Critical Conditions for the Binding of Polyelectrolytes to Small Oppositely Charged Micelles

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Mixed micelles associate with polyelectrolytes of opposite charge to form soluble or insoluble complexes. The interaction takes place abruptly—signaled by a sudden enhancement in scattering—upon an increase of micelle surface charge density, an increase in polymer linear charge density, or a decrease in ionic strength, and involves a microscopic or macroscopic phase change. Because the surface charge state and the dimensions of the mixed micelles may be varied over a wide range, the polyelectrolyte–micelle system provides a useful model for polyelectrolyte–colloid interactions. Turbidimetric titrations have been carried out over a range of ionic strengths for two systems. One is composed of cationic/nonionic micelles of dimethyl-dodecylamine oxide (DMDAO) in the presence of the strong polyanion poly(2-acylamido-2-methylpropanesulfonic acid, sodium salt) (PAMPS) or its lower charge density copolymer with N-vinylpyrrolidone (P(AMPS–NVP)). The other consists of mixed anionic/nonionic micelles of sodium dodecyl sulfate (SDS) and dodecylhexa(oxyethylene) glycol (C12E6) in the presence of the polycation poly(dimethyl)diallylammonium chloride (PDMDAAC). The results provide the ionic strength dependence of the critical micelle composition for polyelectrolyte–micelle association. From these experimental phase boundaries, along with appropriate potentiometric or fluorescence probe measurements, we obtain the critical micelle surface potential. For both systems, the critical surface charge density (σ,) is observed to depend on the square root of the ionic strength (f). This result is particularly meaningful in the DMDAO system, in which the absence of bulky surfactant headgroups means that σ, can be clearly defined. Furthermore, in this work we focus exclusively on the pH and f region in which the micelle stabilizes constant spherical shape. The observations for the DMDAO system may then be compared to relevant theories for the interaction of polyelectrolytes with oppositely charged surfaces. In addition, we suggest a simplified treatment for a spherical charged surface which yields the observed σ, ~ f−1/2 relationship. Analyses of the electrostatic potential decay curves for the systems DMDAO–PAMPS and DMDAO-P(AMPS–NVP) at critical conditions suggest that the mean position of polyelectrolyte binding to the micelle is about 6 Å from the micelle surface and that a potential of +5 mV at this location is required for binding to take place. For mixed micelles of SDS/C12E6 with PDMDAAC, it appears that the oxyethylene head groups obstruct the approach of the polyanion, so that the distance between polyelectrolyte and the sulfonate head groups is more difficult to define.

Introduction

The interaction of polyelectrolytes with oppositely charged particles is an important phenomenon in commercial processes and in biological systems. Some examples of the former are as follows: water treatment by colloidial flocculation with polyelectrolytes,1 flocculation of cellulosic fibers in paper making,2 recovery of mineral suspensions,3 precipitation of bacterial cells with polyelectrets,4 and the stabilization of concentrated preceramic suspensions.5 Examples involving biopolymers include the immobilization of enzymes in polyelectrolyte complexes,6 purification of proteins by selective precipitation and conservation,7 and the nonspecific association of DNA with basic proteins.8

The binding of polyelectrolytes to oppositely charged particles and surfaces has been the subject of extensive theoretical investigation. The adsorption of polyelectrolytes on planar charged surfaces was treated for example by Wiegel,9 by Scheutjens, Fleer, and co-workers,10 and by Muthukumar.11 Odijk considered the binding of a flexible polyelectrolyte to a rigid charged cylinder.12 Without a detailed comparison of these treatments, one may point out that all of them lead to prediction of a phase transition; binding of the polyelectrolyte is predicted to occur abruptly upon sufficient charge of any of the few important variables: ionic strength (f), the charge per polymer repeat unit (q), particle surface charge density (σ), or temperature. The interpretation of the role of the last parameter in these theories is unlikely to survive experimental test, since such important effects as the entropy of released microions, alterations in water structure, and changes in the hydration of ions are not adequately considered. With regard to the other variables, however, it is intuitively obvious that the magnitude of the electrostatic interaction between polyelectrolyte and particle should increase with σ and q and diminish with f, and all treatments agree in this regard. Disagreement appears in the scaling of these variables at critical conditions, but few experimental tests of these relationships have appeared.

