Macromolecules 1988, *21*, 2555–2559

Equilibrium Binding of Mixed Micelles to Oppositely Charged Polyelectrolytes

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ABSTRACT: In aqueous solutions containing poly(dimethyldiallylammonium chloride) (PDMDAAC), sodium dodecyl sulfate (SDS), Triton X-100, and NaCl, the cationic polymer can form equilibrium complexes with the anionic/nonionic mixed micelles. Such molecular aggregates are stable at certain conditions, namely, a well-defined range of anionic surfactant mole fraction for each ionic strength explored. The former variable, defined as $Y = [\mathrm{SDS}]([\mathrm{SDS}] + [\mathrm{Triton\ X\text{-}100}])^{-1}$, dictates the micelle surface charge density, while the latter controls the Debye–Hückel screening length. Solutions containing stable polyion–micelle complexes were studied by turbidimetric titrations, quasi-elastic light scattering (QELS), and ultrafiltration. The QELS autocorrelation decay curves are well fit by two exponentials. The fast decay constant is identical with that observed in polymer-free micelle solutions or in solutions in which complexation is suppressed by high ionic strength and/or low micelle surface charge and may thus be attributed to unbound micelle. The slow decay corresponds to apparent Stokes diameters of ca. 60–120 nm, i.e., 2–4 times larger than the uncomplexed polymer, and therefore arises from intra- or interpolymer micelle complexes. In the presence of 1×10^6 molecular weight PDMDAAC, complexes are retained by a 500 000 "molecular weight cut-off" ultrafiltration membrane, while unbound micelles are not, and consequent changes in the bimodal size distribution are reflected in the QELS results. Turbidimetric titration curves, taken in conjunction with the ultrafiltration/QELS data, suggest that the mixed micelles are compositionally polydisperse, and only those micelles whose composition corresponds to or exceeds some critical surface charge density are involved in the polyion-binding equilibria.

Introduction

Polymer–surfactant complexes appear to be of enduring interest to macromolecular and colloid chemists.[1-5] These systems display self-organization that may in some ways serve as a paradigm for the behavior of biological assemblies. Furthermore, they are conducive to a remarkable range of experimental techniques, such as neutron scattering,[6] fluorescence,[7] dye solubilization,[8] surface tension,[9] potentiometric methods,[10] and turbidimetry.[11]

Literature reports in this area deal preponderantly with either (a) complexes of neutral polymers with ionic surfactant micelles or (b) complexes of polyelectrolytes with oppositely charged surfactants usually below the CMC. (For reviews of these two areas, see ref 12 and 13, respectively.) Relatively little work has been done with ionic surfactants above the CMC in the presence of polyelectrolytes. In a sense, the forces involved are too strong: when the two solutes are of like charge, no interaction occurs; when they are of opposite charge, irreversible phase separation takes place. However, if the micelle surface charge density is attenuated through the incorporation of a nonionic surfactant, elucidation of the association becomes possible.[14]

Strong polyelectrolytes form intermacromolecular coulombic complexes with oppositely charged mixed micelles.[14-18] Under certain conditions, these complexes are formed reversibly, making it possible to study them by solution techniques. Phenomenologically, the most striking features of these systems are that (a) the formation of complexes is relatively insensitive to polymer concentration, total surfactant concentration, or polymer molecular weight; (b) complex formation occurs abruptly when the mole fraction of ionic surfactant in the mixed micelle (Y) attains some critical value (Y_c); and (c) the critical mole fraction (Y_c) varies as the square root of the ionic strength. These relationships are observed consistently for a variety of anionic/nonionic mixed micelles[14,17,19] in the presence of several different polycations[17] and also for cationic/nonionic mixed micelles in the presence of the strong polyanion, sodium polystyrene sulfonate.[20] Taken together, such findings suggest that micelle–polyion complexation is a critical phenomenon, governed solely by coulombic interaction between mixed micelles and polyions, so that the attractive interactions vary directly with the micelle surface charge density (and hence with Y) and with the thickness of the ion atmosphere (electrical double layer) around the micelle (and hence with the inverse square root of the ionic strength). Quasi-elastic light scattering measurements carried out on one particular system, poly(dimethyldiallylammonium chloride) (PDMDAAC) with the nonionic/anionic surfactants Triton X-100/sodium dodecyl sulfate (SDS), indicate that the primary step in complex formation is intramolecular with respect to polymer.[15]

