Structural Elucidation of Soluble Polyelectrolyte–Micelle Complexes: Intra- vs Interpolymer Association

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ABSTRACT: Soluble complexes formed between the strong polycation poly(dimethylallyl ammonium chloride) and mixed micelles of sodium dodecyl sulfate/Triton X-100, in 0.40 M NaCl and at low polymer concentration and excess surfactant concentration, were investigated by a variety of techniques. The results of turbidimetry, static light scattering, dynamic light scattering, dialysis equilibrium, viscometry, and electrophoretic light scattering are discussed in terms of possible structures for the complex in the limit of low polymer concentrations (Cp), and its tendency to associate upon an increase in Cp. The findings from these various studies are consistent with the formation of an intrapolymer complex at low Cp. In this species, the binding of numerous mixed micelles leads to charge reversal and to the formation of a highly extended chain, wherein the dominant influence on polymer dimensions is intermicellar repulsion.

Introduction

Polyelectrolytes form complexes with oppositely charged mixed micelles. 1-11 Whether or not association takes place depends on the polyelectrolyte surface charge density ρ, the polymer linear charge density χ, and the Debye–Hückel ion-atmosphere thickness ε. 1,7,11 The corresponding experimental variables are the fraction of surfactant head groups in the micelle which are charged (Y), the structural polymer charge density 1/b (where b is the distance between charges on the polymer chain), and the ionic strength I. Y is controlled experimentally by adjusting the bulk stoichiometry of the surfactant mixture. For a given polyelectrolyte in some particular ionic strength medium, i.e. at constant b and I, a critical surfactant mole fraction Yc corresponding to a critical micelle surface charge density— is observed; for Y < Yc, no association takes place regardless of the concentration of polymer, Cp, or total surfactant, Cs. To the first order, Yc is independent of polymer molecular weight (MW). 5 Beyond this phase transition point, the system may form soluble polyelectrolyte–micelle complexes, liquid coacervate, or amorphous precipitate. 4 The nature of the complex phase, unlike the conditions for incipient complexation, does depend on Cp, Cs, and MW, 4,8 as well as on the other three variables mentioned.

The structure of soluble polyelectrolyte–micelle complexes is of interest for several reasons. Systems in which polyelectrolytes are adsorbed on the surface of oppositely charged colloids are usually biphasic, but a number of polyelectrolyte–micelle complexes constitute reversible, equilibrium aggregates whose properties may be examined by a wide range of techniques. The effects on the configuration of the adsorbed polymer of inter alia colloid surface charge density, colloid curvature, ionic strength, and polymer charge density may therefore be studied in a variety of ways not possible in truly biphasic systems. From another point of view, polyelectrolyte–micelle complexes represent a degree of self-organization that is remarkable in purely abiotic systems: surfactant molecules, organized in micelles, are bound within the domains of a polyelectrolyte chain, which then may or may not form a higher-order aggregate. 9 In some cases, it appears that a particular association state is much preferred, and the way in which a combination of hydrophobic and electrostatic forces leads to the stabilization of one particular structure has obvious relevance to the understanding of natural supramolecular assemblies. A final question arises regarding the influence of the relative sizes of the colloid and the polymer. Polymer–micelle complexes have been described as a “necklace of beads”, 12 a model that obviously breaks down when the micelle size approaches that of the polymer. It is of interest to consider whether there is a structural discontinuity in the region where the ratio of micelle dimensions to polymer dimensions exceeds unity, and whether the overall structure depends on the absolute or the relative sizes of the two macroionic species.

