

Viscosity of Polyelectrolyte Solutions with Oppositely Charged Surfactant[†]

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The rheological properties of aqueous solutions of poly(acrylic acid) and an oppositely charged surfactant, dodecyltrimethylammonium bromide (C₁₂TAB), are reported. The solution viscosity decreases rapidly as surfactant is added. The effects of polymer molecular weight, polymer concentration, and polymer charge have been studied with no added salt. The results are compared with the predictions of a simple model based on the scaling theory for the viscosity of unentangled semidilute polyelectrolyte solutions in good solvent.¹ This model takes into account two effects of added surfactant. The effective chain length of the polyelectrolyte is shortened when a significant fraction of the length wraps around micelles, and an effective addition of salt arises from the polyelectrolyte and surfactant counterions, further lowering the viscosity. The only parameter used in this model is independently determined using an ion-selective electrode, allowing the model to make a quantitative prediction of solution viscosity for strongly charged polyelectrolytes with no adjustable parameters. Comparison with literature data for weakly charged polyelectrolytes suggests only partial binding of polymer to the micelle surface in this case.

Introduction

Polyelectrolytes and surfactants are often found together in aqueous formulations of cosmetics, detergents, pharmaceuticals, and coatings to simultaneously control surface tension and rheology. Consequently, the interaction between polyelectrolytes and oppositely charged surfactants has been studied extensively. Owing primarily to the strong electrostatic attraction between these species and the release of their condensed counterions on binding,^{2,3} there is a strong thermodynamic driving force for association. This is evidenced by the very low critical aggregation concentration (CAC), the surfactant concentration at which micelles form in the presence of oppositely charged polyelectrolyte chains.^{4–7} The CAC is far below the concentration where surfactant first forms micelles without polymer present, because the polyelectrolyte stabilizes the charge on the micelle surface and no counterions are required to condense on either the micelle or the section of polymer that is associated with the micelle.² Various methods have been employed to determine the CAC, such as surface tension, calorimetry, dye solubilization, and binding isotherm measurements using surfactant-selective, solid-state membrane electrodes. The latter method is used the most because it directly measures the free surfactant activity in the polyelectrolyte solution. The strong interaction causes precipitation at concentrations near the stoichiometric balance point, where equal amounts of surfactants and charged monomers are present. In this study, we focus on solutions with excess polyelectrolyte.

For our study of viscosity effects, a model system of poly(acrylic acid) (PAA) partially neutralized with NaOH and dodecyltrimethylammonium bromide (C₁₂TAB) was chosen. The charge on the polymer is easily changed by the amount of

NaOH added, and this particular mixture has been studied previously.^{7–12} The micelles formed in the PAA/C₁₂TAB system are known to be roughly spherical, with aggregation numbers on the order of 50–100, typical of spherical micelles.^{7–12} This number is similar to the aggregation number of the corresponding surfactant micelles formed in aqueous solutions without polymer present.¹³ Indeed, a specific comparison of aggregation numbers for C₁₂TAB micelles^{3,8} in the presence of sodium polyacrylate (PAA that has been fully neutralized with NaOH, herein termed NaPAA) at various concentrations and levels of NaBr indicates that the aggregation number is 60 ± 4 independent of the amount of NaBr or NaPAA present, virtually identical to the aggregation number of 62 for C₁₂TAB micelles formed with no polymer present.^{3,8}

Furthermore, the CAC has been measured for the NaPAA/C₁₂TAB system. The CAC of C₁₂TAB increases as the concentration of NaPAA is raised^{3,8} because the counterions released from the section of the NaPAA chain that binds to the C₁₂TAB micelle gain less entropy when the Na⁺ ion concentration is raised.^{2,3} In the presence of 10 mM NaPAA with no added salt, the CAC is roughly 0.1 mM.^{3,8} At 100 mM NaPAA the CAC is roughly 0.6 mM,³ and at 1.0 M NaPAA the CAC can be estimated as 3 mM (extrapolating the data in Figure 2 of ref 3).