While we have investigated a range of surfactants and macromolecules, one particular combination—the PDMDAAC/Triton X-100/SDS system mentioned above—has received special attention, because it alone exhibits a broad range of conditions under which one may observe stable (soluble) molecular aggregates, with Stokes radii in the range 200–400 Å.[15,18] At constant ionic strength, I, both the macroscopic turbidity, τ, and the mean apparent Stokes radius, $\bar{R}_{s,\mathrm{app}}$, display maxima as Y increases from the value at which complexation is first observed (Y_c) to the value at which macroscopic phase separation occurs (Y_p). In contrast, other polyion–micelle mixtures (such as PDMDAAC–$C_{12}E_6$/SDS) show an abrupt transition from a homogeneous (noninteracting) system to a macroscopic two-phase system upon an extremely small relative increase in Y, e.g., less than 1% or 2%.

Within the range Y_c–Y_p, complexes formed between PDMDAAC and Triton X-100/SDS mixed micelles exist in equilibrium with the various macromolecular solutes. In evidence of this equilibrium are the observations that turbidity values change reversibly with Y (in both directions), are stable for several days, and are independent of the way in which the solution is prepared.[14] Earlier QELS measurements indicated a very broad distribution of decay constants, suggesting to us a bimodal size distribution,

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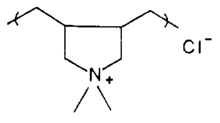
0024-9297/88/2221-2555$01.50/0

presumably corresponding to free micelles in equilibrium with complexes.[15]

In this report we present further results from QELS and from turbidimetric titrations, directed toward elucidation of the polyion–micelle binding equilibria. We have also attempted to use ultrafiltration to separate unbound micelles from complexes. A consistent qualitative model is developed which accounts for the various results.

Experimental Section

Materials. Two samples of PDMDAAC (1) were gifts of Calgon Corp. (Pittsburgh): "Merquat 100" (nominal molecular weight of 2×10^5) and "Cat-Floc" (nominal molecular weight of 1×10^6). Molecular weight values obtained by size exclusion chromatography coupled with low angle light scattering were $\bar{M}_w = 5 \times 10^5$ for the first and $\bar{M}_w = 1 \times 10^6$ for the second.[21] The result for Merquat 100 (hereinafter "PDMDAAC I") is in fair agreement with our own static light scattering measurements in 1.0 M NaCl, giving $\bar{M}_w = 2.8 \times 10^5$. Sodium dodecyl sulfate (SDS) was "Purissima" grade (Fluka). Triton X-100, (*p*-polyethoxylated isooctylphenol, average degree of ethoxylation 9.5) was a gift from Rohm and Haas Co.



(1)

Methods. 1. QELS. A Jodon 20-mW He–Ne laser was focused onto the cylindrical specimen cell maintained at 25.0 °C in a toluene refractive index matching bath. The goniometer and photomultiplier assembly were components of a Malvern RR102 spectrometer. The output of the pulse amplifier discriminator was collected and analyzed with a Nicomp TC-200 computing autocorrelator. All measurements were made at 90° scattering angle with a PMT frontal aperture setting of 0.5 mm. Photon counts were acquired until computed distributions were stable, usually corresponding to a "fit error" of less than 4 and "residual" of less than 10,[22] normally requiring the collection of 30 000 counts above base line.