The range of conditions in which soluble complexes are stable is particularly wide in the system composed of the strong polycation poly(dimethylallyl ammonium chloride) (PDMDAAC), the anionic surfactant sodium dodecyl sulfate (SDS), and the nonionic surfactant Triton X-100 (TX100), in aqueous NaCl solution. Under such conditions, we have previously characterized soluble complexes by viscometry, 1 turbidimetry, 1,3,6,7 quasielastic light scattering (QELS), 2,3,10 and static light scattering, 5 mainly at I = 0.40 M. While these investigations have shed some light on the properties of these species, a well-defined picture of the complex structure has not emerged. Previous QELS measurements on the complex in the polymer concentration range 0.2 < Cp < 1 g/L suggest that the mean apparent Stokes radius (Rs<sup>app</sup>) of the complex is on the order of 40–70 nm, while the polymer alone exhibits Rs<sup>app</sup> = 17 ± 2 nm. 10,11 From somewhat preliminary static light scattering 6 we found Rs for the micelle-free polymer of 40 ± 5 nm (in 0.4 M NaCl); for the complex formed with micelles at Y = 0.35, we found Rs ≥ 40 nm, with considerable sensitivity to the concentration range over which the data were gathered. Under these conditions, the weight-average molecular weight of the complex was more than 20 times larger than that of the polymer alone (2 × 10<sup>6</sup>). Thus, the very large ratio of mass to dimensions seemed to suggest that the complex is very compact.

Despite the foregoing findings, the data available do not effectively discriminate among hypothetical structures such as those shown in Figure 1. The structures shown in Figure 1 may be described as intrapolymer (1A and 1B) or interpolymer (1C) complexes. In 1A, neutralization of
the polyanion charges by association with micelles reduces the intersegmental repulsion and there is some collapse of the polymer chain. In 1B, the repulsive forces among micelles is considered to be a dominating effect and the polymer assumes a more extended configuration than in the absence of surfactant.

A central unanswered question is whether intrapolymer complexes, resembling those proposed by Cabane for complexes of poly(ethylene oxide) and SDS micelles,12 exist under any conditions. Such an intrapolymer complex might then undergo further association to form higher-order complexes. On the other hand, complexes might always be multipolymer and rather polydisperse. Considerations of this type are relevant to the general question of how it is that stable intermacromolecular complexes of finite size are formed. The ambiguity in interpreting the previous results arose in part from the variability of the polymer concentration ranges hitherto employed for the different techniques. In the current work, we report further on turbidimetry, QELS, and static light scattering measurements collected over a wider range of conditions, particularly at very low polymer concentrations. The influence of micelle surface charge density on complex structure has also been explored. In addition, electrophoretic light scattering measurements were carried out to investigate the influence of the number of bound micelles and their average charge state on the charge state of the complex. We have also used dialysis equilibrium to gain some insight into the polyelectrolyte-micelle binding phenomenon and more detailed viscometry than in previous measurements. Taken together, these results lead to a clearer picture of the nature of the aggregated state.

Experimental Section

Materials. Poly(dimethyldiallylammonium chloride) (PDMDAAC) (trade name Merquat 100) was from Calgon Corp. (Pittsburgh, PA) and was diazlyzed (12 000–14 000 nominal MW cutoff) and freeze-dried before use. Sodium dodecyl sulfate (SDS) was Puriss grade from Fluka (Happague, NY). Triton X-100 (Pittsburgh, PA) and was dialyzed (12 000–14 000) against the reference solvent for determination of background scattering. A third difficulty is the possibility that the complex might then undergo further association to form higher-order complexes.
between Results and Discussion.

The sealed cells were secured by rubber bands and placed on a glass plate with a tightly fit membrane. Efflux times were measured with reproducibilities of ±0.05 s or better in a Ubbelohde type glass viscometer operated as part of a Shott AVSN automatic viscometer. Efflux times were measured in 0.40 M NaCl for (a) PDMDAAC at varying concentrations, (b) SDS-TX100 at varying concentrations, and (c) PDMDAAC at varying concentrations in SDS-TX100 at 29.2 g/L for Y = 0.24 and 0.27. Severe difficulties were encountered as foam interfered with detection of the meniscus and could only be overcome with considerable care and patience.

Results and Discussion

Figure 2 shows type 1 turbidimetric titrations at 0.40 M NaCl, at polymer concentrations of (A, top) (from top to bottom) 0.10, 0.20, and 0.30 g/L and (B, bottom) (from top to bottom) 0.05, 0.03, and 0.01 g/L. Insert: schematic illustrating three regimes of polyelectrolyte-micelle interaction.