Aqueous systems containing polyelectrolytes and oppositely charged micelles provide a model for the coulombic interaction of polyelectrolytes and charged colloids,13–15 and the phenomena

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nology of such systems may guide the development of theory.\(^{20}\)

The micelle “surface” charge density (\(\sigma\)) may be varied either by controlling the composition of mixed ionic/nonionic micelles\(^{13-16}\) or by adjusting the pH when the micellar surfactant carries a titratable head group.\(^{17}\) \(\sigma\) may be quantitatively determined by calculations involving the micelle aggregation number and effective head group area contributions, via measurements of the surface potential \(\psi_0\) and application of the Gouy–Chapman equation, or by some similar relationship between \(\sigma\) and \(\psi_0\). This last parameter in turn can be obtained using fluorescent or titratable probes of the micelle surface\(^{15}\) or—in certain cases—by potentiometric titration of the surfactant head group itself. In addition to varying \(\sigma\), it is possible to control the micelle dimensions (and therefore its mean curvature) by controlling the geometry of the surfactant molecules and the micelle composition.\(^{21}\) Of particular interest are changes observed in the aggregation order of the polymer–micelle complex when the relative size of two macromionic species changes.\(^{18}\)

In this study we report on the critical association of a cationic polyelectrolyte with mixed anionic/nonionic micelles of sodium dodecyl sulfate and \(C_{12}E_{8}\) and particularly on the association of anionic polyelectrolytes with micelles of dimethylammonium oxide (DMDAO). The latter system is especially attractive for such studies for several reasons. (1) Most nonionic surfactants have very large headgroups, which confounds the conception of the micelle “surface”; owing to an intense amine oxide dipole, DMDAO on the other hand can form a soluble uncharged micelle even though the headgroup is small. (2) The amine oxide groups may be protonated over the pH range 3 < pH < 9, and from the measurable apparent pK, one may determine the surface potential.\(^{22}\) (3) DMDAO micelles are compact spheres over a reasonable range of pH and ionic strength;\(^{24}\) this simplifies electrostatic considerations. The association of DMDAO with polyanions is found to exhibit a phase transition, which occurs abruptly upon increase in the mean degree of protonation (\(\beta\)) or decrease in ionic strength (\(I\)). At large \(\beta\) or low \(I\) is a liquid conserved; studies with related systems suggest that it arises from the aggregation of polyelectrolyte–micelle complexes whose net charge is close to neutrality.\(^{18}\) The dependence of \(\beta\) on \(I\) at critical conditions may be viewed as a phase boundary and yields the relationship between \(\sigma\) and \(I\). In ref 17, we noted that this dependence changed abruptly in the range of \(\beta\) and \(I\) where the micelle exhibits a transition from spherical to rodlike dimensions. In that work, we reported approximate values for \(\sigma_0\) (based solely on applications of the Gouy–Chapman equation) and provided only a phenomenological account of the interdependence of \(\sigma_0\) and \(I\). We carried out those studies with commercially available samples of sodium poly(styrenesulfonate) (NaPSS), which subsequent characterization data showed to be of uncertain homogeneity.\(^{25}\) In the present study, we deal only with the spherical regime of DMAO micelles (0 < \(\beta < 2.5\); 6.5 < pH < 8) and determine \(\sigma_0\) by use of several procedures. We employ two well-characterized polyanions synthesized specifically for this study. We now place the phase boundary results in the context of available relevant theories and also provide a simple model for binding to a spherically charged colloid, which shows agreement with the phenomenological results. Previously obtained


\(^{22}\) Elemental analysis of dialyzed and freeze-dried samples of the NaPSS polymers used in ref 17 yield degrees of sulfonation ranging from 82 to 86%. This result, along with the occasional turbidity and titration behavior of some of these materials, suggests the possibility of considerable compositional heterogeneity and concomitant uncertainty about the charge density.