The intensity autocorrelation function approximates the infinite time average of the product of the intensity at time t and the intensity at some instant later, $t + \tau$:

$$G^{(2)}(\tau) = \langle I(t)\cdot I(t+\tau)\rangle = A + [1 + \beta|g^{(1)}(\tau)|^2] \qquad (1)$$

where A is the base line and β an equipment-related constant.[23] For a monodisperse spherical particle, the first-order normalized electric field autocorrelation function is a decaying exponential whose rate of decay depends on the diffusion coefficient of the particle:

$$g^{(1)}(\tau) = \exp(-\Gamma\tau) \qquad (2)$$

For a distribution of particles, the above function is integrated over all possible Γ's, with each exponential weighted by the distribution function $F(\Gamma)$:

$$g^{(1)}(\tau) = \int_0^\infty F(\Gamma)\exp(-\Gamma\tau)\,d\Gamma = \sum_i a_i \exp(-\Gamma_i\tau) \qquad (3)$$

There are several techniques employed to solve for the distribution,[24,25] some of which accomplish this inversion through minimization of a least-squares fit. We have used the method of cumulants,[26] nonnegative-constrained least squares (NNLS),[27] and a technique similar to that of Provencher's constrained regularization.[28,29]

2. Turbidimetry. Absorbance measurements were made with a Brinkman PC600 fiber optics probe colorimeter, equipped with a 420-nm filter and a 2-cm path length probe tip. Results were reported as 100 − %T, which is linearly proportional to the true turbidity for %T > 80.

3. Ultrafiltration. Ultrafiltration (UF) experiments were performed by using a 10-mL stirred cell (UHP-25, Micro Filtration Systems, Dublin, CA) operated under 30 psi nitrogen pressure, with a stirrer speed of 300 rpm. The cell was equipped with either a "hydrophilic Type F", nominal molecular weight cut-off (MWCO) 500 000 membrane; or a Type C, 300 000 MWCO membrane (both from Spectrum Medical Industries, Los Angeles). The degree of retention was expressed by the rejection coefficient

$$R = \frac{\ln (C_f/C_0)}{\ln (V_0/V_f)} \qquad (4)$$

where C_f is the solute concentration in the retentate, C_0 the initial solute concentration, V_f the final retentate volume, and V_0 the initial sample volume.

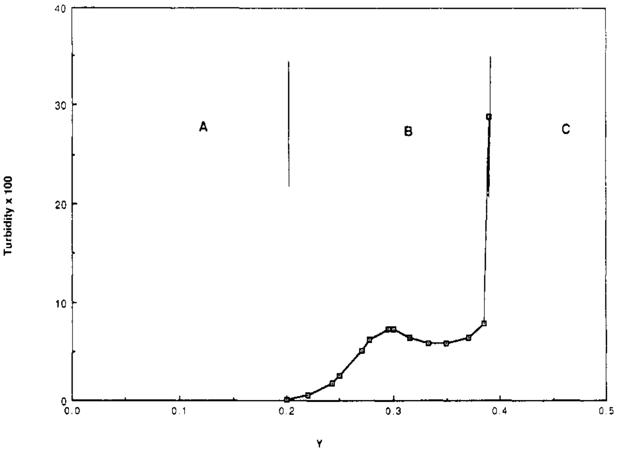


Figure 1. Turbidimetric type I titration of PDMDAAC (1 g L^{-1}) and 31 mM Triton X-100, with 62 mM SDS, in 0.4 M NaCl. Values are corrected for turbidity measured in the absence of polymer. A, B, and C correspond to noninteracting, soluble aggregate formation, and phase separation regimes, respectively.

4. Procedures. Complexes can be generated in several ways. In one procedure, aqueous solutions of PDMDAAC (typically 0.15–2.0 g L^{-1}) containing Triton X-100 (20–70 mM) are "titrated" with SDS (50–100 mM) at constant NaCl concentration, by addition of SDS from a microburet with constant stirring. This mode of addition, referred to as a "type I" titration, corresponds to a continuous increase in the value of Y. In a second method (type II), mixed micelles at constant Y constitute the titrant. Type I titrations reveal the dependence of complex formation on the surface charge density of the mixed micelle, while type II experiments provide information regarding the stoichiometry of complex formation. Lastly, micellar solutions may be titrated with polymer; such "type III" titrations are also conducted at constant ionic strength and Y.