Figure 3. Schematic depiction of hypothetical mixed micelle compositional distributions at different values for the bulk (macroscopic) mole fraction of SDS. 1 provides the micellar stability and micelle composition, while the abscissa corresponds to microscopic (micellar) composition. The shaded areas represent the fraction of micelles that participate in binding to the polymer. Thus, for a bulk SDS mole fraction of Y = 0.21, "active" micelles begin to appear; hence, Y_c = 0.31. Adapted from ref 1. A higher-order complex may be formed.

Figure 3. Schematic depiction of hypothetical mixed micelle compositional distributions at different values for the bulk (macroscopic) mole fraction of SDS. Y_c represents the microscopic critical micelle composition, while the abscissa corresponds to microscopic (micellar) composition. The shaded areas represent the fraction of micelles that participate in binding to the polymer. Thus, for a bulk SDS mole fraction of Y = 0.21, "active" micelles begin to appear; hence, Y_c = 0.31. Adapted from ref 1. A higher-order complex may be formed.
complexes, so the addition of SDS does not lead to an increase in the number or size of scatterers. With progressive addition of SDS, an abrupt increase in turbidity signals bulk phase separation. This observation may be explained on the basis of more efficient and more intimate ion-pairing between the polymer and the micelle at high 

Static and Dynamic Light Scattering. While the results of Figure 2 only permit qualitative hypotheses about complex structure, they serve to guide further light scattering measurements. We suggest that the maxima in the curves at $C_p > 0.5$ g/L correspond to higher-order aggregation; contrariwise, it appears likely that such aggregation is less important in the range $C_p < 0.5$ g/L and that the structure of the complex could be constant with respect to polymer concentration under these conditions. Static light scattering (SLS) and dynamic light scattering of mixtures of PDMDAAC and SDS/TX100 were therefore conducted in 0.40 M NaCl, at low polymer concentrations 0.002 < $C_p$ < 0.01. The total surfactant concentration was maintained near 14 g/L, corresponding to a TX100 concentration of about 25 mM.

Zimm plots for PDMDAAC and SDS/TX100 ($Y = 0.32$), both in 0.40 M NaCl, are presented in Figures 4 and 5, respectively. The increment of refractive index of PDMDAAC was taken as 0.186, as determined by Burkhart. The refractive index of SDS/TX100 was measured as 0.137, using a differential refractometry calibrated with sucrose standards, as described elsewhere. Additional measurements were made for SDS/TX100 at $Y = 0.28$ and 0.35. Light scattering results for PDMDAAC and the mixed micelles are summarized in Table I. The ratio of the radius of gyration to the Stokes radius, $\rho$, is also included, because there is considerable theoretical basis for interpretation of this quantity in terms of polymer chain compactness.

It is of interest to compare the static light scattering results with earlier findings from QELS. The 2-fold difference between $R_g$ and $R_{g_{app}}$ observed for PDMDAAC is expected for polyelectrolytes. This behavior is observed for the complex as well, as shown below. With regard to the micelle, we note that the axial ratio of an ellipsoid with a hydrodynamic radius of 10 nm (as observed) and a minor radius of 5 nm (the value of $R_g$ found for TX100) is about 2.4 so these results are consistent with a moderately elongated micelle. Although the size of the mixed micelles at this ionic strength goes through a shallow maximum with $Y = 0.35$, micelle dimensions are nearly constant with respect to surfactant composition over the range 0.28 < $Y$ < 0.35 of interest here. These compositions were chosen because, as suggested by Figure 2, saturation of the complex occurs at $Y > 0.25$, $Y = 0.28$ is close to the turbidimetric maxima seen for $C_p > 0.5$ g/L, and minima occur in the range 0.32 < $Y$ < 0.35.

SLS and QELS of the complex formed between the mixed micelle and PDMDAAC were carried out under these conditions by the procedures described above. Attempts to measure $dn/dc$ of the complex with a differential refractometer failed because of turbidity.

