

Measurement of Equilibrium Binding of Cationic Micelles to a Polyanion by Membrane Filtration

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The binding of DMDAO micelles to sodium poly(styrenesulfonate) (NaPSS) was studied by turbidimetric titration, membrane filtration, and electrophoretic light scattering. While the first technique indicates the sudden onset of complexation at a well-defined pH_{crit} , micelle binding isotherms obtained by membrane filtration in the vicinity of pH_{crit} reveal binding prior to pH_{crit} . At lower pH, the binding constant increases by an order-of-magnitude with a 20% increase in micelle charge density; the change is abrupt, but not discontinuous. Polyelectrolyte-micelle binding thus appears to follow mass action equilibrium, but with high sensitivity to electrostatic variables.

Introduction

Complex formation between polyelectrolytes and oppositely charged surfactants has been the subject of ongoing research effort.^{1–14} An important aspect of this problem is the determination of the binding isotherm.^{6,7} The binding isotherm, generally expressed as the relationship between the moles of bound surfactant per mole polymer residue and the free surfactant concentration, contains information on both the nature of the binding process and the structure of the complex. However, in the case of polyelectrolyte–surfactant complexes, the interpretation of such data requires assumptions about the nature of the bound species. For the most part, binding studies have been carried out with the assumption that binding ligand is exclusively monomeric surfactant. Under such conditions, specific surfactant ion electrodes have been used extensively. For example, Hayakawa and Kwak⁶ reported isotherms for the binding of dodecyltrimethylammonium ions (DTA) by sodium dextran sulfate (DxS) and sodium poly(styrenesulfonate) (NaPSS) and reported that the binding constant (K) decreased strongly with increasing ionic strength and was larger for NaPSS than

that for DxS. The difference in K was attributed to the role of hydrophobic interactions in the NaPSS-DTA system. Recently, Liu et al.⁷ investigated the binding of sodium poly(2-acrylamide-2-methylpropane sulfonate) and mixed cationic surfactants of dodecylpyridinium chloride and tetradecylpyridinium chloride, also using a surfactant selective electrode. The binding isotherms for this system were interpreted in terms of synergistic effects.

While the preceding studies focused on surfactant systems below the critical micelle concentration (cmc), surfactant concentrations are well above the cmc in most systems of technological or biological interest. In addition, the binding of micelles to polyelectrolyte can be used to experimentally test⁹ theoretical treatments of polyelectrolyte–colloid interactions. The binding of polyelectrolytes to micelles is different from their binding to monomeric surfactants as demonstrated, for example, by an abrupt change in the turbidimetric response to the addition of surfactant depending on whether the added surfactant solution is barely above or just below the cmc.¹⁰ In part because the binding of micelles to polymers cannot be followed by surfactant electrodes which are not functional above the cmc, there are few reports of micelle–polymer binding isotherms. Xia et al.⁸ used equilibrium dialysis to obtain binding isotherms for poly(dimethyl-diallylammonium chloride) (MW ca. 2×10^5) with mixed micelles of sodium dodecyl sulfate (SDS) and Triton X-100 (TX100) and found approximately 20 micelles bound per polymer chain at $I = 0.1$; since 30 days of dialysis were required to ensure dialysis equilibrium, that experimental approach is inconvenient. Nevertheless, the measurement of such isotherms and corollary information about stoichiometry, binding constants and cooperativity provide important insights into these systems.