In UF/QELS experiments, a 10.0-mL aliquot of a solution containing 0.55 g L^{-1} of PDMDAAC II and 38 mM Triton X-100, with SDS concentration ranging from 11.4 to 22.3 mM ($0.23 < Y < 0.37$), always in 0.4 M NaCl, was placed in the stirred UF cell. Nitrogen pressure was applied, and 3.0 mL of ultrafiltrate was collected directly into the light scattering cell, at a typical flow rate of 0.1 mL min^{-1}. QELS was carried out on the ultrafiltrate, retentate, and sample prior to ultrafiltration. Similar experiments were performed on polymer-free solutions. After QELS measurements, each solution was diluted 50 to 1 by weight, and UV spectra were obtained with a Hewlett-Packard 8450 A diode array spectrophotometer, in order to quantitate the concentration of Triton X-100.

Results and Discussion

The type I turbidimetric titration presented in Figure 1 reveals three regimes. Below Y_c, turbidity, viscosity, and QELS measurements both show no interaction between polymer and surfactant.[12,13] At Y_p, reversible precipitation takes place. Between Y_c and Y_p, a maximum is commonly observed in both the turbidity and the mean apparent diameter from QELS. Preliminary electrophoretic measurements suggest that charge reversal may accompany such maxima. In this work, we focus on the regime between Y_c and Y_p, which corresponds to complexes in

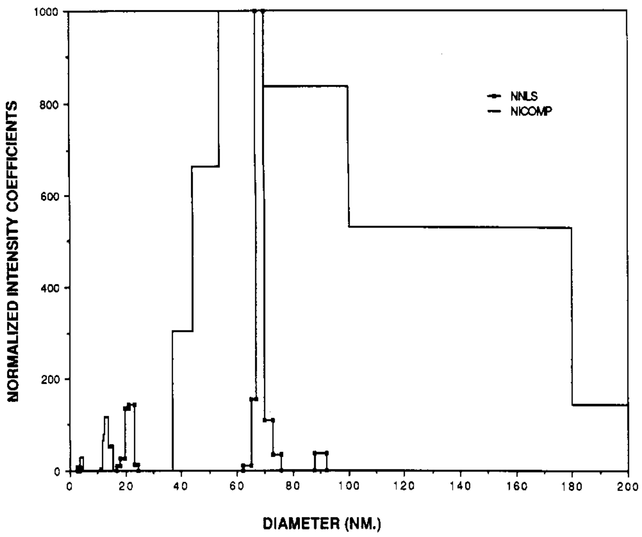


Figure 2. Comparison of apparent distribution of Stokes diameters, using NNLS and Nicomp programs, for PDMDAAC I (1.5 g L^{-1}) Triton X-100 (20 mM)/SDS at $Y = 0.22$ and $I = 0.20$ M.