Table I. Light Scattering Results for PDMDAAC and for SDS/TX100 Mixed Micelles, in 0.40 M NaCl

<table>
<thead>
<tr>
<th></th>
<th>$M_w$</th>
<th>$R_g$</th>
<th>$R_{g_{app}}$</th>
<th>$\rho$</th>
<th>$A_2$, mol mL/g^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMDAAC</td>
<td>$1.5 \times 10^5$</td>
<td>28.7</td>
<td>15</td>
<td>1.9</td>
<td>$1.1 \times 10^{-3}$</td>
</tr>
<tr>
<td>SDS/TX100</td>
<td>$Y = 0.28$</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SDS/TX100</td>
<td>$Y = 0.32$</td>
<td>9.5</td>
<td>2.3</td>
<td>$-2.2 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>SDS/TX100</td>
<td>$Y = 0.36$</td>
<td>22.2</td>
<td>9</td>
<td>2.5</td>
<td>$-3.5 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Figure 4. Zimm plot for PDMDAAC in 0.40 M NaCl.

Figure 5. Zimm plot for SDS/TX100 at $Y = 0.32$, in 0.40 M NaCl.
**Figure 6.** Zimm plot for the complex formed between PDMDAAC and mixed micelles of SDS/TX100 at $Y = 0.28$, in 0.40 M NaCl.

### Table II. Light Scattering Results for Complexes Formed between PDMDAAC and SDS/TX100 Micelles of Varying Composition in 0.40 M NaCl

<table>
<thead>
<tr>
<th>$Y$</th>
<th>$10^6 M_w$</th>
<th>$R_x$ nm</th>
<th>$R_g^{000}$ nm$^2$</th>
<th>$\rho$ (mol mL$^{-1}$/g$^2$)</th>
<th>$10^4 A_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.28</td>
<td>7.3</td>
<td>44.3</td>
<td>20.5</td>
<td>2.2</td>
<td>7.4</td>
</tr>
<tr>
<td>0.32</td>
<td>10.5</td>
<td>51.0</td>
<td>25</td>
<td>2.0</td>
<td>9.3</td>
</tr>
<tr>
<td>0.36</td>
<td>15.1</td>
<td>52.5</td>
<td>25</td>
<td>2.1</td>
<td>5.8</td>
</tr>
</tbody>
</table>

$^a C_p = 0.01$ g/L.

Effects. Since the complex is composed of polymer and micelle, $(dn/dc)_x$ of the complex may be written as:

$$
\frac{dn}{dc}_x = \frac{1}{1 + \beta} \frac{dn}{dc}_p + \frac{\beta}{1 + \beta} \frac{dn}{dc}_m
$$

(1)

where the subscripts $x$, $p$, and $m$ represent complex, polymer and micelle, respectively. $\beta$ represents the mass ratio of bound micelle to polymer. According to the observed large turbidity, $\beta > 1$ is expected. Therefore, we used the value of $(dn/dc)_m$ in eq 2 for $(dn/dc)_x$. The resulting Zimm plot is shown for $Y = 0.28$ in Figure 6. Data of similar quality were obtained at $Y = 0.32$ and 0.36. Parallel QELS measurements were made at $C_p = 0.01$ g/L, under identical conditions of $I$ and $Y$. In order to obtain the size of the complexes, the correlation functions were fitted according to a two-exponential decay, as given by

$$
g(t) = a_1 \exp(-D_1 q^2 t) + a_2 \exp(-D_2 q^2 t)
$$

(2)

where $q$ is the amplitude of the scattering vectors, $D_1$ and $D_2$ are the diffusion coefficients for the free micelle and complex, respectively, and $a_1$ and $a_2$ are constants. From each value of $D$ we obtain the Stokes radius $R_S$ from the Einstein equation

$$
R_s = kT/6\pi \eta D
$$

(3)

where $k$ is the Boltzmann constant, $T$ the absolute temperature, and $\eta$ is the viscosity of the solvent. QELS results are summarized in Table II.

