Complex Formation between Polyelectrolyte and Oppositely Charged Mixed Micelles: Static and Dynamic Light Scattering Study of the Effect of Polyelectrolyte Molecular Weight and Concentration

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ABSTRACT: Dynamic light scattering, static light scattering, and turbidimetry were used to investigate the effect of polyelectrolyte molecular weight and concentration on complex formation between a strong polyelectrolyte, poly(dimethyldiallylammonium chloride) (PDMDAAC), and oppositely charged mixed micelles of Triton X-100 (TX100) and sodium dodecyl sulfate (SDS). The hydrodynamic radius (Rh) of the complexes is about twice those of the PDMDAAC from which they are formed, while the radius of gyration (Rg) of the complexes remains essentially unchanged. This suggests that the complex formed is compact. With increasing polyelectrolyte concentration, intrapolymer complexes transform to interpolymer complexes. The interpolymer complexes are not stable and in time phase separate (coacervate). Although the polyelectrolyte molecular weight has only a small effect on the structure of the complex in the intrapolymer complex region, the interpolymer complex transition depends strongly upon the molecular weight of the polyelectrolyte. The polyelectrolyte concentration at which the transition occurs decreases with increasing polyelectrolyte molecular weight. If the polyelectrolyte molecular weight is low enough, this sharp transition is not observed, and no associative phase separation is observed.

Introduction

Complex formation between polyelectrolytes and oppositely charged surfactants has been a subject of intense research effort for both fundamental and technological reasons. Knowledge acquired from the study of polyelectrolyte–surfactant interactions can be applied to important industrial and biological processes. For example, the interaction of polyelectrolytes with oppositely charged micelles may serve as a useful model system for polyion–colloid systems. Such systems are represented in a wide range of situations including water purification and precipitation of bacterial cells with polycations17 and in a wide range of situations including water purification and precipitation of bacterial cells with polycations,17 and the stabilization of preceramic suspensions.18 In the biological realm, they are central to the immobilization of enzymes in polyelectrolyte complexes16 and the purification of proteins by selective precipitation and coacervation.19–23 The fundamental interactions that govern the nonspecific association of DNA with basic proteins24,25 must also be identical to the ones that control the binding of charged colloids to oppositely charged polyelectrolytes.

Until recently, most of the published studies on polyelectrolyte–surfactant complexes involved surfactants at such a low concentration that free micelles do not exist in the system, mainly because of the difficulties arising from phase separation. The interaction between polyelectrolytes and oppositely charged surfactants is dominated by strong electrostatic forces, although hydrophobic interactions may play a secondary role.2,5,3,6 These forces cause the association to start at a very low surfactant concentration, known as the critical aggregation concentration (cac), which is usually a few orders of magnitude lower than the critical micelle concentration (cmc) of the free surfactant. Unlike the situation for nonionic polymer–ionic surfactant systems, the complex usually cannot coexist with free micelles because precipitation is observed as the addition of ionic surfactant brings the polyelectrolyte close to charge neutralization.26,27 Therefore, phase separation effects result in the restriction of most studies of strong polyelectrolytes with oppositely charged surfactants to surfactant concentrations below or not much higher than the cmc.

Dubin and co-workers28–30 have demonstrated that the strong electrostatic interaction could be attenuated by using mixed micelles of nonionic and ionic surfactants. Thus Dubin and Oteri29 showed that the interaction between poly(dimethyldiallylammonium chloride) (PDMDAAC) and mixed micelles of sodium dodecyl sulfate (SDS) and Triton X-100 (TX100) takes place only when a critical molar ratio Y, of SDS to TX100 has been reached, where Y is defined as Y = [SDS]/[(SDS) + (TX100)], and is proportional to the average mixed micelle surface charge density. In addition to the phase transition at Y, corresponding to the reversible formation of soluble polyelectrolyte–mixed micelle complexes, Dubin and Oteri29 observed a second phase transition, corresponding to bulk phase separation, at a higher Y value, denoted by Y,. Y, usually exceeds Y, by about 50–100%. The region between Y, and Y, represents a range of micelle surface charge density where soluble, reversible complexes could form. At moderate or high polyelectrolyte concentration, a maximum in the turbidity versus Y curve is observed between Y, and Y,. The soluble complex formation as well as its dependence upon ionic strength, polyelectrolyte concentration, and surfactant concentration has been studied by Dubin and co-workers using a variety of techniques.

