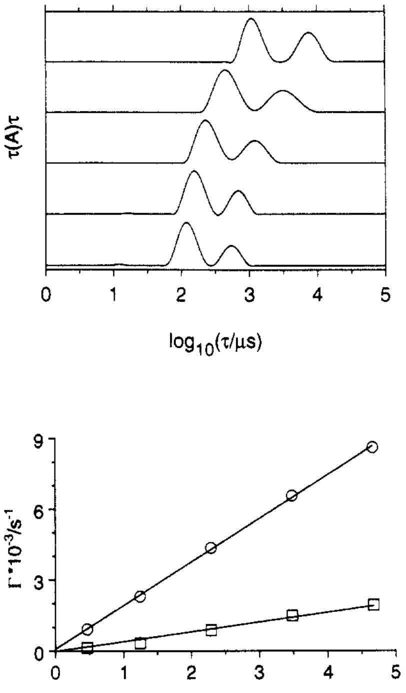

Figure 3. (a, top) Relaxation time distributions for CTAB/NaPSS (concentration ratio 1.2) as a function of angle without added salt. Angles from top to bottom: 30, 50, 70, 90, and 110°. Conditions: C_{NaPSS} = 0.083%; 25 °C. (b, bottom) Relaxation rates (Γ/s^{-1}) from ILT results for the data in Figure 3a plotted as a function of scattering vector (q) squared.

Table 1. Effective Diffusion Coefficients for the Fast and Slow Modes at Different Surfactant/Polyion Ratios (*C*(NaBr) = 0 and Temperature 25 °C)

10^4C(NaPSS)/g mL^{-1}	$10^{12}D_{fast}$/m^2 s^{-1}	$10^{12}D_{slow}$/m^2 s^{-1}
	a. 1.2 Ratio	
0.833	11.3	
1.67	11.8	
2.50	12.6	1.1
3.33	13.6	1.9
4.17	13.5	2.0
6.67	15.5	2.9
7.50	16.3	2.5
8.33	17.0	2.9
9.17	16.9	2.0
10.0	17.9	2.7
	b. 0.9 Ratio	
0.833	10.6	
1.67	11.4	
2.50	12.2	
3.33	13.0	
4.17	13.9	1.7
6.67	17.7	2.9
7.50	17.5	2.6
8.33	18.1	3.2
9.17	19.2	3.7
10.0	20.2	4.0
	c. 0.6 Ratio	
0.833	10.9	
1.67	13.4	
2.50	14.7	
3.33	16.4	
4.17	17.1	
6.67	20.6	
7.50	22.2	1.1
8.33	23.6	3.2
9.17	24.1	4.4

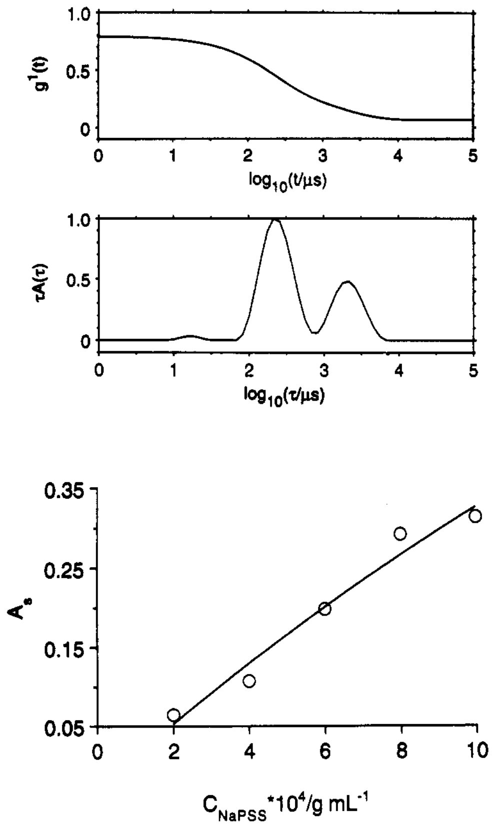

Figure 4. (a, top) Field correlation function ($g_1(t)$) and corresponding ILT results for NaPSS (zero CTAB) in 10 mM NaBr. Conditions: 25 °C and angle 90°; C_{NaPSS} = 0.08%. (b, bottom) Slow mode amplitude as a function of NaPSS concentration (zero CTAB).