For an extensive number of oppositely charged polyelectrolyte/micelle systems,^{8–14} we have observed that complex formation resembles a phase transition phenomenon, as predicted by theoretical treatments for the interaction of polyelectrolytes with oppositely charged colloidal surfaces^{15–18} This means, for example, that at some fixed ionic strength, micelles bind to polyelectrolytes

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only when their surface charge densities exceed some critical value σ_c (regardless of the total concentration of either macroion). However, these observations were mainly based on changes of turbidity or the apparent hydrodynamic radius of the complex as a function of micelle surface charge density σ . Observed increases in scattering intensity or particle size with σ cannot easily be correlated with shifts in the complex formation equilibrium (i.e., increase in the equilibrium constant) since the complex itself can assume different association states with different dimensions. Measurements of fluorescence quenching when pyrene-tagged polyanions complex with quencher-containing cationic micelles¹⁹ suggest that the increase in binding at σ_c is in fact not abrupt, but extraction of binding constants from such data is highly model-dependent. The theoretical treatments which indicate that binding resembles a phase transition phenomenon apply to flat surfaces, i.e., to colloidal particles above 1 μm . On the other hand, binding of polyions to small particles (counterions or ligands) is a mass action equilibrium phenomenon. Since small micelles occupy a position intermediate between large counterions and colloids, it is natural to question whether binding of micelles to polyions resembles more closely a phase transition or a mass action equilibrium. It is therefore of interest to establish the abruptness of the increase in binding by directly measuring the binding constant in the region of micelle surface charge density corresponding to the onset of optically detected complex formation.

In the present study, we investigate the binding of dimethyldodecylamine oxide (DMDAO) micelles to sodium poly(styrenesulfonate) (NaPSS) at different micelle surface charge densities. DMDAO is a nonionic-cationic surfactant, whose micelle composition can be modulated by changing its degrees of protonation through pH adjustment.^{20,21} Thus, our system is comprised of polyanion and nonionic/cationic mixed micelles. To avoid the excessive equilibrium times of dialysis, we use membrane filtration to obtain the binding isotherms at different degrees of protonation of DMDAO and different ionic strengths. These results, in conjunction with potentiometric titration and electrophoretic light scattering, are used to examine the nature of the binding and the structure of the complex for the DMDAO/NaPSS system.

Experimental Section

Materials. *N,N*-Dimethyldodecylamine oxide (DMDAO) was from Sigma (St. Louis, MO), purity > 97%. Sodium polystyrenesulfonate (NaPSS, $M_w = 2.5 \times 10^5$) was synthesized by radical polymerization of styrene sulfonate and purified as previously described.²² Standard NaOH and HCl solutions and NaCl were from Fisher Scientific (Pittsburgh, PA). Mill-Q water was used throughout the work.

Potentiometric Titration. The relationship between pH and the degree of protonation β of DMDAO micelles was obtained by pH titration of 50mM DMDAO using a Beckman $\phi 34$ pH meter equipped with a Beckman combination electrode, at $25 \pm 1^\circ\text{C}$, under N_2 and magnetic stirring, using procedures described elsewhere.²¹

Turbidimetric Titration. Turbidimetric titrations were carried out at $25 \pm 1^\circ\text{C}$ by adding 0.100–0.500M HCl to mixed solutions of 0.1 g/L NaPSS and 5–100 mM DMDAO at fixed ionic strengths, monitoring pH and turbidity simultaneously. Turbidity measurements, reported as $100 - T\%$, were carried

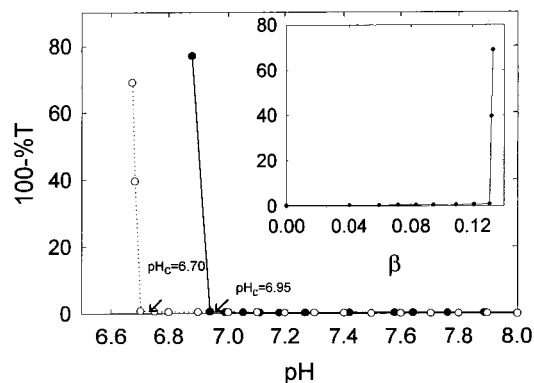


Figure 1. Turbidimetric titration of 0.1 g/L NaPSS and 50mM DMDAO at $I = 0.1$ (●) and 0.2 (○). Inset: $100 - T\%$ vs β for 0.1 g/L NaPSS and 50mM DMDAO at $I = 0.2$.

out at 420 nm using a Brinkmann PC 800 Probe Colorimeter equipped with a 1 cm path length fiber optics probe. The measured turbidity values were corrected by subtracting the turbidity of a polymer-free blank. The pH and turbidity values were recorded after the values became stable for about 2 min.