One parameter that has received relatively little attention in studies of polyelectrolyte–surfactant complex formation is the polyelectrolyte molecular weight.31 Using turbidimetry, Dubin et al.32 indicated that the molecular weight of PDMDAAC did not exhibit a significant effect on PDMDAAC/TX100–SDS complex formation but did observe that Y, decreased slightly with increasing molecular weight of poly(sodium styrenesulfonate)

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(NaPSS), in the presence of mixed micelles of TX100 and dodecyltrimethylammonium bromide.\textsuperscript{38} Lindman and co-workers studied the effect of polyelectrolyte molecular weight on the phase behavior of mixtures of alkyltrimethylammonium bromide (C\textsubscript{12}TAB) and the anionic polysaccharide hyaluronic acid. The tendency toward phase separation increased slightly with increasing polyelectrolyte molecular weight; only a slight change was observed in the phase diagram. Recently, Choi and Kim\textsuperscript{41} studied the interaction between poly(acrylic acid) (PAA) and TX100-SDS complexes via the excluded volume effect. It is thus interesting to study the change of complex formation as the size of one of the components, polymer or micelle, changes. PDMDAAC/TX100-SDS should be a good candidate since the hydrodynamic radius (R\textsubscript{h}) of the free micelles could reach ca. 50 nm,\textsuperscript{47} while the range of R\textsubscript{h} for available PDMDAAC fractions is around 4.5–26 nm.\textsuperscript{48} A second interesting parameter in polyelectrolyte–surfactant complex formation is the polyelectrolyte concentration (C\textsubscript{POL}) expressed in this paper as the weight ratio of PDMDAAC to surfactant. This parameter is usually a determining factor for intra-\textsubscript{US} intercomplex formation. Dubin and co-workers\textsuperscript{34–36} have indicated that an intrapolymer complex forms in the PDMDAAC/TX100–SDS system at low C\textsubscript{POL}, while at high C\textsubscript{POL} an interpolymer complex could form. However, the PDMDAAC used in those studies was polydisperse. Since polyelectrolyte molecular weight could influence intra-\textsubscript{US} interpolymer complex formation, narrow molecular weight distribution samples should be preferable in such studies. In addition, it is particularly interesting to see if an interpolymer complex is the precursor of phase separation.

A series of PDMDAAC fractions with narrow molecular weight distribution has been obtained by preparative gel permeation chromatography (GPC).\textsuperscript{46} These fractions were characterized by static and dynamic light scattering, viscosity, GPC, and electrophoretic light scattering. In the present study we explore the effect of polyelectrolyte molecular weight and concentration on PDMDAAC/TX100–SDS complex formation.

**Experimental Section**

**Materials.** A commercial sample of PDMDAAC, Merquat 100 from Calgon Corp. (Pittsburgh, PA), with a nominal molecular weight of 200K and polydispersity of M\textsubscript{w}/M\textsubscript{n} \~ 10 was fractionated via preparative GPC, and the fractions were characterized by static and dynamic light scattering, viscosity, GPC, and electrophoretic light scattering.\textsuperscript{48} Table 1 shows the molecular characteristics of the PDMDAAC fractions used in this study. TX100 was purchased from Aldrich and SDS from Fluka. Ionic strength was adjusted by using NaCl from Fisher. Milli-Q water was used throughout this work. TX100, SDS, and NaCl were used without further purification.

The Merquat 100 sample used in this study was dialyzed through a membrane with a nominal 12K–14K cutoff. Therefore, it is expected that the molecular weight distribution index M\textsubscript{w}/M\textsubscript{n} should be much smaller than 10.