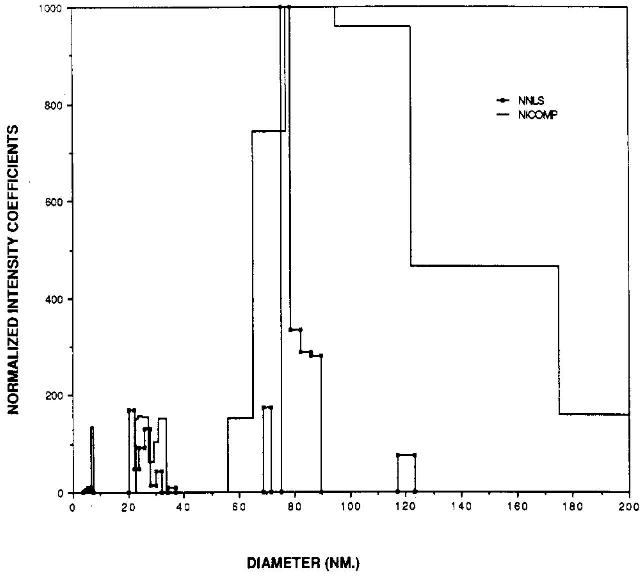


Figure 3. Comparison of apparent distribution of Stokes diameters, using NNLS and Nicomp programs, for PDMDAAC I (1.5 g L^{-1}) Triton X-100 (20 mM)/SDS, at $Y = 0.24$ and $I = 0.20$ M.

equilibrium with their components.

Quasi-Elastic Light Scattering. From cumulant analysis of the autocorrelation function, we obtained the particle size variance for PDMDAAC + mixed micelles in 0.2 M NaCl. At $Y < Y_c$ (0.18), the variance is approximately 0.2; above $Y = 0.18$, the variance increases dramatically to 0.5–0.6. This value is too large to correspond to any realistic monomodal distribution.

In Figures 2–4 are shown histograms obtained from the Nicomp "canned software", a modification[28] of the constrained regularization technique of Provencher et al.[29] All of these histograms, measured for PDMDAAC I/Triton X-100/SDS in 0.4 M NaCl at $Y > Y_c$ (0.23), display pronounced bimodal distributions. The smaller of the two modes, presumably unbound micelles, falls with the range of dimensions obtained by the cumulants method for the polymer-free mixed micelles: 12–30 nm mean apparent diameter at $I = 0.4$, $0.2 < Y < 0.3$.[13] In contrast, the median diameter of the complex ranges from 60 to 80 nm. The extreme breadth of this mode is believed to be a consequence of the limited set of Γ values allowed by the program over the range of Stokes diameters covered here, and not a representation of the true distribution.

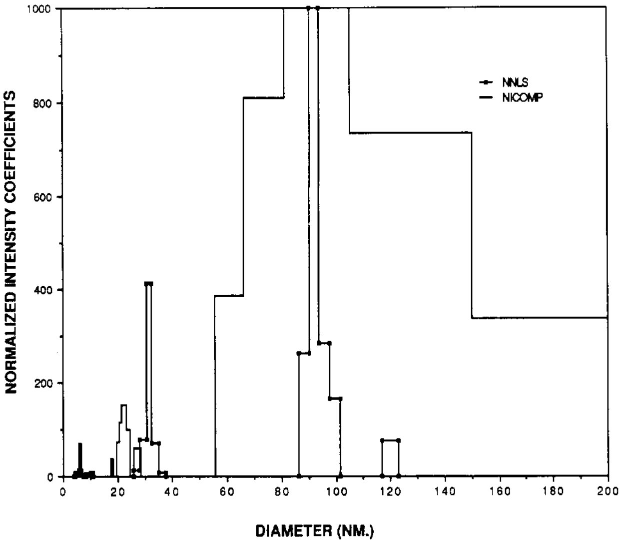


Figure 4. Comparison of apparent distribution of Stokes diameters, using NNLS and Nicomp programs, for PDMDAAC I (1.5 g L^{-1}) Triton X-100 (20 mM)/SDS, at $Y = 0.26$ and $I = 0.20$ M.