From the data in Tables I and II, we observe that the dimensions of the complex are on the order of 50–70% larger than the polymer’s. On the other hand, the molecular masses are greater than those of either micelle or polymer by factors of 35–100. This result suggests a high degree of compactness for the complex. On the other hand, the quantity $\rho = R_y/R_5$ increases from 1.9 for the polymer alone, to 2.1 ± 0.1 for the complex. From theory, $\rho = 0.778$ for hard spheres and is predicted to be 1.5 for flexible chains in a good solvent and 1.78 for flexible chains in a good solvent. The value of $\rho$ may be expected to be significantly larger for polyelectrolytes, as observed by PDMADAC. For ellipsoids with appreciable axial ratios, such as the (polymer-free) mixed micelles, $\rho > 2$ is easily attained. The fact that $\beta$ values for the complex are intermediate between those of the polymer and the micelle suggests that the complex is more extended than the free polymer.

It is of interest to note that the mass increases by 50% as $Y$ increases from 0.32 to 0.36, while the dimensions are unchanged. This must be explained by an increase in the micelle binding constant, which increases the mean number of bound micelles. As recently pointed out by Stahlberg et al. the binding of a macroion to an oppositely charged surface includes a repulsive osmotic term: the lack of charge symmetry between the two surfaces along with the requirement for electroneutrality means that some counterions must reside between the two surfaces, so there is an osmotic effect that keeps the surfaces apart. In the present case that leads to a rather loose binding between the high linear charge density polycation and the lower charge density mixed micelle. We suggest that charge symmetry is more nearly attained upon an increase in $Y$. This leads to stronger micelle binding, and therefore an increase in the number of bound micelles per polymer chain, and hence an increase in complex $M_w$.

**Electrophoretic Light Scattering.** ELS results for mixed micelles and for complexes with PDMADAC, in 0.40 M NaCl, are shown in Figure 7. As expected, the mobility of the complex is less negative than that of the mixed micelle and, in fact, is zero close to the point of the inception of binding, $Y$. The mobility of the micelle is seen to be a linear function of $Y$. Since the mobility is the ratio of the charge to the friction factor, we can write for
the micelle mobility

\[ U_m = \frac{q_m}{f_m} = \frac{n_{av} e Y}{f_m + N_{av} Y} \]  

where \( n_{av} \) is the mean micellar aggregation number and \( e \) is the electronic charge and where the effect of counterion binding to the micelle is neglected. The linear dependence of \( U_m \) on \( Y \) indicates that there is little change in \( n_{av} \) or \( f_m \) with \( Y \), consistent with the MW and \( R_g \) results in Table I. The \( Y \) dependence of the mobility of the complex is nearly linear and, interestingly, is displaced by almost a constant amount from the curve for the micelles. If we assume that the mobility of the complex is the sum of contributions from the bound micelles and the polymer and we assert that the contribution of \( N \) bound micelles to the friction factor is simply \( N f_m \), then we can write

\[ U_s = \frac{q_p}{f_p + N f_m} - \frac{N n_{av} e Y}{f_p + N f_m} \]  

where \( U_s \) is the mobility of the complex, \( q_p \) is the net charge of the polymer, \( f_p \) is the polymer contribution to the friction factor of the complex, and \( N \) is the number of micelles bound per polymer chain. The difference between the mobilities of the complex and the micelle is then

\[ \Delta U = \frac{q_p f_m + n_{av} e f_p Y}{f_m (f_p + N f_m)} \]  

Since the charge on the polymer, \( q_p \), is larger by about a factor of 10 than the charge on the micelle, \( n_{av} e \), and \( f_p \) is not very much larger than \( f_m \), the first term in the numerator of eq 6 is large relative to the second, and \( \Delta U \) does not show much dependence on \( Y \). From the large MW of the complex, we know that \( N \) is large, therefore \( N f_m \gg f_p \). Then eq 5 reduces to

\[ U_s \approx \frac{q_p}{f_p + N f_m} - \frac{n_{av} e Y}{f_m} \]  

The weak curvature in the \( U_s \) vs \( Y \) plot can best be explained by an increase in \( N \) with \( Y \). This is consistent with the fact that the MW of the complex doubles as \( Y \) increases from 0.28 to 0.36, as shown in Table II. Counterion binding to the micelle, neglected in the preceding analysis, may also be one reason for the curvature.