Centrifugal Filtration. The Centrifugal Filter Device (CFD) from Millipore Co. (Bedford, MA) is composed of two parts: an inner reservoir and an outer tube, separated by a high-flux polysulfone membrane. Various concentrations of DMDAO were mixed with 0.2 g/L NaPSS of the same volume and same ionic strength as the DMDAO. After adjusting the pH, the mixture was stirred for 2 h, then centrifuged in the CFD, using a 100000 nominal molecular weight limit (NMWL) CFD membrane; or a 300000 NMWL membrane for DMDAO at 50mM or more or at high ionic strength where micelle size is large. To avoid perturbation of complexation equilibria, the centrifugal speed and time were typically about 1 min at 1500 rpm so that only one-third of the solution was collected in the outer tube.

After centrifugation, 1 mL of the outer solution was diluted 10-fold with salt solution, stirred for 1 h, adjusted to pH 8 (protonation degree $\beta \approx 0$) with 0.500M NaOH and then titrated to pH 4 ($\beta \approx 0.8$) with 0.200M HCl under N_2 . The HCl volume consumed was recorded as V_{sample} . Polymer-free DMDAO solutions were similarly prepared and titrated. The HCl volume consumed was found to be linear with initial DMDAO concentration. On this basis, calibration curve, and V_{sample} , the DMDAO concentration in the outer tube was determined and assumed to be equal to the concentration of free DMDAO in the inner reservoir. The concentration of bound DMDAO in the inner reservoir could then be obtained.

Electrophoretic Light Scattering (ELS). ELS was carried out at $25 \pm 0.1^\circ\text{C}$ using a DELSA 440SX apparatus (Coulter). The electric field was applied at a constant current of 8–14 mA to a 1 mL sample in an electrophoretic cell that has a rectangular cross section connecting the hemispherical cavities in each electrode. The measured electrophoretic mobility, U , was the average value at the upper stationary layer for the four scattering angles (8.6, 17.1, 25.6, and 34.2°).²³

Results and Discussion

Turbidimetric titrations were carried out to establish appropriate conditions for the measurement of equilibrium binding. The dependence of turbidity on pH for 50mM DMDAO and 0.1 g/L NaPSS at ionic strengths $I = 0.1$ and 0.2 is shown in Figure 1. The onset of binding appears to occur at pH = 6.95 for $I = 0.1$ and 6.70 for $I = 0.2$. Since pH_c for polyelectrolyte-micelle binding is independent of surfactant concentration,^{10,24} we used pH 6.95 at $I = 0.1$ and pH 6.70–7.50 at $I = 0.2$ for further studies.

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(24) We have measured pH_c for the systems of 5–100mM DMDAO and 0.1 g/L NaPSS at ionic strengths of 0.1–0.8. We obtained the same pH_c for 5–100mM DMDAO at fixed ionic strength.

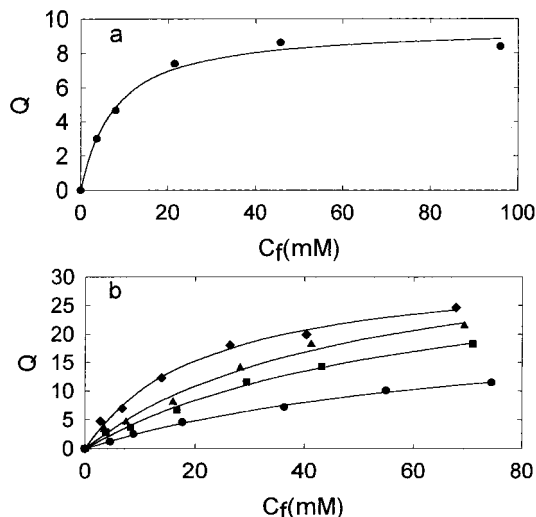


Figure 2. Binding isotherm of DMDAO micelles to NaPSS. (a) pH 6.95, $I = 0.1$; (b) $I = 0.2$, pH 7.50 (●), pH 6.95 (■), pH 6.80 (▲), and pH 6.70 (◆).