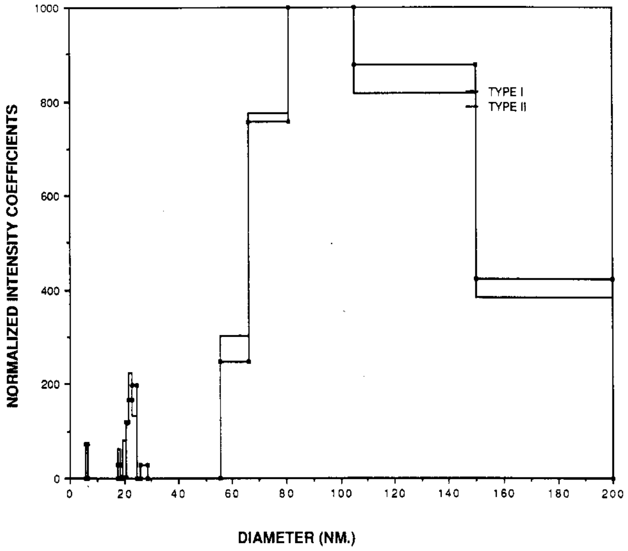


Figure 5. Apparent distributions of Stokes diameters for PDMDAAC I (1.5 g L^{-1})/Triton X-100 (20 mM)/SDS, at $Y = 0.30$, $I = 0.40$ M, prepared by either type I or type II titration.

Since the algorithm employed in the Nicomp software is not documented, we have also employed the published NNLS method,[27] with the results shown in Figures 2–4. The values for the "free micelle" mode are 30–50% larger than with the Nicomp program. However, both routines yield reproducible and well-separated bimodal size distributions, and the median values for the apparent diameter of the aggregate mode (70, 80, and 90 nm for $Y = 0.22$, 0.24, and 0.26, respectively) are very close for the two procedures.

It is possible to prepare complex-containing solutions either by addition of SDS to polymer/nonionic micelle solutions (type I titration) or by addition of micelles at constant Y (type II titration). Figure 5 shows QELS results for two solutions, identical with respect to all solute concentrations but differing, as noted above, with regard to sequence of addition. The identity of the apparent size distributions is further evidence for the equilibrium nature of polymer–micelle association.

The identification of two modes, representing free micelle and complex, respectively, suggests the possibility of

Table I
Assignment of Summed Normalized Intensity-Weighted Coefficients from QELS for Ultrafiltration Samples

	initial solution		final retentate	
Y	aggregate mode	unbound micelle mode	aggregate mode	unbound micelle mode
0.23 (Y_c)	0.07	0.93	0.46	0.54
0.25	0.54	0.46	0.69	0.31
0.27	0.69	0.31	0.69	0.31
0.31	0.68	0.32	0.69	0.31
0.37	0.69	0.31	0.68	0.32

determining equilibrium binding parameters if these two species can be quantitated. For example, one could determine the concentration of free micelles as a function of total surfactant concentration in a type II titration. It should be possible to correct the intensity weighted distributions such as those in Figures 2–5 to yield mass-weighted distributions. Mass ratios determined in this way for mixtures of latexes are found to be reasonably accurate with respect to true concentrations. However, the dependence of polarizability on diameters may be more complicated for species differing in solvation as much as those studied here.

Ultrafiltration. Complexes formed between PDMDAAC I and mixed micelles are completely retained by ultrafiltration membranes with mean pore diameters of 28 nm (e.g., 300 000 molecular weight cut-off), as indicated by QELS measurements of the ultrafiltration. Mixed micelles, however, are also partly retained by this membrane. The rejection coefficient, R, was 0.65 for mixed micelles in polymer-free solution. Use of the nominal 500 000 MWCO membrane (mean pore diameter 45 nm) reduced R to $\leq$0.05 for micelles but allowed some permeation of complex. Consequently, PDMDAAC II, molecular weight ca. 1×10^6, was employed at a concentration $C_p = 0.55$ g L^{-1}. Complexes formed from this polymer in 0.4 M NaCl exhibit an apparent mean diameter from QELS of 250 nm and are completely retained by the 500 000 MWCO membrane. As noted above, Y_c and Y_p are insensitive to polymer molecular weight; in this ionic strength, $Y_c = 0.23$ and $Y_p = 0.40$ (see Figure 1).

QELS analyses of ultrafiltrate solutions exhibited a single mode with mean apparent diameter of 26 ± 2 nm, attributable to mixed micelle. Histograms for the initial solution and for the retentate also showed this same band, along with one centered around an apparent diameter of 200–300 nm, corresponding to the complex. The equivalent hydrodynamic diameter of PDMDAAC II in 0.4 M NaCl, calculated from the value of $[\eta]M = 2 \times 10^6$ dL mol^{-1} is about 70 nm. The QELS results thus suggest either that the polyion is considerably extended in the complex or (less likely, in our opinion) that the complex contains several polymer molecules.