It should be noted that, although the relative amplitude of the slow mode in Figure 2 is significant ($\approx$0.3), the corresponding weight concentration of the cluster mode is small. Thus, if the ratio of the diffusion coefficients of the two modes is $\approx$1:10 (corresponding to a ratio of the molecular weights of about 100 (taking $D \sim M^{-1/2}$)), the weight concentration ratio (C_{slow}/C_{fast}) $\approx 3 \times 10^{-3}$.

Figure 4a shows an autocorrelation function with the corresponding ILT result for the pure polymer NaPSS in 10 mM NaBr. Figure 4b shows the progressive increase in the relative amplitude of the slow mode with PSS concentration. It has been proposed that the formation of multichain domains (clusters) is responsible for the presence of the slow mode in salt-free NaPSS solutions. Apparent dimensions of the domains are of the order of 100 nm, irrespective of molecular weight, indicating that a variable number of chains is involved in each domain. It was concluded that the slow mode for the pure polyelectrolyte in salt-free conditions arises from electrostatic interactions between chains. Filtration through 0.1-μm filters thus has only a small effect on the amplitude of the slower mode which is interpreted as due to distortion of the multichain domains.[41]

We also note here the study by Ise and co-workers[42] of the dynamic aspects of ordering in latex suspensions, a phenomenon which was also observed in DLS experiments. Ordered and disordered structures were observed on the microscopic level, and the motion of the particles in the ordered structures was shown to differ from that for the free particles.

Figure 5a depicts ILT distributions for different complex concentrations, where the surfactant/polyion weight concentration ratio is maintained constant at 1.2 without added salt. While the correlation function is close to a single exponential at the lowest concentration, the relative amplitude of the slow component increases strongly with increasing concentration.

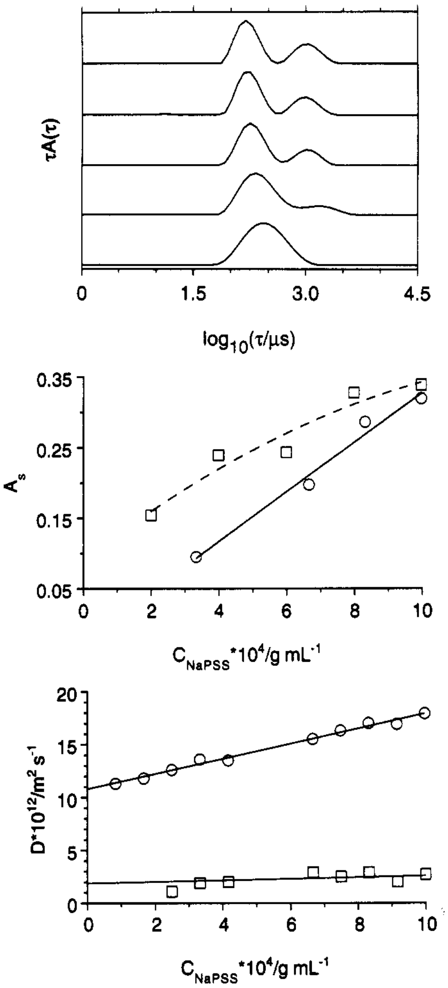

Figure 5. (a, top) Inverse Laplace transform results for CTAB/NaPSS; ratio = 1.2 without added salt. NaPSS concentrations (bottom on top): 1.67×10^{-4}, 3.33×10^{-4}, 6.67×10^{-4}, 8.33×10^{-4}, 10.0×10^{-4} g/mL. (b, middle) Relative amplitude of the slow mode from Figure 5a as a function of C_{NaPSS}: zero added salt (circles); 100 mM NaBr (squares). Conditions: 25 °C, angle 90°. (c, bottom) Diffusion coefficients for fast and slow modes as a function of concentration: single chain complex (circles); multichain clusters (squares). Conditions: CTAB/NaPSS ratio = 1.2; zero added salt.