Binding isotherms for $I = 0.1$ and 0.2 were obtained over the range of pH's noted above. Figure 2a shows the result for $I = 0.1$ and pH 6.95 ($\beta = 0.08$), as a plot of moles of bound surfactant per mole polymer residue, Q , vs unbound surfactant concentration C_f . The result is fit by Hill's equation²⁵

$$Q = k_1 C_f^z / (1 + k_2 C_f^z) \quad (1)$$

where k_1 is a constant, and k_2 is the binding constant. The empirical exponent z indicates the binding process cooperativity, taking on values < 1 , 1, or > 1 , for anticooperative, noncooperative, or cooperative binding, respectively. The results for Figure 2a are $k_1 = 1.30$, $k_2 = 0.14$, and $z = 1$. From the saturation value, $Q_{\max} = 9$, and assuming a micelle aggregation number of 100,²⁰ we can calculate the maximum number of micelles bound per polymer chain, i.e., the number of binding sites, as $n = 110$. As shown in Figure 2b, an increase in ionic strength to $I = 0.2$ in the pH range 7.50–6.70 leads to a decrease in binding constant, as expected due to increased screening. The increase in n to $160 < n < 320$ with increased ionic strength resembles the result obtained by Xia et al.²⁶ for binding of SDS micelles to high molecular poly-(oxyethylene). This can be explained as a consequence of the shielding of the electrostatic repulsion among bound micelles.

As seen in Figure 3 for $I = 0.2$, the binding constant increases gradually between $\beta = 0.02$ and 0.11, then rapidly above $\beta = 0.11$. As stated above, theoretical treatments for the binding of polyelectrolytes to oppositely charged surfaces predict the onset of binding at a critical surface charge density. In previous studies of polyelectrolyte-micelle systems we interpreted abrupt changes in turbidimetry and light scattering at well-defined micelle surface charge densities in terms of this framework. Figure 3 shows that the binding indeed increases by almost an order of magnitude with a 20% change in β at $\beta \approx \beta_c$. On the other hand, some binding appears to take place even below β_c . This indicates that the binding of micelles to polyelectrolyte may resemble a mass action equilibrium, but one for which the local cooperativity, in which a

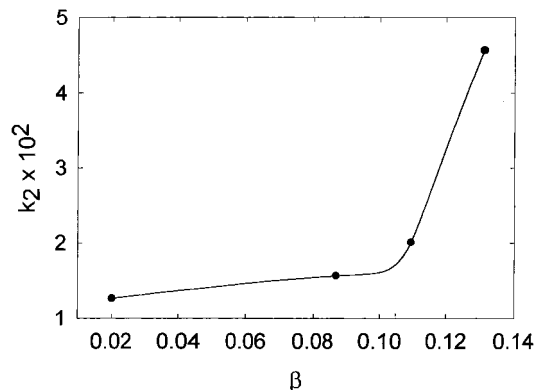


Figure 3. The dependence of micelle binding constant on micelle degree of protonation β , for DMDAO-NaPSS system at $I = 0.2$.

sequence of polymer segments bind as a cooperative unit,¹⁴ leads to quasi-discontinuous behavior of the binding constant.

Some information about complex structure may be deduced from the measured values of n , assuming aggregation numbers on the order of 100 for the bound micelles. At $\beta = 0.13$, $n = 320$, corresponding to a complex molecular weight 7×10^6 . While this value is large, Xia et al.⁸ reported the MW of complexes formed between PDMDAAC and SDS/TX100 mixed micelles to be about 10^7 at $I = 0.4$ and in the limit of low polymer concentration ($c_p = 0.01$ g/L). These high MWs are consistent with cryo-TEM pictures of the PDMDAAC-SDS/TX100 system at $I = 0.4$,²⁷ which reveal that dense micelle-rich regions form within the domains of polymer chains without any particular organization or restructuring of the micelles.