The histograms reported above are based on the coefficients a_i in eq 3, each of which is proportional to the intensity of scattered light attributed to species with decay constant Γ_i. The sum of coefficients within the range of decay constants corresponding to free micelles, divided by the sum of all coefficients, should thus be proportional to the fraction of detected light arising from scattering by unbound micelles. While we hesitate to attempt a formal quantitation of these two species in this manner, we suggest that the fraction of histogram coefficients falling in the small-diameter mode is proportional to the fraction of micelles not bound to polyion.

Results for this QELS analysis for retentate and initial solutions are shown in Table I, for varying values of Y. We note that the shape of apparent size distribution is invariant with Y above $Y = 0.27$. From $Y = 0.23$ to 0.27, both the absolute and relative scattering due to complex increases with Y. Also, ultrafiltration modifies the distribution only for $Y \leq 0.25$.

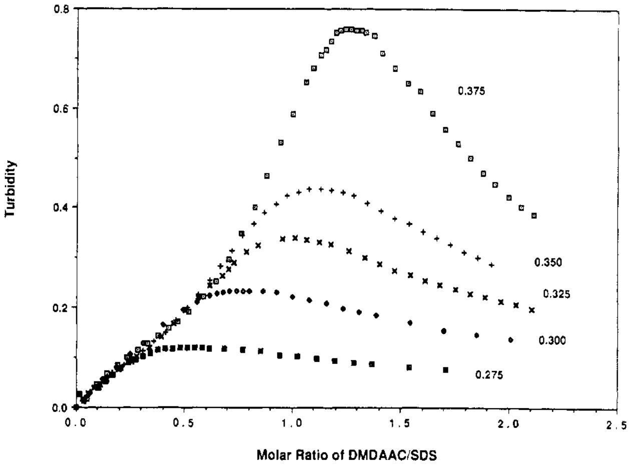


Figure 6. Turbidimetric (type III) titrations of Triton X-100/SDS (total surfactant concentration 70 g L^{-1}) in 0.40 M NaCl with PDMDAAC I (titrant concentration 10 g L^{-1}) at Y values shown.

These observations can be explained on the basis of the compositional heterogeneity of the mixed micelles. Anionic–nonionic mixed micelles are strongly nonideal,[30] and the composition of the mixed micelle is expected to differ substantially from that of the monomeric surfactant. Such nonideal behavior is a reflection of steric and coulombic interactions among the surfactant head groups. In the present case, bulky Triton X-100 head groups generate significant steric repulsion, while the repulsive interactions among SDS head groups is a complex function of ionic strength and Y.[31] One consequence of highly nonideal mixing may be micellar compositional polydispersity. This phenomenon has been specifically addressed for mixtures of C_mEO_n nonionic polyethers and SDS by Ogino and co-workers[32] who have shown that extensive polydispersity—possibly approaching bimodality—occurs when m is small and n is large.[33]

The implications of micelle compositional heterogeneity vis-à-vis our findings will now be considered. Let us assume that there is a critical micellar surface charge density, σ_c, required for complex formation. Below Y_c, no micelles have $\sigma \geq \sigma_c$; above a certain value of Y (Y^*), all micelles have $\sigma > \sigma_c$. The initial increase in turbidity just above Y_c, in Figure 1, thus corresponds to an increase in the concentration of micelles with $\sigma > \sigma_c$. We suggest that $Y^* \cong 0.27$ in the current system. Below $Y = 0.27$, then, micelles with $\sigma < \sigma_c$ do not participate in the binding equilibrium and are preferentially ultrafiltered. Their removal leads to a large decrease in the fraction of the scattered light due to unbound micelles at $Y = 0.23$ (from 93% to 54%). At $Y = 0.25$, fewer micelles have $\sigma < \sigma_c$, so their removal reduces the fraction of scattered light due to unbound micelles just from 46% to 31%. At yet larger values of Y, all micelles participate in the binding equilibrium. Removal of these "active" micelles perturbs the equilibrium which is subsequently restored by dissociation of the complex.