\(^{25}\) Dubin, P. L.; Zhang, H. Unpublished work.


Figure 1. Structure of polyelectrolytes used in this study.

results for the system \(C_{12}E_{8}-SDS/PDMDAAC\) are used to calculate \(\sigma_0\) for that system in order to demonstrate the general nature of the dependence of \(\sigma_0\) on \(I\).

Experimental Section

DMDAO, “purum” grade from Fluka (Happague, NY), was found to contain 1.3% H\(_2\)O by Karl Fisher titration. pH titration in acetic acid with HClO\(_4\) to the acid end point only consumed 97.2% of the theoretical amount of acid, from which it was concluded that the surfactant was partially in the salt form, perhaps because of adsorption of CO\(_2\). Therefore, solutions of DMDAO were adjusted by addition of NaOH to pH ca. 11 prior to titration with HCl. \(C_{12}E_{8}\) was purchased from Nikko Chemical Co. (Tokyo). SDS was puriss grade from Fluka (Happague, NY). Poly(dimethylidylylammonium chloride) (PDMDAAC), a strong polycation, was a commercial sample (“Merquat 100”) from Calgon (Pittsburgh, PA). After dialysis and freeze-drying, the weight-average molecular weight was determined by light scattering as 2.5 \(\times\) 10\(^5\).\(^{23}\) A homopolymer of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) (Lubrizol Corp., Wickliffe, OH) was prepared by free radical polymerization of a 10 wt % solution of the neutralized monomer in deionized water at 65°–70 °C, under \(N_2\) with Na\(_2\)SO\(_4\) and (NH\(_4\))\(_2\)SO\(_4\) (both from Aldrich) as initiator. The molecular weight (MW), estimated from the measured intrinsic viscosity of 1.21 dL/g in 0.50 M NaCl, was 6 \(\times\) 10\(^5\) (using the relationship\(^{26}\) \(\eta_p = 1.95 \times 10^{-3} (M_w)^{0.83}\)). A copolymer of AMPS with N-vinylpyrrolidone (NVP) (Altrod) was prepared by a similar procedure. The intrinsic viscosity in 0.50 M NaCl was 3.30 dL/g, indicating a MW of ca. 2 \(\times\) 10\(^6\). Elemental analysis showed a ratio of AMPS:NVP of 64:36 (mole basis). Structures of these three polymers are in Figure 1.

The relationship between pH and the degree of protonation of DMDAO micelles (\(\beta\)) was obtained by pH titrations of 50 mM DMDAO using an Orion Model EA 920 meter equipped with an Orion glass/combination Ross electrode. The pH was first adjusted to 10.9 with 1.0 M NaOH, then titrated under \(N_2\) atmosphere with 0.500 M HCl. After correction by subtraction of the titration curve of a surfactant-free blank,\(^{27}\) the \(\beta = 1\) equivalence point was determined by fitting the titration data at low pH to a cubic equation, differentiating it manually, and setting the second derivative to zero. The \(\beta = 0\) end point was obtained from a plot of the first derivative of the raw titration data. All other measurements involving DMDAO were carried out in the regime of low ionic strength, \(I < 0.3\), to ensure spherical micelle dimensions.\(^{24,27}\)