**Dynamic Light Scattering.** The type I titration procedure was followed to bring Y to 0.30. Such solutions were diluted 10 times by using 0.40 M NaCl, to yield final solutions with a typical C\textsubscript{POL} value of (PDMDAAC) = 0.0466 g/L (unless otherwise indicated) and (TX100) = 3.11 mM (fixed throughout this study). Since the cmc of TX100–SDS mixed micelles is expected to be less than 0.2 mM, i.e., at least 15 times smaller than the surfactant concentrations employed here, the system we studied is a polyelectrolyte–micelle system. The diluted solutions were passed through 0.45-\textmu m filters (Life Science Products). Most of the dynamic light scattering measurements were carried out at 24 ± 1 °C and at angles from 45 to 120° using a Brookhaven Instruments system equipped with a 72-channel digital correlator (BI-2030AT) and an Omnichrome air-cooled 200 mW argon ion laser operating at a wavelength in vacuum \lambda\textsubscript{0} = 488 nm.

In the self-beating mode of dynamic light scattering, the measured photoelectron count autocorrelation function G(\tau, q) for a detector with a finite effective photocathode area has the form\textsuperscript{49–51}

\[
G(\tau, q) = N_\text{s}(\pi b)^{1/2} (1 + b g(1)(\tau, q) q^2) \tag{1}
\]

where g(1)(\tau, q) is the first-order scattered electric field (E\textsubscript{0}) time correlation function; \tau, the delay time; \langle \tau \rangle, the mean counts per sample; N\textsubscript{s}, the total number of samples; A (=N\textsubscript{s}(\pi b)^{1/2}), the base line; b, a spatial coherence factor depending upon the experimental setup and taken as an unknown parameter in the data fitting procedure; and q = (4\pi n/\lambda\textsubscript{0}) sin(\theta/2), with n and \theta being the refractive index of the scattering medium and the scattering angle, respectively.

For a solution of polydisperse particles, g(1)(\tau, q) has the form\textsuperscript{49}

\[
g(1)(\tau, q) = \int_0^\infty G(\tau, q) e^{-\gamma t} \gamma d\gamma \tag{2}
\]

where G(\Gamma, q) is the normalized distribution of line width \Gamma measured at a fixed value of q. In the present study, a CONTIN algorithm was used to obtain the average \Gamma and its distribution of the complex mode and the free micelle mode.\textsuperscript{42}

The average line width \Gamma\textsubscript{w} at a finite concentration C and a finite value of q is related to the translational diffusion coefficient at infinite dilution and q → 0 extrapolation, D\textsubscript{w} by\textsuperscript{53}

\[
\Gamma_w = D_0 q^2 (1 + f R_g q^2)^{-1} (1 + k_\text{e} C) \tag{3}
\]

where f is a dimensionless number which depends upon the chain structure, polydispersity, and solvent quality; R\textsubscript{g} is the radius of gyration; and k\textsubscript{e} is an average system-specific second virial (diffusion) coefficient which combines the hydrodynamic and thermodynamic factors. Therefore, to get D\textsubscript{w} both extrapolations

| Table 1. Description of the PDMDAAC Fractions Used in This Study |
|--------------------------|--------------------------|
| fraction no. | 10^{-3}M\textsubscript{w} | fraction no. | 10^{-3}M\textsubscript{w} |
| 2 | 1400 | 9 | 110 |
| 3 | 1300 | 10 | 50 |
| 8 | 800 | 11 | 22 |
| 15 | 200 |
of \( C \rightarrow 0 \) and \( q \rightarrow 0 \) are required. The hydrodynamic radius, \( R_h \), can then be obtained by using the Stokes–Einstein relation

\[
D_q = k_B T / (6 \pi \eta R_h)
\]

(4)

where \( k_B \) is the Boltzmann constant; \( T \) is the absolute temperature; and \( \eta \) is the solvent viscosity.

In the present study, only one concentration is used because it is not known to what extent dilution could affect the structure of the complex. No extrapolation to infinite dilution was performed. Therefore, the \( R_h \) values presented in this paper are only apparent values. However, the concentration of PDMDAAC in this study is fairly low (typical value 0.0466 g/L). Therefore, the lack of concentration extrapolation should not introduce a significant error.