Figure 5b shows the trend in the relative amplitude of the slow mode as the NaPSS complex concentration is increased at zero added salt and in 100 mM NaBr, respectively. The concentration dependence of the diffusion coefficients for the two modes is depicted in Figure 5c. The slopes of these lines are conventionally represented in terms of a hydrodynamic virial coefficient, k_D, which is proportional to the interaction strength:

$$D = D_0(1 + k_D C + ...) \qquad (4)$$

where k_D equals $2A_2M - k_f - 2v_2$. Here A_2 is the second virial coefficient related to the pair interaction potential, k_f describes the concentration dependence of the friction factor (f), and v_2 is the partial specific volume of the solute (for the surfactant/polyion complex). It is implicit in the use of eq 4 that the polyion/surfactant complex does not change its composition over the concentration range used. The linearity of the plots in Figure 5c justifies this assumption.

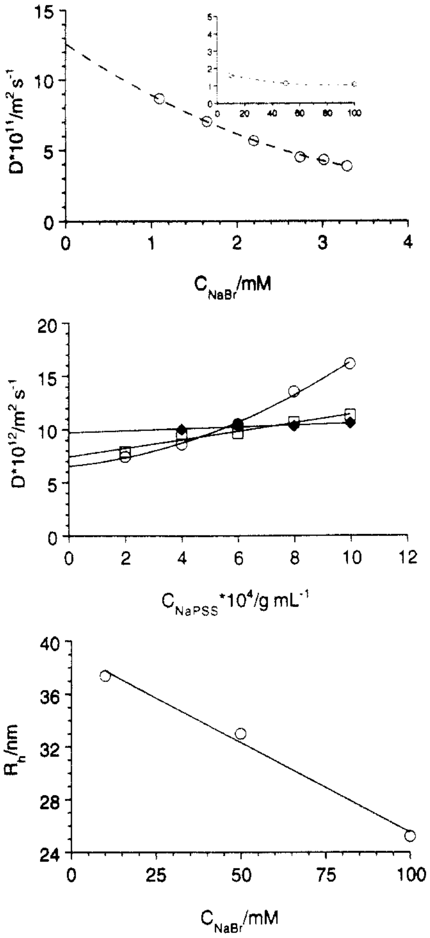

Figure 6. (a, top) Diffusion coefficient for NaPSS versus NaBr concentration. Conditions: C_{NaPSS} = 0.1% (≈5 mM); measurements at 25 °C and angle 90°. The inset shows data over a more extended range of salt concentrations. (b, middle) Diffusion coefficients for NaPSS in the absence of CTAB at different NaBr levels: 10 mM (circles); 50 mM (squares); 100 mM (diamonds). (c, bottom) Hydrodynamic radii derived from the intercepts in Figure 6b plotted as a function of added NaBr.

Figure 6a shows the decrease in the polyion diffusion coefficient (here at a fixed NaPSS concentration of 0.1%) as a function of NaBr concentration in the absence of CTAB. D decreases with increasing ionic strength owing to screening effects which strongly influence the interaction potential between fixed charges, and thus this curve has a qualitative resemblance to Figure 1 showing the influence of added surfactant. At very low concentrations of added salt (<1 mM), the DLS measurements become increasingly difficult since the scattering from the solutions is only a little in excess of that of the pure solvent. Figure 6b shows the diffusion coefficients for NaPSS at various ionic strengths as a function of NaPSS concentration. As pointed out above with reference to eq 4, the concentration dependence in plots such as Figure 6b is influenced partly by the virial term and partly by the competing concentration dependence of the friction factor, both effects becoming increasingly important as the concentration of added salt is reduced, and this leads to nonlinearity in the limit of zero added salt. At infinite dilution the value of the intercept (D_0) increases with increasing NaBr since the coil radius contracts due to the screening of the fixed charges.

Figure 6c shows the corresponding change in R_h of the coil as the NaBr concentration is increased; see also Table 2.