The quasi-transitional behavior observed in Figure 3 is consistent with recent simulations and with experimental findings on other systems. Stoll²⁸ and co-workers carried out simulations for charged spheres interacting with oppositely charged polyelectrolytes and observed an onset of binding when the ionic strength decreased, occurring at a well-defined ionic strength, but not discontinuously. Hashidzume et al.²⁹ measured the fluorescence change when anionic/cationic micelles containing solubilized pyrene bind to a polycationic quencher, poly(4-vinylpyridinium hydrochloride). From time-resolved quenching studies, they obtained the lifetime for micelles bound to polymers (residence time) as a function of micelle charge and ionic strength. At $I = 0.10$, the residence time was found to change from 0.6 to 2.0 μ s upon a 25% increase in micelle surface charge density. The magnitude of this change in residence time with micelle surface charge density is similar to the magnitude of the change in the binding constant seen in Figure 3.

Electrophoretic light scattering (ELS) was used to measure the mobility μ of DMDAO and its complexes with NaPSS. At pH 6.95 ($\beta = 0.08$) and $I = 0.1$ we found $\mu = -8 \times 10^{-3}$ μ m cm/V s. As has been pointed out by Imae,³⁰ the electrophoretic mobility for DMDAO at $\beta = 0$ is negative because of the adsorption of chloride ions on micellar surfaces arising from the interaction of polarized amine oxides with hydrated chloride ions. The ability of chloride ions to depress the micelle surface charge

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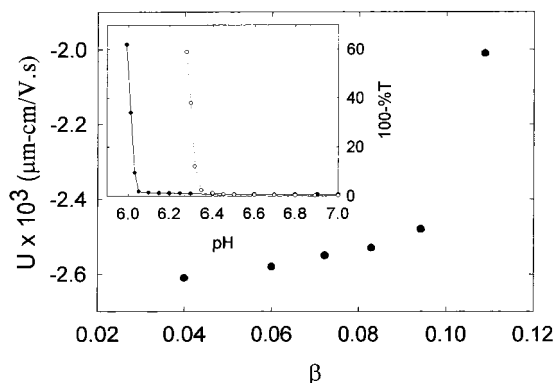


Figure 4. The electrophoretic mobility of DMDAO–NaPSS complexes as a function of micelle degree of protonation at $I = 0.2$. NaPSS concentration: 0.1 g/L. DMDAO: 50 mM. Inset: Turbidimetric titration of 50 mM DMDAO and 0.1 g/L NaPSS at $I = 0.8$ M NaCl (●) and 0.8 M NaNO₃ (○).

density is also reflected in the turbidimetric titrations of DMDAO/NaPSS in 0.8M NaCl vs 0.8M NaNO₃ shown in the insert of Figure 4. At pH = 6.2, for example, micelles bind to NaPSS in NaNO₃ but not in NaCl, because their effective charge is less positive in NaCl (we can also

consider this in terms of the relative ease with which NaPSS displaces NO₃⁻ from the micelle, compared to Cl⁻). With increasing β , the number of protonated headgroups first equals and then surpasses the number of bound chloride ions; thus micelle mobility reaches zero at $\beta = 0.1$, and then becomes positive. Figure 4 shows that electrophoretic mobilities measured for DMDAO–NaPSS at $I = 0.2$ become less negative with increasing β . The measured values of μ are complicated and reflect the combined contributions from free polymers and micelles, as well as complex; however, the last component is the strongest scatterer and so dominates the electrophoretic light scattering signal. Therefore, the increasingly positive mobilities can be attributed to an increase in the number of micelles bound per polymer chain. The rapid change observed in the vicinity of $\beta = 0.1$ is thus consistent with the quasi-transition observed by membrane equilibrium.

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