The dimensions of the DMDAO micelles were measured by dynamic light scattering with 90° detection, using one of two systems. The first was composed of a Jodon 20-mW He:Ne laser, a Malvern RR102 spectrometer, and a Nicomp T1000D 64 channel autocorrelator interfaced with an Epson Equity II computer (this system and experimental procedures have been previously described\(^{13}\)). The second was an Oros Model dp-801 QELS instrument (Biotage, Charlottesville, VA) equipped with a 7-\(\mu\)L sample cell maintained at 26.5 ± 0.4 °C, a 30-mW solid-state laser (780 nm), and an actively quenched avalanche photodiode. For either instrument, samples of DMDAO, 30–100 mM, adjusted to the desired pH and ionic strength, were filtered through 0.2-\(\mu\)m Anotec filters prior to data collection. There were no significant
Critical Conditions for the Binding of Polyelectrolytes

Figure 2. "Type 1" turbidimetric titrations: (A) PAMPS-DMDAO (axis above); ionic strengths (from left to right) 0.25, 0.20, 0.15, and 0.10 M. (B) PDMDAAC-C12E6/SDS (axis below). Ionic strengths (from left to right) 0.05, 0.10, 0.20, 0.40, 0.60, and 0.80 M. Polymer concentration 0.50 g/L, C12E6 concentration 20 mM.

differences between the mean apparent diffusivities obtained using the two different instruments.

"Type 1" turbidimetric titrations for PDMDAAC in the presence of polyamions were carried out as follows. PDMDAAC (50 mM) and 0.50 g/L polymer were combined at the desired ionic strength (adjusted with NaCl) and at pH ca. 9. HCl (0.499 M) was added with a Gilgore 200-ml microburet, and the pH and transmittance were simultaneously monitored, the latter at 420 nm using a Brinkmann colorimeter, equipped with a 2 cm path length fiber optics probe. Distilled water was used to set the colorimeter to 100% T prior to each titration. Measured values of 100 – ST (linearly proportional to the turbidity for ST > 90) were corrected by subtraction of a blank, consisting of a polymer-free solution. The pH at which an abrupt increase is observed (see Figure 2A) is defined as pHc and corresponds to the onset of complex formation. From pH titration curves obtained as mentioned above, pHc was converted to \( \beta_c \). In the case of the SDS/C12E6 - PDMDAAC system, the micelle surface charge density is controlled by Y, the mole fraction of SDS in the mixed micelle. Therefore, type I titrations were carried out by adding 40 mM SDS to a solution of 0.50 g/L PDMDAAC and 20 mM C12E6, with both titrant and solution adjusted to the appropriate ionic strength by addition of NaCl. 100 – ST readings were corrected by subtraction of turbidity values for a polymer-free blank. \( Y_c \) was determined as the surfactant composition at which an abrupt turbidity is initiated (see Figure 2B). Surface potentials of C12E6/SDS micelles at \( I \) and \( Y \) corresponding to the critical conditions defined as in Figure 2B were determined by means of fluorescent or potentiometric probes, as previously reported.

Results and Discussion

Phase Boundaries. Critical conditions for complexation may be described by a phase boundary, as shown in Figure 3, in which we plot the dependence of \( Y_c \) on ionic strength for the system PDMDAAC-SDS/C12E6. As noted previously, such phase boundaries are independent of the concentration of polymer or micelle. This is because they reflect only the local interaction of a sequence of polymer segments with the micelle surface, which has a surface charge density \( \sigma \). The dependence of \( \sigma \) on \( Y \) is given by

\[
\sigma \sim A_N + (A_A - A_N) Y
\]

(1)

where \( A_N \) and \( A_A \) are the effective molecular head group areas of nonionic and anionic surfactants, respectively. (With units of esu/cm² for \( \sigma \) and cm²/molecule for \( A \), the proportionality constant is the charge per ionic headgroup.) Since \( A_N \) and, especially,

Figure 3. Dependence of critical micelle composition on ionic strength for PDMDAAC-C12E6/SDS (from data of Figure 2B). The homogeneous solution phase exists to the right and below the line.