Figure 7 shows the data for the surfactant/polymer complex (weight concentration ratio 1.2) at added salt concentrations of 10 and 100 mM NaBr. There is a progressive increase in the cluster mode amplitude with increasing polyion concentration which is most pronounced in 100 mM salt. Comparison of Figures 2 and 4a shows that, at the same polymer concentration (0.08% NaPSS) and at the same ionic strength of 10 mM, the clusters are considerably larger (R_h ≈ 175 nm) for the polyion in the absence of surfactant compared to the CTAB/NaPSS complex system (R_h ≈ 84 nm). Furthermore, the cluster mode has a greater relative amplitude with increasing (a) CTAB/PSS ratio and (b) total concentration of the CTAB/PSS complex. These compositional shifts move the system closer to phase separation. The most likely explanation is that the clusters originate from hydrophobic interactions between the complex chains and represent incipient phase separation. Increasing the NaBr concentration tends to reduce chain solvation but also increases the screening of the charge–charge interactions. A higher relative surfactant concentration reduces the charge on the complex polyion toward the limit of 65% neutralization, above which value the complex phase separates. Possibly the clusters originate from a small number of surfactant micelles which are associated with two or more polymer chains.

The temperature dependences of the hydrodynamic radii are shown in Figure 8a for the NaPSS single chain complex and the multichain clusters; see also Table 2. Multichain clusters are present in both systems (with and without CTAB) in addition to the single chain complex. The contraction observed with increasing temperature for both the single chain and the clusters is significantly greater

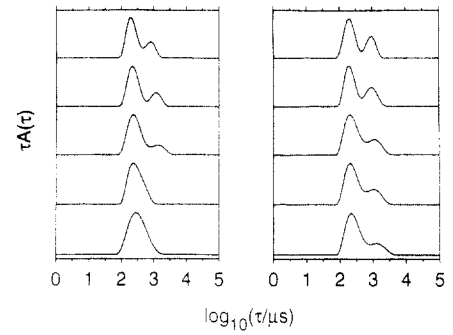

Figure 7. Inverse Laplace transform results for the CTAB/NaPSS ratio 1.2 in 10 mM NaBr (left) and 100 mM NaBr (right). Concentrations from bottom to top: 2 × 10^{-4}, 4 × 10^{-4}, 6 × 10^{-4}, 8 × 10^{-4}, and 10 × 10^{-4} g mL^{-1}. Measurements at 25 °C and angle 90°.

Table 2. Diffusion Coefficients at Infinite Dilution and Hydrodynamic Radii for the NaPSS/CTAB Complexes (Temperature 25 °C)

a. C(NaBr)/mM	CTAB/NaPSS ratio	$10^{12}D_0$/m^2 s^{-1}	R_h/nm
0	0.6	7.84	31.3
0	0.9	9.66	25.4
0	1.2	10.8	22.8
50	0.6	9.28	26.4
50	0.9	10.8	22.7
50	1.2	11.2	21.8

b. C(NaBr)/mM	$10^{12}D_0$/m^2 s^{-1}	R_h/nm
0	10.8	22.8
10	10.9	22.6
50	11.2	21.8
100	12.0	20.4

c. t/°C	$10^{12}D_{0,fast}$/m^2 s^{-1}	$R_{h,fast}$/nm	$10^{12}D_{0,slow}$/m^2 s^{-1}	$R_{h,slow}$/nm
25	10.8	22.7	1.90	129
35	15.4	20.4	2.90	108
45	21.1	18.5	5.38	72.7

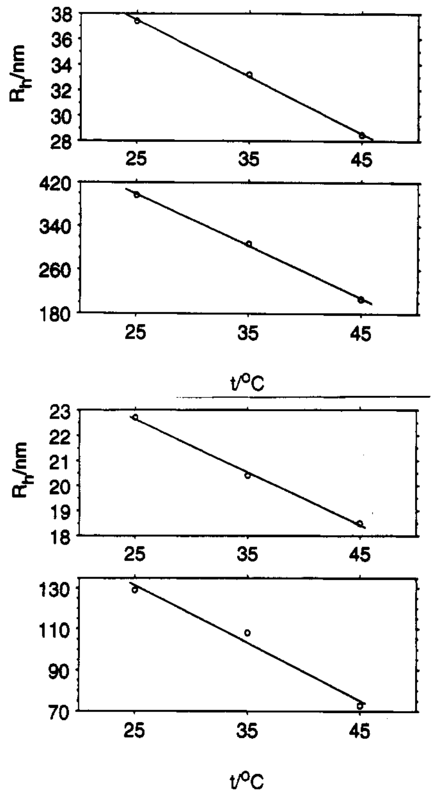

Figure 8. (a, top) Temperature dependence of the hydrodynamic radius for NaPSS with no CTAB present in 10 mM NaBr. (b, bottom) Plots analogous to those in Figure 8a for the CTAB/NaPSS ratio 0.9 in 50 mM NaBr.