At low polyelectrolyte concentrations with no added salt, there is a semidilute unentangled solution regime that spans a wide concentration range. Addition of surfactant to such solutions lowers the viscosity dramatically.^{14–21} In 1984, Abuin and Scaiano¹⁴ showed that this viscosity reduction is far stronger than the simple charge screening resulting from addition of monovalent salt. In this paper, a simple viscosity model is introduced to predict the reduction of the viscosity of a polyelectrolyte solution upon addition of oppositely charged surfactant, based on the scaling theory for viscosity of unentangled semidilute polyelectrolyte solutions.¹ The model ac-

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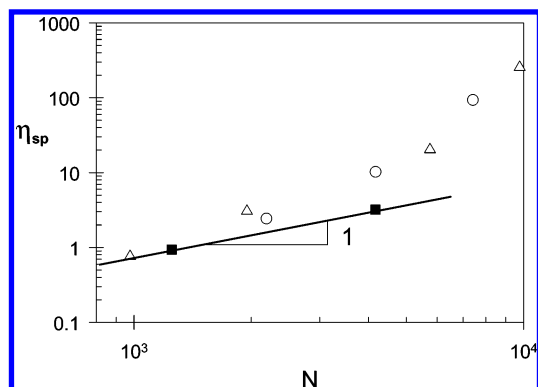


Figure 1. Chain length dependence of specific viscosity in the semidilute regime at $c_p = 2$ mM for poly(acrylic acid) partially neutralized with NaOH ($\alpha = 0.5$, filled squares), sodium poly(2-acrylamido-2-methylpropanesulfonate) ($\alpha = 1$, open circles²⁴), and sodium poly(styrenesulfonate) ($\alpha = 1$, open triangles²²).

counts for both changes in the effective chain length of the polyelectrolyte when it wraps around the exterior of the spherical micelles and changes in ionic strength resulting from surfactant and polyelectrolyte counterions. The model makes quantitative predictions of viscosity based solely on a parameter determined from ion-selective electrode measurements of activity for the polyelectrolyte's counterion. It is important to point out that we only treat solutions with a stoichiometric excess of charged monomers relative to the oppositely charged added surfactant.

Background Theory

A Zimm model for the viscosity of dilute polyelectrolyte solutions has been proposed by Dobrynin et al.¹ The specific viscosity η_{sp} is predicted to scale as the $4/5$ power of the degree of polymerization N and to decrease as monovalent salt (with molar concentration c_s) is added:

$$\eta_{sp} \equiv \frac{\eta - \eta_s}{\eta_s} \approx N^{4/5} \left[1 + \left(\frac{2c_s}{fc_p} \right) \right]^{-3/5} \quad c_p < c^* \quad (1)$$

The solution viscosity is η , η_s is the solvent viscosity, f is the fraction of monomers bearing an effective charge, and c_p is the molar concentration of monomers. Hence, the term in parentheses is the ratio of concentrations of small ions from added salt ($2c_s$) and the free counterions from the polyelectrolyte (fc_p). The overlap concentration c^* is the crossover concentration between the dilute and semidilute regimes.¹

A Rouse model for the viscosity of unentangled semidilute polyelectrolyte solutions has also been proposed by Dobrynin et al.¹ This scaling theory predicts that the specific viscosity η_{sp} of unentangled polyelectrolyte solutions is proportional to the degree of polymerization N of the chains and decreases with addition of monovalent salt (with molar concentration c_s):

$$\eta_{sp} \approx N \left[1 + \left(\frac{2c_s}{fc_p} \right) \right]^{-3/4} \quad c^* < c_p < c_e \quad (2)$$

This equation holds for concentrations above the overlap concentration but below the entanglement concentration c_e . The dependence of specific viscosity on added salt has been found to be quantitatively described by eq 2 over wide ranges of salt and polyelectrolyte concentrations.²² In particular for poly(acrylic acid) in the high salt limit ($2c_s \gg fc_p$) it has been shown²³ that $\eta_{sp} \propto c_s^{-0.7}$ and $\eta_{sp} \propto f^{0.6}$ showing that the scaling theory¹ is reasonable. Figure 1 shows that the viscosity data in