**Static Light Scattering.** If we take the PDMDAAC/TX100-SDS complex as a solute and the free (unbound) TX100-SDS mixed micelles in 0.4 M NaCl as a solvent (the concentration of the free micelles, although in large excess when compared with PDMDAAC, is not known in the present study), the excess Rayleigh ratio \( R(q) \) of the complex at finite \( q \) and finite complex concentration \( C \) has the form

\[
H' C_q / R(q) = (1 / M_w \times (1 + R_h^2 q^2 / 3) + 2 A_2 C \times \text{dn}/\text{dc})
\]

(5)

where \( M_w \) is the weight-averaged molecular weight of the complex, \( A_2 \) is the second virial coefficient; and \( H' \) is a constant. Then, \( R_h \) can be estimated from \((3 \times \text{slope/intercept})^{1/2}\) in a plot of \( 1/(I(q) \times q^2) \) vs \( q^2 \).

In the limit of \( q \rightarrow 0 \), eq 7 can be written as

\[
I(q \rightarrow 0) \approx H' C_q M_w \times (\text{dn}/\text{dc})^2
\]

(8)

It is further assumed that \( C = \beta C_p \), where \( \beta \) is the degree of binding, i.e., the mass of surfactant bound per unit mass polyelectrolyte (this assumption should be reasonable if TX100-SDS is in large excess). Then eq 8 can be written as

\[
I(q \rightarrow 0) \approx H' \beta C_q M_w \times (\text{dn}/\text{dc})^2
\]

(9)

Therefore, in a plot of \( I(q \rightarrow 0) \) vs \( C_p \), if the slope is changed it implies \( M_w \) and/or \( \text{dn}/\text{dc} \) is changed. For example, if interpolymer complexes start to form with increasing \( C_p \), an increased slope change should be observed.

Static light scattering measurements were performed at 24 ± 1 °C and at angles from 25° to 145° along with dynamic light scattering measurements on the same solutions as described above. The excess scattered intensity from complexes was estimated by subtracting the scattered intensity of TX100-SDS micelles without PDMDAAC and at the same concentration as in the PDMDAAC/TX100-SDS system. This disregards the fact that some micelles are bound to PDMDAAC. However, since the surfactant was in excess, i.e., the weight ratio of surfactant to PDMDAAC, \( w_{\text{surfactant}} / w_{\text{PDMDAAC}} \), is generally greater than 30, this approximation may be reasonable. Further evidence supporting this approximation can be found in the Results and Discussion. All the excess scattered intensity values presented in this paper are from extrapolation \( q \rightarrow 0 \).

**Results and Discussion**

Figure 1 shows the results from type I titrations in 0.4 M NaCl. The shapes of the curves are very similar to previous results using polydisperse PDMDAAC samples. No turbidity increase is observed until \( Y \) reaches \( Y_c = 0.23 \), regardless of the PDMDAAC molecular weight. Above \( Y_c \), soluble complex starts to form. When \( Y \) reaches \( Y_p \) (around 0.38–0.42), phase separation occurs. The curves for 200K < \( M_w \) show maxima between \( Y_c \) and \( Y_p \). \( Y_p \) is also little affected by the PDMDAAC molecular weight. Such phenomena suggest that the initial complex formation process at \( Y_c \) mainly involves short polymer segments, although the structure of the complex as detected from more sensitive light scattering techniques may be dependent upon PDMDAAC molecular weight as discussed later. It is noted that the changes in the titration curves with increasing PDMDAAC molecular weight are very similar to those observed with increasing PDMDAAC concentration, i.e., \( 100 - \% T \) is increased with either increasing polyelectrolyte molecular weight or increasing polyelectrolyte concentration. This can be understood from eq 8, which indicates that the scattered intensity is proportional to both concentration and molecular weight of the complex.

One noticeable feature in Figure 1 is that the maximum is only obvious when PDMDAAC molecular weight is higher than about 110K. It is interesting that the PDMDAAC fraction with \( M_w = 110K \) has a hydrodynamic size of ~9 nm, which is also the size of free TX100-SDS micelles, as previously shown or as obtained by dynamic light scattering results, discussed below. The information from turbidity measurements provides the range of \( Y \) for soluble complex formation. The light scattering results presented below are all from systems with \( Y = 0.30 \) and 0.4 M NaCl.

Figure 2 shows the dependence on PDMDAAC molecular weight of \( R_h \) of the PDMDAAC/TX100-SDS complex as well as that of the accompanying unbound micelles from CONTIN analysis of the dynamic light scattering results. The \( R_h \) value of ca. 9 nm for free micelles is in agreement with previous results. The size of the complex increases with increasing PDMDAAC molecular weight, while the size of the free TX100–SDS micelles remains essentially unchanged.