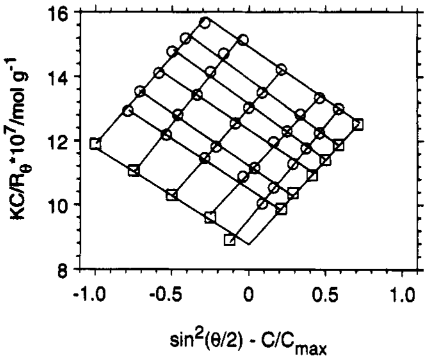

Figure 9. Zimm plot for CTAB/NaPSS systems. Conditions CTAB/NaPSS ratio 0.6, 50 mM NaBr at 25 °C. Derived data are listed in Table 3.

Table 3. Averaged Radii of Gyration, Second Virial Coefficients, Molecular Weights, Overlap Concentrations, and R_g/R_h Values for the Complexes in 50 mM NaBr (Temperature 25 °C)

CTAB/ NaPSS ratio	R_g/nm	10^4A_2/mol mL g^{-2}	$10^{-6}M_w$	C*/g L^{-1}	R_g/R_h
0.6	52.6	1.93	1.4	3.8	2.0
0.9	60.4	0.77	2.3	4.1	2.7
1.2	53.5	≈0	2.3	6.0	2.5

in the case of the NaPSS alone compared to the NaPSS/CTAB complex (Figure 8b).

Intensity Light Scattering Results. The presence of clusters complicates the application of static light scattering since the total intensity of the scattering is then due to more than one component. The radius of gyration and molecular weights evaluated and listed in Table 3 are thus average values for the total system. Figure 9 shows a Zimm plot for the CTAB/PSS ratio 0.6 in 50 mM NaBr. As the ratio increases and the overall charge of the complex is reduced, the concentration dependence of the reduced scattering becomes smaller. There is also a trend toward phase separation when the electrostatic interactions are progressively screened out by increasing the NaBr concentration. This is shown, for example, by the greater relative amplitude of the cluster mode at the higher salt concentration in Figure 7 as well as the change in k_D (k_D = 0.47 L g^{-1} at 10 mM and 0.22 L g^{-1} at 100 mM).

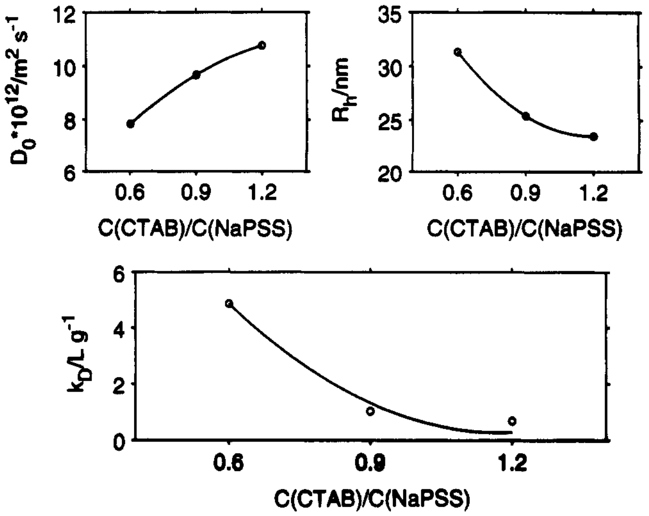

Figure 10. (a, top left) Diffusion coefficient at infinite dilution (D_0), (b, top right) hydrodynamic radius (R_h), and (c, bottom) hydrodynamic virial coefficient (k_D) as a function of the CTAB/NaPSS ratio. Conditions: data at 25 °C and zero added salt.