<table>
<thead>
<tr>
<th>I, M</th>
<th>( Y_c )</th>
<th>( R_0, \AA )</th>
<th>( \Psi_{HHC} )</th>
<th>( \Psi_{DA} )</th>
<th>( 10^2 \rho_{HHC} )</th>
<th>( 10^2 \rho_{DA} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.056</td>
<td>72</td>
<td>-12</td>
<td>-11</td>
<td>2.1</td>
<td>2.0</td>
</tr>
<tr>
<td>0.10</td>
<td>0.095</td>
<td>75</td>
<td>-18</td>
<td>-8.8</td>
<td>-4.5</td>
<td>-2.2</td>
</tr>
<tr>
<td>0.20</td>
<td>0.145</td>
<td>91</td>
<td>-20</td>
<td>-13</td>
<td>-6.6</td>
<td>-4.2</td>
</tr>
<tr>
<td>0.40</td>
<td>0.230</td>
<td>137</td>
<td>-21</td>
<td>-10.6</td>
<td>-9.4</td>
<td>-4.7</td>
</tr>
<tr>
<td>0.60</td>
<td>0.285</td>
<td>194</td>
<td>-22</td>
<td>-11</td>
<td>-11.7</td>
<td>-5.8</td>
</tr>
</tbody>
</table>

*From QELS. †From \( \rho \) of HHC probe solubilized in micelle. ‡From \( \rho \) of dodecanoic acid probe solubilized in micelle. §From columns 3 and 4, via eq 2. ¶From columns 3 and 5, via eq 2.

\( A_N \) are complex functions of \( Y \) and \( I \), so we measure the surface potential \( \psi \) and then deduce \( \sigma \) via the linearized Gouy-Chapman (G-C) equation for a sphere of radius \( a \)

\[
\sigma = (\psi_{0}/4\pi)(\kappa + 1/\alpha)
\]

where \( \kappa \) is the solvent dielectric constant. In the case of SDS/C12E6 micelles, \( \psi_{0} \) may be measured using amphiphilic probe molecules, namely dodecanoic acid (DA) and heptadecylhydroxyoxycoumarin (HHC), by a procedure described elsewhere. Under conditions of \( I \) and \( Y \) corresponding to the phase boundary of Figure 3, the HHC probe yields potentials ranging from -12 to -22 mV as one progresses along the phase boundary in the direction of increasing \( Y \), while \( \psi_{0} \) for the DA probe under the same set of conditions is virtually constant at -11 ± 1 mV. This difference is probably a result of the greater hydrophobicity of HHC which allows the probe to reside in the more interior region of the micelle, closer to the mean locus of the sulfonate groups; the DA head group, on the other hand, may hydrogen-bond to the polyether head groups and is likely to be more distal with respect to the micelle core. We proceed to evaluate \( \sigma \) with both sets of data, using values for the radii of the mixed micelles obtained by QELS. Application of the linearized G-C equation for spherical particles then yields the surface charge densities shown in Table 1.

In Figure 4, we plot the ionic strength dependence of \( \sigma \) obtained with the two probes. It can be seen that both sets of data reveal, within experimental error, a linear dependence of \( \sigma \) on \( I^{1/2} \) (the regression coefficient for the data obtained with DA probe is better

(28) The dimensions of the C12E6/SDS mixed micelles suggest that a cylindrical model could be more realistic. Numerical solutions of the expression analogous to eq 2 for cylindrical colloids were carried out. For \( I < 0.4 \), the results were identical, but at the largest ionic strength, the approximation of spherical geometry introduces ca. a 10–15% negative error in calculated values of \( \sigma \). Corrections for this would slightly improve the linearity of the plots in Figure 3.