The complex is electrically neutral at \( Y = 0.26 \). From this result we may estimate \( N \), as follows. The micelle aggregation number is about 350 with a corresponding formal net charge of about 90. If the complex contains a single polymer chain with a net charge of about 1200, then the number of bound micelles required to compensate this charge is approximately 15. The mass of this hypothetical complex would be about 3 million. A rough extrapolation from the MW values of the complex obtained at \( Y = 0.28, 0.32, \) and 0.38 to \( Y = 0.26 \) is about 5 million. This calculation makes a number of assumptions, including the hypothesis that the bound micelle has the same structure as the free one; dye solubilization studies do suggest that there is no major restructuring of the micelle on complex formation. A second, and less likely, assumption is the absence of counterion binding to the micelle. Evidence from Figure 7 against this supposition is seen as follows.

A linear extrapolation of the data for the micelle to lower \( Y \) gives the unlikely result of zero mobility at \( Y = 0.15 \); in fact, the plot must exhibit curvature at lower \( Y \) to keep this from happening. While such effects can be partly due to changes in micelle size and shape,25 it also seems likely that the ratio of micelle charge to aggregation number is not a linear function of \( Y \) because of counterion binding. Other studies on mixed micelle systems (mainly at low ionic strength) suggest a decrease in the degree of cation "dissociation" \( \alpha \) with increasing surfactant content.26 Reduction of the net charge of bound micelles by a decrease in \( \alpha \) increases the complex MW calculated via the charge neutrality argument made above, bringing that estimate even closer to the observed value.

With increasing \( Y \), the electrophoretic mobility becomes progressively more negative, as would be expected. However, the magnitude of the change in \( U \) is greater than would be predicted from the increasingly negative micelle charge; i.e. the slope of the curve for the complex is larger than that for the micelle alone. As pointed out above, this can be best be understood in terms of an increase in the number of micelles bound per polymer chain, corresponding to an increase in the micelle—polyion binding constant with increasing \( Y \). This change is reflected in dialysis equilibrium results, as described below.

**Dialysis Equilibrium.** On the basis of the assumption that the concentration of unbound micelles on the polymer side of the dialysis cell is the same as the total concentration of micelles on the polymer-free side of the membrane, we can determine the concentration of bound and free micelles in the polymer compartment. The high ionic strength employed allows us to neglect the Donnan effect in the analysis of the dialysis data. Figure 8A presents the results obtained at a polymer concentration of 1 g/L, in 0.40 M NaCl, for \( Y = 0.32 \) and 0.38, as a plot of the mass of bound surfactant (as millimoles of TX100) per gram of polymer, \( Q \), vs surfactant concentration \( C_S \). Taken at face value, the results suggest a saturation at (TX100) > 25 mM (i.e. above \( C_S = 17 \) g/L total surfactant). In the case of \( Y = 0.32 \), the saturation value of \( Q = 7 \) is consistent with only 4–5 micelles bound per polymer chain, which calls into question either the MW obtained by static light scattering or the assumption that the complex involves a single polymer chain. This result also contradicts electrophoretic light scattering results, because complexes in which the number of bound micelles per polymer chain is less than 10 cannot have a net negative charge. There is reason to believe that saturation is not attained under the conditions of the dialysis equilibrium experiment when the weight ratio of total surfactant to polymer is \( C_S/C_P = 30 \) (the upper limit of conditions in Figure 8A). Furthermore, the large size of the micelles (\( R_g^{NP} = 9 \) nm at \( Y = 0.34 \)) reduces the rate of dialysis and thus the certainty that equilibrium has been attained. Figure 8B displays results obtained at a lower polymer concentration, 0.15 g/L, at \( Y = 0.14 \) and
in mixed micelle "solvent" is obtained, i.e. 3 times greater than exploration, at this time it may not contribute to the cell is two small to measure with precision. We must then structural characterization of the complex formed at infinite dilution of polymer, in excess micelle.