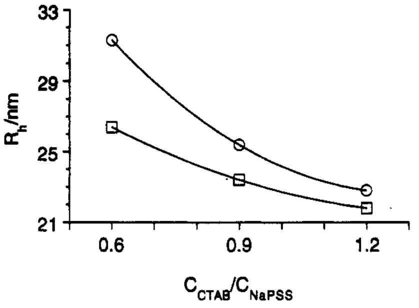

Figure 11. Plots of hydrodynamic radius versus the CTAB/NaPSS ratio at zero added salt (circles) and 50 mM NaBr (squares). Conditions: measurements at 25 °C.

Conformation of the Polyion/Surfactant Complex. The changes in conformation of the surfactant/polyelectrolyte complex are revealed by the values of the hydrodynamic radius of the single chain complex which are summarized in Table 2 and are illustrated in Figure 10. The changes in k_D are also illustrated in the figure.

The coil contracts strongly with increasing surfactant/polyion ratio (see Table 2). This contraction is strong when doubling the surfactant concentration (31 nm at molar ratio 0.34) to 23 nm (molar ratio 0.68) with no added salt (Figure 11). This contraction may be compared with the decrease in R_h of the complex (molar ratio 0.68) when going from zero added salt to 100 mM NaBr (23–20 nm) (Figure 12). In 50 mM NaBr the contraction of the complex is less pronounced: 26 nm (molar ratio 0.34) to 22 nm (molar ratio 0.68), as seen in Figure 11. These results show that the contraction of the polyion coil produced by interaction with CTAB is considerably stronger than the effect produced by screening with a high concentration of simple salt. In order to form a stable polyion/micelle complex, there must exist a strong mutual interaction between the polyion and the small spherical surfactant micellar aggregates, partly to optimize the interactions between the oppositely charged species and partly to maximize contacts between the hydrophobic moieties of

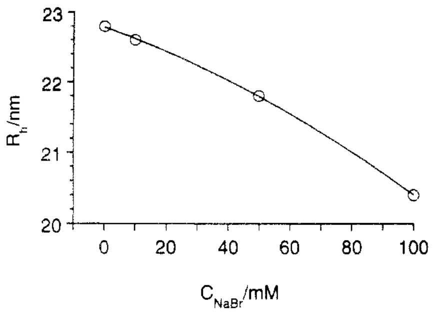

Figure 12. Hydrodynamic radius for CTAB/NaPSS ratio 1.2 as a function of added NaBr. Conditions: 25 °C and angle 90°.

the polystyrene chain and the hydrocarbon parts of the micellar aggregate. Stabilization of the complex thus requires maximization of the interaction surface between the small micelles and the chain, which will result in an overall compact conformation of the polyion complex. This behavior may be anticipated for flexible chain polyions [for example, it is also found to be the case with poly(methacrylic acid)][20] and conversely should be less pronounced for stiff polyelectrolytes. Similar conclusions have been arrived at by other workers using other indices. Thus a reduction in polyion extension was earlier indicated by the low viscosity of the NaPSS/DoTAB complex in comparison with the viscosity of the solution of the polyion alone.[19] The mutual interactions between the polyion and the surfactant micelles mean that the polymeric component also has a striking effect on the conformation of the micelles formed. Thus, it may be recalled that in the absence of polymer and above the cmc, CTAB micelles grow strongly in solution on the addition of salt owing to the screening of intermicellar interactions favoring micellar growth. This behavior is well documented and light scattering studies[43-46] revealed that long threadlike micelles are formed. Imae and Ikeda[43] showed, for example, that the persistence length of the CTAB micelles is 47 nm, indicating substantial extension of the long micellar chains. Above the overlap concentration (C^*) there are clear analogies with the behavior of linear polymer chains, for example, in the similarity with the scaling relationships which are followed for semidilute polymer solutions in good solvents.[44-46] The situation changes dramatically in the presence of a polymer since the formation of long threadlike micelles of the surfactant is then inhibited and the formation of spherical micelles is favored. Thus, for example, Brackman and Engberts[47] found that when polymer (poly(propylene oxide) or poly(vinyl methyl ether)) is added to the viscoelastic solutions of cetyltrimethylammonium salicylate (CTASal), the solution then displays normal Newtonian behavior with a water-like viscosity. The micelles apparently undergo a transition from a rodlike conformation to a spherical one, with the polymer wrapped around the surfactant/water interface, thereby minimizing unfavorable core–water contacts at the surface. The effect of the polyelectrolyte NaPSS is probably of a similar nature with the surfactant CTAB examined here. In the present system, the changes in R_h with increasing surfactant/polyion ratio are accompanied by changes in the parameter k_D in eq 4, which primarily reflects a reduction in the pair interaction potential embodied in A_2. Thus with zero added salt, k_D for the complex decreases from 4.86 to 0.68 L g^{-1} as the ratio CTAB/NaPSS is increased from 0.6 to 1.2. The change is less pronounced in 50 mM NaBr (0.33–0.18 L g^{-1}), as the interactions are then already strongly screened.