TABLE II: Dimensional and Electrostatic Properties of DMDAO Micelles at pH and Ionic Strengths Corresponding to Critical Conditions for Binding of PAMPS

<table>
<thead>
<tr>
<th>I, M</th>
<th>pH</th>
<th>$\beta$</th>
<th>$\psi_0$, mV</th>
<th>$R_s$, Å</th>
<th>$R^*$, Å</th>
<th>$n'$</th>
<th>$10^3\sigma_\gamma$, esu cm$^{-2}$</th>
<th>$10^2\sigma_{GC}$, esu cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>6.98</td>
<td>0.08</td>
<td>10.7</td>
<td>28</td>
<td>95</td>
<td>3.3</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>6.88</td>
<td>0.10</td>
<td>11.8</td>
<td>31</td>
<td>110</td>
<td>5.0</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>6.77</td>
<td>0.12</td>
<td>13.0</td>
<td>35</td>
<td>135</td>
<td>6.5</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>6.68</td>
<td>0.15</td>
<td>14.6</td>
<td>39</td>
<td>170</td>
<td>8.0</td>
<td>5.8</td>
<td></td>
</tr>
</tbody>
</table>

* At critical conditions (determined from "type 1" turbidimetric titration of polyanion–micelle solution. * From pH$_{crit}$ in conjunction with titration curve. * From $-2.303 (k_BT/e) (pK_a - pK_b)$ (see ref 21). * By QELS. * From analysis of titration data (see ref 21). * By interpolation of static light scattering data from ref 22. * From $\sigma_{crit}$/4$n'a^2$. * From eq 2.

Figure 4. Dependence of critical micelle surface charge density on the square root of ionic strength for the system PDMDAAC–SDS/C12E6. From data of Figure 3, heptadecylhydroxyoxamamin is used as a probe for the micelle surface potential (lower curve) or dodecaneic acid (upper curve).

Figure 5. *Phase boundary* for DMDAO–PAMPS (open symbols) and DMDAO–NVP–AMPS (filled symbols) expressed as the ionic strength dependence of the critical degree of protonation of the micellar surfactant.

Figure 6. Dependence of micelle surface charge density on ionic strength for DMDAO with PAMPS (lower curve) and PAMPS–NVP (upper curve), from data of Figure 5. Regression coefficients of fitted lines: 0.992 (lower curve) and 0.999 (upper curve).

6 show the dependences of $\sigma_{crit}$ on I for both PAMPS and P(AMPS–NVP).

The linear dependence of $\sigma_{crit}$ on $I^{1/2}$ in Figure 6 confirms the result reported above for the PDMDAAC–SDS/C12E6 system of reversed charge. We will first discuss this functional relationship, namely that $\sigma_{crit}$ varies linearly with $\kappa$, the Debye–Hückel parameter. We may compare this phenomenological result with several theoretical treatments for the binding of polyelectrolytes to oppositely charged colloids whose surfaces may be treated as charged planes, namely those of Wiegel, Evers et al., and a modification of Wiegel's treatment by Muthukumar. Considering the adsorption of a charged macromolecule on a surface with a weak opposite charge, Wiegel found a phase transition characterized by the expression

$$\lambda q = k_B T(5.7985)\epsilon^{3/2}/48\pi$$

where $q$ is the charge on a polymer repeat unit, $k_B$ the Boltzmann constant, $\epsilon$ the dielectric constant of the medium, and $I$ the length...
of a repeat unit. For a given polymer at constant temperature, eq 3 then gives (since ξ is only weakly dependent on κ) \( \sigma_c \sim \kappa^4 \), a distinctly different result from what we observe in Figures 4 and 6. More recently, Muthukumar modified the Wiegel treatment by considering the effect of the ion-strength dependence on the polymer configuration. This leads to a result identical to eq 3, except that \( P \) is replaced with \( H_0 \), where \( H_0 \) is the q-dependent step length, also given by \( lx^2 \), with \( \alpha \) being the Flory expansion factor. Since \( \alpha \) varies inversely with ion strength, hence inversely with \( \kappa \), the \( \kappa \) dependence on \( \sigma_c \) is substantially diminished but not necessarily to the first power in \( \kappa \). The presence of a polymer expansion term also leads to a molecular weight effect: since \( H_0 \) increases with MW, so does \( \sigma_c \), yielding the result that lower MW polymers (with smaller \( H_0 \) ) bind more strongly.\(^{11} \)