Figure 3 shows the dependence of \( R_h \) for complex and for PDMDAAC (without TX100–SDS) on PDMDAAC molecular weight. The \( R_h \) values of the complexes are about twice those of the PDMDAAC from which they are formed. Figure 4a shows some representative angular distribution of scattered intensity from complexes, and Figure 4b presents similar double-logarithmic plots for...
Figure 3. Dependence of $R_g$ of complex upon PDMDAAC molecular weight. For comparison, the $R_g$ values of pure PDMDAAC (without TX100 and SDS) are also shown.

Interestingly, the $R_g$ values are very close to those of the pure PDMDAAC fractions. This indicates that the overall PDMDAAC conformation does not change much upon complex formation; i.e., no significant chain expansion occurs. TX100-SDS micelles appear to occupy the space between the PDMDAAC segments. It is known that such a process will increase $R_g$ because mobile solvent molecules inside the PDMDAAC coils are replaced by bound, immobile micelles, while the geometric $R_g$, which is largely dependent upon the topological conditions, remains largely unchanged. Therefore, the complex formed is very compact, a conclusion also drawn earlier by Dubin and co-workers from light scattering measurements of Merquat 100/TX100-SDS. Chu and co-workers observed similar phenomena for the bovine serum albumin (BSA)-polysaccharide conjugate, they found that the molecular weight of the conjugate (3500 K) was about 7 times larger than that of the pure polymer (530 K), yet $R_g$ values were comparable: $R_g \sim 54$ nm for the conjugate and $\sim 50$ nm for the polymer.

The reason for the compact structure of the complex formed between polyelectrolyte and oppositely charged mixed micelles may be discussed in terms of thermodynamic quantities. Complex formation could be controlled by at least four factors. One of the electrostatic interaction between polyelectrolyte and oppositely charged mixed micelles. This enthalpy change is the main driving force for complex formation and depends strongly upon the structure of polyelectrolyte and micelles, ionic strength, and temperature. On the other hand, binding gives rise to an entropy loss of the polyelectrolyte chains, $\Delta S_{\text{config}}$. This loss may be compensated, to some extent, by the release of bound counterions from micelle and polyion. $\Delta S_{\text{config}}$ increases with increasing flexibility of the polyelectrolyte chains (note that the flexibility also depends upon the ionic strength). If a polyelectrolyte is already rather rodlike, this loss will not be significant. $\Delta S_{\text{config}}$ will be minimized if the binding takes place in such a way that the polyelectrolyte chain conformation remains largely unchanged during complex formation. The third factor is the excluded volume effect (steric effect) of the bulky micelles, which tends to expand the polyelectrolyte chain. The magnitude of this factor increases with micelle size. In a system where only monomeric surfactant is involved, as is the case in most literature research, this factor should not be significant. The fourth factor is the electrostatic repulsion of bound micelles given that the binding of micelles to the polyelectrolyte chain is unlikely to neutralize the charge on the micelle surface completely. This factor has an effect similar to micelle excluded volume on complex structure but depends strongly upon ionic strength. The final structure of the complex depends upon the relative magnitude of these four factors.

In the present system of PDMDAAC/TX100-SDS in 0.4 M NaCl, the electrostatic repulsion among bound micelles is probably not a significant factor because of the high ionic strength. The conformation of PDMDAAC in
0.4 M NaCl is close to that of a flexible random coil. Therefore, it is likely that the final structure of the complex in the present system depends upon the excluded volume factor and the entropy loss factor. The compact structure of the complex suggested by Figures 3 and 4 points to the entropy factor; i.e., the PDMDAAC chain tries to retain the original overall conformation during complex formation to minimize entropy loss, and the micelles tend to occupy the space between PDMDAAC chains. The excluded volume effect can also be seen from Figures 3 and 4; i.e., the overall slope of the curves is decreased upon complex formation. This tendency is more obvious at low PDMDAAC molecular weight, and there appears to be a transition point around PDMDAAC $M_w = 110K$, in agreement with the turbidity results. With decreasing molecular weight, the size of PDMDAAC becomes comparable to or even smaller than that of the micelles. The micelles cannot stay inside the PDMDAAC chain domain without large perturbation of the chain conformation. Thermodynamically, the most favorable case is for some of the bound micelles to reside at the outside boundary of the PDMDAAC domain. In this case, the total number of such “distal” bound micelles is likely to be greater for high molecular weight PDMDAAC due to the larger accessible space. But if this number is divided by the number of PDMDAAC repeating unit, the number of micelles bound per PDMDAAC repeating unit should be larger for low molecular weight PDMDAAC fractions, which gives rise to larger increase in both $R_b$ and $R_e$. A depiction of complexes formed from high and low molecular weight PDMDAAC fractions is shown in Figure 5.