Influence of Added Salt. The surfactant/polyion complex contracts with increasing concentration of added salt, as is shown in Table 2 and in Figure 12 for the hydrodynamic radius as a function of NaBr concentration; this change is paralleled by a decrease in k_D from 0.68 (zero added salt) to 0.22 L g^{-1} (100 mM). This result is in agreement with the general finding that the cac is increased on addition of salt to the surfactant/polymer system; i.e. the interaction is reduced. This trend is, however, opposite to that usually displayed with surfactant micelles for which salt addition produces a lowering of the cmc. The salt apparently serves to screen the electrostatic interactions and also to stabilize the bound micelles in the complex.

Comparison with Surfactant/Neutral Polymer Interaction. One of the main differences observed in the present system in comparison with the previously studied PEO/SDS system[48] is that the solubility of the complex polyion is dependent on a minimum charge density. In the present system, this means that a level of surfactant representing about 65% charge neutralization corresponds to the maximum loading of CTAB and that compositions corresponding to the PEO complex accompanied by an excess of surfactant cannot exist. In the latter, in contrast, the PEO chain is progressively charged up to the point of saturation, whereafter free micelles are formed in the surrounding solution, and this leads to screening by the excess counterions. The resulting pronounced maxima in the complex hydrodynamic radius, viscosity, second virial coefficient, and k_D value found with increasing SDS concentration in the SDS/PEO system are thus not observed with CTAB/PSS. Neither is a peak in the relaxation time distributions observed for the pure surfactant.

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References and Notes

(1) Saito, S. *Kolloid Z.* **1957**, *154*, 19.
(2) Fishman, M. L.; Eirich, F. R. *J. Phys. Chem.* **1971**, *75*, 3135.
(3) Mattice, W. L.; Harrison, W. H. *Biopolymers* **1976**, *15*, 559.
(4) Zana, R.; Lianos, P.; Lang, J. *J. Phys. Chem.* **1985**, *89*, 41.
(5) Carlsson, A.; Karlström, G.; Lindman, B. *Langmuir* **1986**, *2*, 536.
(6) Hanna, H. S.; Somasundaran, P. *J. Colloid Interface Sci.* **1979**, *70*, 181.
(7) Law, J. P., Jr.; Kunze, G. W. *Soil Sci. Soc. Am. Proc.* **1966**, *30*, 321.
(8) Howler, W. F. *Clays Clay Miner.* **1970**, *18*, 97.
(9) Basenkova, V. L.; Zubkova, Yu. N. *Khim. Tver. Topl. (Moskow)* 1977, *11*, 137.
(10) Przhegorlinskaja, R. W.; Zubkova, Yu. N. *Khim. Tver. Topl. (Moscow)* **1978**, *12*, 125.
(11) Isemura, I.; Imanishi, A. *J. Polym. Sci.* **1958**, *33*, 337.
(12) Jones, M. N. *J. Colloid Interface Sci.* **1967**, *23*, 36.
(13) Sarker, D. K.; Doty, P. *Proc. Natl. Acad. Sci. U.S.A.* **1966**, *55*, 981.
(14) Grourke, M. J.; Gibbs, J. H. *Biopolymers* **1967**, *5*, 586.
(15) Satake, I.; Yang, J. T. *Biochem. Biophys. Res. Commun.* **1973**, *54*, 930.
(16) Taber, J. J. *Pure Appl. Chem.* **1980**, *52*, 1323.
(17) (a) Cabane, B. *J. Phys. Chem.* **1977**, *81*, 1639. (b) Cabane, B.; Duplessix, R. *J. Physique* **1982**, *43*, 1529.
(18) Smith, M. L.; Muller, N. *J. Colloid Interface Sci.* **1975**, *52*, 507.
(19) Abuin, E. B.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6274.
(20) Chu, D.; Thomas, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 6270.
(21) Hayakawa, K.; Kwak, J. C. T. *J. Phys. Chem.* **1982**, *86*, 3866.
(22) Lange, H. *Kolloid Z. Z. Polym.* **1971**, *243*, 101.
(23) Schwuger, M. J.; Lange, H. *Proc.—Int. Congr. Surf. Act. Agents, 5th* **1968**.