Turbidimetric Type III Titrations. Concentrated mixed micelle solutions (70 g L^{-1}) were titrated with polymer, in 0.40 M NaCl, at values of Y ranging from 0.275 to 0.375. Results are shown in Figure 6, where the concentration of added polymer is expressed as the molar ratio of polymer repeating units to SDS, i.e., N/S. At low concentration of added polymer, the data conform to a single line and then systematically diverge. For all values of Y, a maximum in turbidity is observed upon progressive addition of polymer. These maxima are displaced toward higher polymer concentration with increasing Y.

The initial linear portion occurs under conditions of excess micelles, so that added polymer is stoichiometrically converted to complex. One might at first expect that the affinity of micelles for polyion should depend on Y; consequently, the turbidity should increase with Y. In order to explain why this is not observed at low polymer concentration, we refer again to two hypotheses put forward in the explanation of ultrafiltration results. First, a critical micellar surface charge density, σ_c, is required for polyion binding. (Results to be published elsewhere indicate that complex formation occurs at a critical micelle surface potential of about -20 mV.[19]) The corresponding micellar composition is y_c; i.e., all micelles with $y > y_c$ participate in binding equilibria. Second, we suggest that the micelles are compositionally polydisperse. Thus, the number of "active" micelles, with $y > y_c$, increases continuously with Y (the bulk composition), as well as with the total surfactant concentration. The stoichiometry of this system therefore depends on the ratio of the concentration of polymers to *active* micelles. The initial concentration of active micelles is thus lowest for $Y = 0.275$, and the departure from linearity of the turbidity curve in this case occurs when all these micelles have been bound by polymer so that further polymer addition has little effect. As Y increases, so does the concentration of active micelles. Consequently, so does the concentration of polymer required to reduce the free active micelle concentration to the point where conversion of polymer to complex is no longer complete.

Marked increases in turbidity are observed for $Y \geq 0.325$ at polymer concentrations above those corresponding to ca. 85% T. These large turbidities correspond to coacervation, the formation of a second liquid phase. It seems likely that coacervation may occur only when many complexes are electrically neutral, and this condition requires some sort of stoichiometry. When this stoichiometry is exceeded by the addition of excess polymer, the active micelles presumably are redistributed among the available polyions. Complexes then would acquire a net positive charge, coacervates could disperse, and the turbidity would diminish, as is observed.

Conclusions

The results obtained are consistent with a model for which the central feature is a critical micelle surface charge density for polyion binding. This charge density, σ_c, corresponds to a microscopic micellar composition, y_c, which is the fraction of surfactant molecules in a micelle that must bear a charge in order for complex formation to occur, and is expected to vary inversely with the ionic strength. We postulate that, in mixtures of SDS and Triton X-100, micelles are compositionally disperse. The stoichiometric or measured mole fraction, Y, is then an average value. The onset of turbidity at Y_c corresponds to the presence of some small concentration of micelles with $y > y_c$, this concentration of "active" micelles increasing rapidly with Y.

In the absence of bulk-phase separation, polyelectrolyte and active micelles appear to be in equilibrium with a molecular polyion–micelle complex. We are at present attempting to characterize this complex by static light scattering, fluorescence, and size exclusion chromatography.

Acknowledgment. Support from the National Science Foundation (Grant DMR-8507479) and from the Petroleum Research Fund. (Grant 17656-B7-C) is gratefully acknowledged, as is assistance from S. C. Johnson & Son, Inc.

Registry No. PDMDAAC, 26062-79-3; SDS, 151-21-3; Triton X-100, 9002-93-1.

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