Figure 6 compares the CONTIN distribution of complex formed from polydisperse Merquat 100 with that from a PDMDAAC fractions. Qualitatively, the two complex peaks are similar. This can again be explained from the dependence of complex size upon PDMDAAC molecular weight indicated in Figure 3, which suggests that lower molecular weight fractions do not form low molecular weight complex.

Figure 7 shows the effect of $C_p$ on $R_b$ and $R_e$ of the complex for the 590K fraction. With increasing $C_p$, $R_b$ and $R_e$ change very little until $z = W_{PDMDAAC}/W_{surfactant} \approx 0.028$. Above 0.028, $R_b$ and $R_e$ increase sharply. It is noted that $z = 0.09$ corresponds to a 1:1 charge ratio of PDMDAAC to TX100–SDS.

Figure 8 shows the excess scattered intensity (extrapolated to $q \to 0$) of the complex as a function of $z$. After subtraction of the contribution from the mixed micelles, the values of $I$ below $z = 0.028$ approach zero as $z \to 0$. This suggests that our use of scattered intensity from a polymer-free solution as the background correction is a good approximation.

Figure 8 shows a linear dependence on $C_p$ of the excess scattered intensity from complexes up to $z = 0.028$, at which point the slope increases sharply. Consideration of Figure 8 along with Figure 7 indicates that below $z = 0.028$, only intrapolymer complexes are formed. The number of complexes increases with increasing $z$, while the size and the molar mass of complexes remain unchanged. Above $z = 0.028$, interpolymer complexes start to form. Both
Figure 9. Dependence of $R_b$ of complex upon $z$ (PDMDAAC ($M_w=1400K$)).

Figure 10. Dependence of $R_b$ of complex upon $z$ (PDMDAAC ($M_w=50K$)).

Figure 11. Excess scattered intensity (from extrapolation $q \to 0$) of complex as a function of $z$ (PDMDAAC($M_w=50K$)).

Concluding Remarks

This paper elucidates the effect of polyelectrolyte molecular weight and polyelectrolyte concentration on complex formation with mixed micelles. The light scattering results indicate that the complexes are very compact. With increasing polyelectrolyte concentration, intrapolymer complexes change to interpolymer complexes, which appear to be precursors of associative phase separation (coacervation). Although polyelectrolyte molecular weight is not a significant factor for the structure of complex in the intrapolymer complex region, the intra- to interpolymer complex transition depends strongly upon the polyelectrolyte molecular weight; i.e., the polyelectrolyte concentration at which the transition occurs decreases with increasing polyelectrolyte molecular weight. If the polyelectrolyte molecular weight is low enough, high molar mass interpolymer complexes cannot be observed and associative phase separation does not occur. This may explain why high molecular weight polyelectrolyte is preferred for high protein recovery ratio based on polyelectrolyte–protein complex formation.

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References and Notes

(2) Goddard, E. D. Colloids Surf. 1986, 19, 301.


(37) The effect of the molecular weight of nonionic polymers on polymer-surfactant complex formation has been reviewed by Goddard and by Lindman and co-workers. Generally, a minimum nonionic polymer molecular weight is required for complex formation. Above this value, a weaker interaction could be observed. However, it has to be noted that, although the techniques used are similar, complex formation from nonionic polymers and surfactants may be very different from that from polyelectrolytes and oppositely charged surfactants. The complex from nonionic polymers and charged surfactants has a charge accumulation, while the complex formation from polyelectrolytes and oppositely charged surfactants involves charge neutralization. The driving force for the two is thus different.