I is formed by isoionic addition of polymer to a solution of polymer concentration $C_p = 1$ g/L, $Y = 0.32$ (O) and 0.38 ($\Delta$), in 0.40 M NaCl: (B) $C_p = 0.15$ g/L, $Y = 0.14$, in 0.10 M NaCl. The solid line in (B) is the best fit to Hill's equation.

$I = 0.10$ M (at this lower value of $Y$, the micelles are smaller, which therefore accelerates the approach to dialysis equilibrium). The results (obtained after 50 days of dialysis) are well fit by Hill's equation:

$$ Q = \frac{k_1 C_s^{z_1}}{1 + k_2 C_s^{z_2}} $$

shown by the solid line in Figure 8B for $z = 2.4$, $k_1 = 3.7$, and $k_2 = 0.2$. The value of $z > 1$ indicates that the binding is cooperative, and the saturation value of $Q = 15$, obtained at $C_s/C_p \approx 50$ g/g, is consistent with approximately 20 micelles bound per polymer chain.

The light scattering, electrophoresis, and viscosity experiments are carried out at—or extrapolated to—$C_s/C_p$ in excess of 600. It is impossible to carry out the dialysis experiment under the same conditions for technical reasons: the change in UV absorption in the polymer-free cell is too small to measure with precision. We must then recognize that the dialysis experiments correspond to stoichiometries different than those in the light scattering/hydrodynamic studies and the structures of the complexes formed under these two different sets of conditions may differ. Although the dialysis technique merits further exploration, at this time it may not contribute to the structural characterization of the complex formed at infinite dilution of polymer, in excess micelle.

Viscometry. Plots of reduced specific viscosity vs concentration are shown in Figure 9 for (a) mixed micelle, (b) PDMDAAC, and (c) complex. In the last case, complex is formed by isoionic addition of polymer to a solution of SDS-TX100. If the concentration used is that of polymer alone, an intrinsic viscosity of 180 cm$^2$/g for the polymer in mixed micelle "solvent" is obtained, i.e. 3 times greater than $[\eta]$ in 0.40 M NaCl. However, the addition of polymer may be viewed as an increase in the concentration of the complex, along with a diminution of the surfactant concentration of the solvent medium. Assuming $\beta = 36$ (as determined from light scattering), we can calculate the effective mass concentration of the complex, i.e. $C_p(\beta)$, which is the concentration used for the complex in constructing the viscosity plot of Figure 9. We must also correct for the reduction in solvent viscosity that comes from the removal of surfactant upon complex formation. This correction was performed by using the viscosity of the effective micellar solvent as the solvent viscosity. The effective micellar solvent is a pure micelle solution with a micelle concentration of $C_m - C_p(\beta)$, where $C_m$ and $C_p$ are the concentrations of the micelle and polymer, respectively, in the complex solution. The value of $C_m - C_p(\beta)$ is the free micelle concentration in the complex solution. With this correction, we obtain the viscosity plots shown in Figure 9, along with $[\eta] = 13$ cm$^2$/g for the complex. This intrinsic viscosity is remarkably small, which suggests a high degree of compactness. However, it is important to point out that "compactness" deduced from low $[\eta]$ means that the effect on solution viscosity per unit mass of solute is small, and this may arise either from reduced chain dimensions or, as is more likely in the present case, from large mass per contour length. We may use the measured viscosity in conjunction with the molecular weight as obtained from light scattering to calculate the viscosity radius as