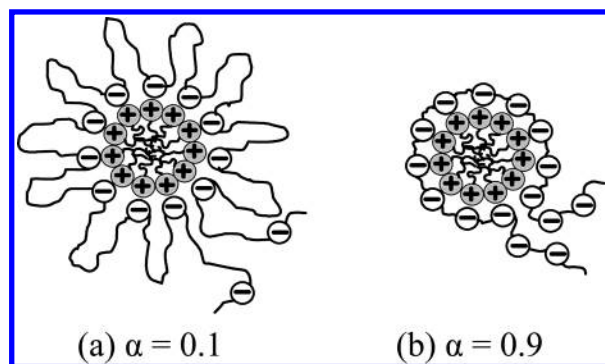


Figure 2. Schematic illustration of the interaction of a surfactant micelle with oppositely charged polyelectrolytes of different neutralization extents. The counterions of the surfactant and of the polyelectrolyte section associated with the micelle are free in solution (not shown).

the semidilute unentangled regime have the dependence on the degree of polymerization predicted by eq 2. However, it is important to realize that, once the polyelectrolytes become entangled (for $c > c_e$), eq 2 no longer applies, as demonstrated by the other polyelectrolyte viscosity data shown in Figure 1 at higher degrees of polymerization.

As oppositely charged surfactant is added to a polyelectrolyte solution, the viscosity of the solution is lowered by two effects. First, the polyelectrolyte loses some of its effective chain length in wrapping around the exterior of the surfactant micelles. We assume that one neutralized monomer is bound to each surfactant headgroup in the micelle as shown schematically in Figure 2. We further assume that neither the placement of charges along the polyelectrolyte chain nor the fraction of neutralized monomers is altered by the interaction with the micelle. The polyelectrolyte chain will wrap efficiently around the micelle, using a section of chain containing a number of neutralized monomers that is equal to the aggregation number of the micelle.

As shown in Figure 2, the polyelectrolyte wastes a lot less chain length wrapping around the micelle for $\alpha = 0.9$ than for $\alpha = 0.1$, where α is the degree of neutralization, defined as the molar ratio of added NaOH and acrylic acid monomer. In the section of chain bound to the micelle surface, the monomers that have not been neutralized simply exist as loops extending from the bound neutralized monomers on the micelle surface.

If c is the concentration of surfactant, the fraction of polyelectrolyte monomers tied up with micelles is $c/(\alpha c_p)$, so the fraction of polyelectrolyte monomers that are free from micelles (proportional to the effective polyelectrolyte chain length) is $1 - c/(\alpha c_p)$. The second effect is that the ionic strength (the concentration of free ions) in solution increases as surfactant is added. These ions consist of polyelectrolyte counterions released upon interacting with the surfactant micelle, and counterions of surfactant molecules. We assume that, for each surfactant molecule bound to a polyelectrolyte monomer, there is effectively one salt molecule added to the solution, comprising the polyelectrolyte monomer's counterion and the surfactant's counterion. Since in most cases the CAC is very small, practically all added surfactant is bound to the polyelectrolyte, making the effective salt concentration c , the concentration of added surfactant. The number density of free polyelectrolyte counterions also diminishes as surfactant is added because the fraction of the chain bound to micelles no longer has free counterions. We assume that the fraction of free counterions on the remaining (unbound) sections of chain is the same as without added surfactant, making the number density of free counterions $fc_p[1 - c/(\alpha c_p)]$. The ratio of salt ions to free

polyelectrolyte counterions ($2c_s/fc_p$) in eqs 1 and 2 becomes $2c/(fc_p[1 - c/(\alpha c_p)])$. Equations 1 and 2 are therefore modified to describe the viscosity of polyelectrolyte solutions as oppositely charged surfactant is added:

$$\frac{\eta_{sp}(c)}{\eta_{sp}(0)} = \left[1 - \left(\frac{c}{\alpha c_p}\right)\right]^{4/5} \left[1 + \frac{2c}{fc_p \left[1 - \left(\frac{c}{\alpha c_p}\right)\right]}\right]^{-3/5} \quad c_p < c^* \quad (3)$$

$$\frac{\eta_{sp}(c)}{\eta_{sp}(0)} = \left[1 - \left(\frac{c}{\alpha c_p}\right)\right] \left[1 + \frac{2c}{fc_p \left[1 - \left(\frac{c}{\alpha c_p}\right)\right]}\right]^{-3/4} \quad c^* < c_p < c_e \quad (4)$$

$\eta_{sp}(c)$ and $\eta_{sp}(0)$ are the specific viscosities of polymer with and without added surfactant, respectively. In both eqs 3 and 4, the first term accounts for the reduction in chain length that is effectively lost in wrapping the polyelectrolyte chain around the micelle using consecutive neutralized monomers along the chain to bind to each surfactant headgroup in the micelle (Figure 2). The second term accounts for the change in ionic strength resulting from the surfactant counterions and polyelectrolyte counterions that are released into the solution when the surfactant binds to the polyelectrolyte.² We will see below that f can be determined from measurements with an ion-selective electrode, allowing eqs 3 and 4 to predict the solution viscosity with *no adjustable parameters*.