(24) Gettings, J.; Gould, C.; Hall, D. G.; Jobling, P. L.; Rassing, J.; Wyn-Jones, E. *J. Chem. Soc. Faraday Trans. 2* **1980**, *76*, 1535.
(25) Xia, J.; Dubin, P. L.; Kim, Y. *J. Phys. Chem.* **1992**, *96*, 6805.
(26) Dubin, P. L.; Rigsbee, D. R.; Gan, L.-M.; Fallon, M. A. *Macromolecules* **1988**, *21*, 2555.
(27) Dubin, P. L.; Thé, S. S.; Gan, L.-M.; Chew, C. H. *Macromolecules* **1990**, *23*, 2500.
(28) Almgren, M.; Hansson, P.; Mukhtar, E.; van Stam, J. *Langmuir* **1992**, *8*, 2405.
(29) Thalberg, K.; Lindman, B. *J. Phys. Chem.* **1989**, *93*, 1478.
(30) Hayakawa, K.; Kwak, J. C. T. In *Cationic Surfactants*; Rubingh, D. N., Holland, P. M., Eds.; Marcel Dekker: New York, 1991; p 189.
(31) In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; CRC Press, Inc.: Boca Raton, FL, 1993.
(32) (a) Vink, H. *Makromol. Chem.* **1981**, *182*, 279. (b) Unpublished results.
(33) Nicolai, T.; Brown, W.; Johnsen, R. M.; Stepánek, P. *Macromolecules* **1990**, *23*, 1165.
(34) Jakes, J. *Czech. J. Phys.* **1988**, *B38*, 1305.
(35) Provencher, S. W. *Makromol. Chem.* **1979**, *180*, 201.
(36) Pike, E. R.; Pomeroy, W. R. M.; Vaughan, J. M. *J. Chem. Phys.* **1975**, *62*, 3188.
(37) Koene, R. S.; Mandel, M. *Macromolecules* **1983**, *16*, 973.
(38) Drifford, M.; Dalbiez, J.-P. *J. Phys. Chem.* **1984**, *88*, 5368.
(39) Koene, R. S.; Mandel, M. *Macromolecules* **1983**, *16*, 220.
(40) Mandel, M. In *Dynamic Light scattering: the Method and some Applications*; Brown, W., Ed.; Oxford University Press: Oxford, U.K., 1993.
(41) Sedlak, M. *Macromolecules* **1993**, *26*, 1158.
(42) Ito, K.; Nakamura, H.; Yoshida, H.; Ise, N. *J. Am. Chem. Soc.* **1988**, *110*, 6955.
(43) Imae, T.; Ikeda, S. *J. Phys. Chem.* **1986**, *90*, 5216.
(44) Candau, S. J.; Hirsch, E.; Zana, R. *J. Colloid Interface Sci.* **1985**, *105*, 521.
(45) Delsanti, M.; Moussaid, A.; Munch, J. P. *J. Colloid Interface Sci.* **1993**, *157*, 285.
(46) Appel, J.; Porte, G. *Europhys. Lett.* **1990**, *12*, 185.
(47) Brackman, J. C.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1990**, *112*, 872.
(48) Brown, W.; Fundin, J.; da Graça Miguel, M. *Macromolecules* **1992**, *25*, 7192.