$$ R_\eta = (3M[\eta]/10\pi N_A) ^{1/3} $$

This quantity is sometimes referred to as "the equivalent hydrodynamic radius" but we prefer the term "viscosity radius" in order to avoid confusion with the dimension obtained from diffusivity, the Stokes radius. Both $R_\eta$ and $R_s$ are "equivalent" dimensions, since they are based on theories for spheres, but are nevertheless of demonstrated utility. Using for the molecular weight the value of 7 x 10$^6$ measured at $Y = 0.28$ in Table II, we obtain $R_\eta = 34$ nm, very nearly in agreement with the Stokes radius of 21 nm measured by dynamic light scattering for the complex at $Y = 0.28$. Thus the low value of $[\eta]$ is compensated for by the large value of $M$; this result is consistent with a chain with a moderately large persistence length, but with a large ratio of mass to hydrodynamic volume.
Speculations on the Structure of the Soluble Complex at Low Polymer Concentration. There is clear evidence for the formation of higher aggregates at large solute concentration, which may be envisioned as the precursors of condensation. In this work we focus on the complexes formed at low $C_p$; with the exception of the dialysis experiments, all results refer to $C_p < 0.5$ g/L. These complexes are extremely massive, with $M_\infty$ ranging from 7 to 15 million as $Y$ increases from 0.28 to 0.36. For an intrapolymer complex, these values would correspond to an increase in the number of bound micelles per polymer chain from 35 to 70 upon an increase in $Y$. Under the same conditions both the Stokes radius and the radius of gyration increase about 20%, i.e. from about 50% larger than the value for the free polymer to 60–80% larger. At $Y = 0.24$ and 0.27, the intrinsic viscosity measurements correspond to viscosity radii in good agreement with the Stokes radii. The electrophoretic mobilities show that the extent of micelle binding at $Y$ causes a rapid increase in the magnitude of the (negative) $\xi$-potential of the complex.

The extraordinarily high $M_\infty$ values seen at large $Y$ might seem to suggest a multipolymer complex; however it would be difficult to understand how such a complex could exhibit the stability with respect to aggregation in the limit of very low polymer concentration that would be necessary to yield regular Zimm plots. Furthermore, the positive second virial coefficient of the complex is not consistent with a highly self-aggregating system. These results and the good agreement between the hydrodynamic radii obtained in the limit of zero $C_p$ from viscometry, and at $C_p = 0.01$ g/L from QELS, suggest that the complex structure is invariant in this $C_p$ range, which is more consistent with an intrapolymer structure. In order to explain the magnitude of $R_g$ and $R_g^{0^0}$, we refer to the extended intrapolymer structure of Figure 1B. Although the hydrodynamic dimensions of the free polymer are not a great deal larger than those of the free micelle, it is important to keep in mind that the contour length of the polymer is ca. 50–100 times larger than either of these.

In the limit of excess surfactant, saturation of the polymer with micelles can be attained, especially at high $Y$. The intense binding of the micelles to the polymer produces, via steric and electrostatic intermicellar repulsive effects, a strong chain expansion and near-doubling in $R_g$. To conceptualize the structure of the complex in an intuitively reasonable manner, we may imagine that micelles tend to be oriented with their major axes parallel to the average direction of the local bound polymer segments, in order to minimize their surface curvature in the vicinity of the bound polymer chain. The chain itself is highly extended on a local scale but, because of the high ionic strength, exhibits flexibility at distances that are large compared to the micelle dimensions. The same intermicellar repulsions that produce chain expansion also lead to interparticle repulsion, and the second virial coefficient for the complex is positive, and just ca. 50% smaller than $A_2$ for PDMDAAC. In contrast to PDMDAAC, the mass:contour length ratio is very large.

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References and Notes

14. In the Nicomp software, "fit error" is obtained from the square of the errors between the fitted and measured autocorrelation functions, normalized with respect to particle size, while "residual" is the coefficient obtained for the decay constant of an infinitely large particle, commonly attributed to "dust events".
27. The effect of this approximation on $M_\infty$ for the complex ($M_c$) is difficult to assess directly; however, in separate work in 0.10 M, under which conditions the mixed micelle is small enough to allow dialysis equilibrium studies, the number of micelles bound per polymer chain so determined was in good agreement with $M_c$ in that solvent. This is circumstantial evidence for the validity of this approximation.