This result is contrary to experimental findings we have reported elsewhere, namely that \( \beta \) varies inversely with MW, at least in the regime of 1 in which DMDAO micelles are rodlike.\(^{12} \)

A Simple Model. The situation under consideration here is represented schematically in Figure 7. The stippled area represents the region in which the potential due to the colloid surface exceeds \( k_BT/e \). Its dimensions depend on the colloid surface charge, curvature, and \( \kappa \). (Note that this is not the Debye-Hückel ion atmosphere, whose thickness does not depend on \( \kappa \).) A sequence of polymer segments occupies a position alongside a colloid surface, in a configuration which does not substantially reduce its entropy. One of these sequences with a net charge \( Z_p \) becomes attached to the colloid surface with a change in electrostatic interaction energy \( (W_{d}) \). If this energy is such that \( W_{d} > k_BT/\kappa \), we propose that there will be binding accompanied by the measurable phase transition. It is clear that \( W_{d} \) should depend on \( Z_p \), and hence on \( \kappa \). The magnitude of \( Z_p \) depends also on the potential in the vicinity of the head group charged surface and on the thickness of the region of high potential surrounding the particle, which in turn increases with the colloid surface charge density and decreases with theionic strength. Thus, \( W_{d} \) should increase with \( \kappa \) and decrease with \( \kappa \), consistent with our finding that \( \sigma_c \sim \kappa^3/\kappa \).

To treat the model more quantitatively, while avoiding complicated mathematical formulations, we begin with the rather severe assumption that the energetics of the cooperative binding of the segment sequence with net charge \( Z_p \) to an oppositely charged sphere can be approximated by the binding of an equivalent point charge \( Z_p \). This assumption will be most valid when the distance between the bound polymer segments and the colloid surface is at least a few Debye lengths. The binding energy is then

\[
W_{d} = Z_{d} \int E(x) \, dx = -Z_{d} \int \frac{d\phi}{dr} \, dr
\]

where \( E \) is the electric field at a distance \( x = r - a \) from the colloid surface. Solving eq 4 we obtain

\[
W_{d} = Z_{d} \psi_{d}(a)
\]

which from eq 2 may be written as

\[
W_{d} = Z_{d} (4\pi \sigma/c_{0})(\kappa + 1/a)^{-1}
\]

Ionic strength becomes less certain at very low concentrations of added salt because of the difficulty of assessing the contributions of the surfactant and polymers to I. However, increases in the salt concentration in this micellar system are accompanied by drastic changes in micelle dimensions, which would complicate attempts to evaluate treatments such as those described above. Future experiments will focus on systems in which well-defined colloidal geometry can be maintained over a range of \( \alpha \) and \( I \).

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Registry No. DMDAO, 1643-20-5; PAMPS, 55141-01-0; P(AAMPS-NVP), 53845-64-0; SDS, 151-21-3; C12E6, 3055-96-7; PDMDAAC, 26062-79-3.

Conformational Characteristics of Short Poly(ethylene oxide) Chains Terminally Attached to a Wall and Free in Aqueous Solution