The specific viscosity predicted by eq 3 reaches zero when the concentration of added surfactant (c) equals the total concentration of charged monomers in the solution (αc_p). At this point all polymer chains are charge-balanced by added surfactant and precipitate from solution, so the viscosity of the solution equals the viscosity of water.

Experimental Section

Sample Preparation. PAA samples (with $M = 90000$ and 300000 , reported by the manufacturer) were obtained from Polysciences as 25% solutions in water. The polymers were exhaustively dialyzed with deionized distilled water by using a dialyzer with a spiral membrane that only allows species with $M < 3000$ to pass through (Amicon). Following dialysis, the polymer was freeze-dried and then vacuum-dried at 40°C . C₁₂-TAB from Aldrich (99% purity) was recrystallized twice from absolute ethanol and dried under vacuum.

A stock solution of PAA was prepared in deionized distilled water and then titrated with NaOH to the desired degree of neutralization, α . Then the surfactant solution with suitable concentration was slowly added using a micropipet while the solution was gently stirred. This was done to prevent the solution from premature precipitation if the surfactant concentration gets too high locally. This is important, since the strong interaction between opposite charges leads to the irreversible formation of a water-insoluble PAA/C₁₂TAB complex. The concentration was then adjusted to the final concentration by adding deionized distilled water. In this study, the concentrations of PAA were $c_p = 0.01, 0.10$, and 1.0 M (moles of monomer per liter) with $\alpha = 0.30, 0.50$, and 0.90 . For both molecular weights, the concentrations studied are all lower than the concentration where entanglement effects become important.

Viscosity Measurement. Viscosity measurements were made using two commercial rheometers. A controlled-strain-rate Contraves LS-30 viscometer with a concentric cylinder geometry

TABLE 1: Experimentally Determined Parameters Needed for the Viscosity Prediction of Eqs 3 and 4 for the Poly(acrylic acid)/C₁₂TAB Data Presented in Figures 3–5

α	f^a	$\eta_{sp}(0)(90\text{ K})$			$\eta_{sp}(0)(300\text{ K})$
		10 mM	100 mM	1.0 M	10 mM
0.3	0.14	2.11	6.78	39.01	6.02
0.5	0.18	2.49	8.25	54.84	7.27
0.9	0.23	2.75	8.32	77.06	

^a Measured with a sodium-selective electrode for $M = 90000$ at $c_p = 10$ mM.

was used to measure viscosities less than 3 P. The temperature was controlled at $25.0 \pm 0.2^\circ\text{C}$ using a temperature-controlled water bath surrounding the measuring cup in addition to the standard circulating water inside the cup holder. Additionally, some measurements were made using a Rheometrics stress rheometer equipped with a large concentric cylinder geometry, described in detail elsewhere.²⁵ All three rheometers were calibrated with Newtonian standard fluids of appropriate viscosity. All solutions in this study were found to be Newtonian at shear rates in the range of $0.02\text{--}100\text{ s}^{-1}$, and hence, measurements at different shear rates were averaged to determine the viscosity.

Fraction of Effectively Charged Monomers, f . The counterions of PAA used in this study are sodium ions (Na^+); therefore, the fraction of effectively charged monomers can be determined from the ratio of free sodium ion concentration and the polymer concentration of the solution without added surfactant. The free sodium ion concentration is measured using a sodium-selective electrode (Orion). This electrode is equipped with a glass sensing membrane that measures the activity of sodium ions in solution. When it comes in contact with a solution containing sodium ions, an electrical potential develops across the membrane surface. The measured potential E determines the activity a of sodium ions, according to the Nernst equation²⁶

$$a = \exp[(E - E_o)\mathcal{F}/RT] \quad (5)$$

where E_o is the difference between the standard potentials of the indicator and reference electrodes and \mathcal{F} is the Faraday constant. The electrode was calibrated using vacuum-dried sodium bromide (NaBr) solutions in deionized distilled water. While eq 5 expects a slope of 59.1 mV per decade of Na^+ concentration (assuming an activity coefficient of unity), we measured 60.8 mV per decade of Na^+ concentration, and used this for calibrating the electrode to give the concentration of free sodium ions in solution. The fraction of polyelectrolyte monomers that are effectively charged (with free counterions) f is shown along with the specific viscosities of the PAA solutions without added surfactant, $\eta_{sp}(0)$, in Table 1.