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Many systems of practical importance contain short polymer chains terminally attached at interfaces. Such systems include sterically stabilized colloids, coated surfaces, compatibility enhancers, micelles, and biological membranes. Although it is generally accepted that for very short chains the well-known polymer scaling laws apply, the lower limit of applicability of such laws cannot be easily established a priori. For an aqueous solution of poly(ethylene oxide) (PEO), a system of considerable fundamental and practical importance, we have studied the lower limit of validity of polymer scaling laws for isolated PEO chains free in solution and attached at one end to an inert and impenetrable planar interface (a wall). For this purpose, we have utilized the rotational isomeric state (RIS) model to describe the conformations of PEO chains in water over the temperature range 0-100 °C. The root-mean-square end-to-end distance of free PEO chains ranging in length from 3 to 18,000 bonds was calculated exactly using Flory's serial matrix multiplication method. For the terminally attached PEO chains, this exact method cannot be utilized due to the spatial symmetry breaking induced by the wall. Consequently, we have used a Monte Carlo approach to the RIS model to calculate the root-mean-square end-to-end distance of attached chains ranging in length from 3 to 900 bonds. We find that polymer scaling laws are applicable within an uncertainty of a few percent for fairly short PEO chains. Specifically, the shortest free PEO chain that satisfies scaling with a 2% accuracy has 12 bonds, while the shortest attached chain has 30 bonds. It is also interesting to note that we find a weak temperature variation of the root-mean-square end-to-end distance over the temperature range studied for both free and attached chains. Our results are valid under 0-solvent conditions, as well as over a range of good-solvent conditions. A discussion of the implications of these new findings for modeling micelles containing alkyl poly(ethylene oxide) \( (C_xE_y) \) nonionic surfactants in aqueous solution, as well as for interpreting results of force measurements between two surfaces coated with \( C_xE_y \) surfactants and immersed in water, is also presented.

I. Introduction

Many systems of technological importance contain chain polymer molecules attached at one end to an interface.1 The interface may be a solid surface or the interfacial region between two liquids, between liquid and air, or between melts or solutions of homopolymers. The mechanism of chain attachment depends on the nature of the interface; for example, for solid surfaces, the chain end may be chemically bonded to the surface (end-grafted chain). Depending on the type of interface and method of attachment, a number of important physical systems are encountered. These include the following: (i) colloids sterically stabilized by end-grafted chains, where solid particles are protected against flocculation by attaching grafted chains that have more affinity for the solvent than for each other, (ii) polymeric surfactants, macromolecules composed of a polar end group attached to a hydrocarbon chain that is insoluble in polar solvents, which due to their amphiphilic nature reside preferentially at oil-water interfaces and can therefore be utilized as emulsifiers as well as agents to lower interfacial tensions, and (iii) polymer compatibilizers, macromolecules formed from two dissimilar polymers joined end to end ( diblock copolymers), which due to their special chemical architecture adsorb preferentially at interfaces between the constituent polymers and are therefore capable of stabilizing microdomains of one incompatible homopolymer in another.

Most fundamental work in these and related systems has assumed that the polymer chains are sufficiently long to allow the use of theoretical concepts and methodologies from polymer science, such as polymer scaling laws, which are expected to be valid in the limit of infinitely long chains.2 However, it is noteworthy that the systems described in i-iii above often contain relatively short chains. In particular, an important class of systems of this type involves nonionic surfactants of the alkyl poly(ethylene oxide) \( (C_xE_y) \) family. The \( C_xE_y \) molecules, which are among the most widely studied nonionic surfactants, are linear chains composed of two dissimilar blocks: the hydrophobic tail \( C_x \), an alkane block having \( i \) carbon atoms (or \( i = 1 \) bonds) in the backbone, and the hydrophilic head \( E_y \), a poly(ethylene oxide) (PEO) block having \( j \) ethylene oxide units (or \( 3j \) bonds) in the chain. In many of the investigations involving these surfactants, both \( i \) and \( j \) are less than 20. In other words, the chains of interest contain less than 100 bonds. For such relatively short chains, the validity of polymer scaling laws is no longer warranted. This observation is particularly relevant for two areas that involve short chains. One is the interpretation of recent experiments involving the measurement3 of forces between two surfaces coated with \( C_xE_y \) nonionic surfactants and immersed in aqueous solution, with the \( E \) chains exposed to the aqueous solvent.4,5 The other one is the developement of theoretical account of theoretical and experimental aspects of long-chain polymers attached at one end to interfaces (polymer brushes), see: Milner, S. T. Science 1991, 251, 905.


(3) For a review on surface force measurements, see: Israelachvili, J.; McGuiggan, P. M. Science 1988, 241, 795.

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