Results

For all of the semidilute unentangled solutions studied, the viscosity of PAA solutions decreases upon adding C₁₂TAB. By using eq 4 with the values of parameters reported in Table 1, the specific viscosities of various concentrations of PAA ($M = 90,000$) with added C₁₂TAB were calculated and shown as lines in Figures 3 and 4. The prediction also works well with the higher molecular weight PAA sample ($M = 300,000$) as shown in Figure 5.

As shown in Figures 3–5, the predictions of η_{sp} are in good agreement with experimental data for all three concentrations

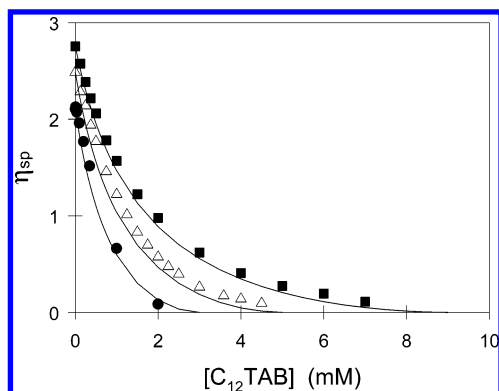


Figure 3. Specific viscosity of $c_p = 10$ mM PAA ($M = 90000$) as a function of added $C_{12}TAB$ with $\alpha = 0.3$ (filled circles), $\alpha = 0.5$ (open triangles), and $\alpha = 0.9$ (filled squares) compared with the predictions of eq 4 with the parameters listed in Table 1 (lines).

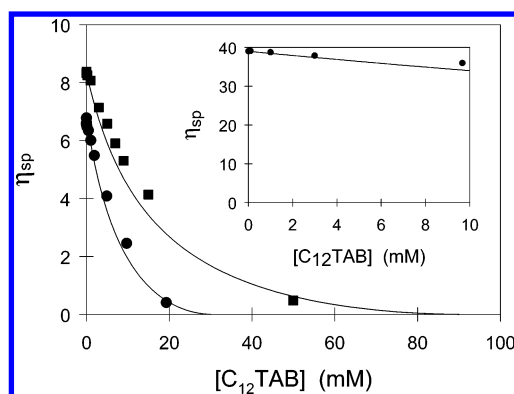


Figure 4. Specific viscosity of $c_p = 100$ mM PAA ($M = 90000$) as a function of added $C_{12}TAB$ with $\alpha = 0.3$ (circles) and $\alpha = 0.9$ (squares) compared with the predictions of eq 4 with the parameters listed in Table 1 (lines). The inset is for $c_p = 1.0$ M PAA solutions with $\alpha = 0.3$.

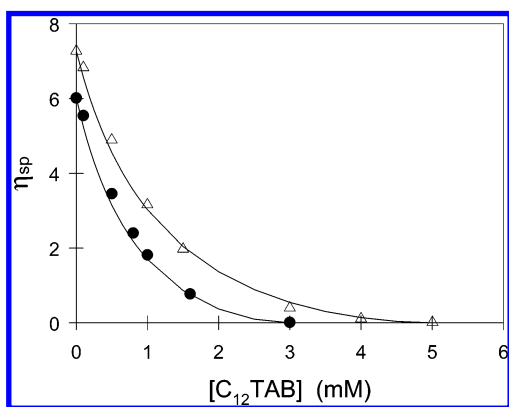


Figure 5. Specific viscosity of $c_p = 10$ mM PAA ($M = 300000$) as a function of added $C_{12}TAB$ with $\alpha = 0.3$ (filled circles) and $\alpha = 0.5$ (open triangles) compared with the predictions of eq 4 with the parameters listed in Table 1 (lines).

and two different molecular weights of PAA, despite the fact that f was determined for PAA with $M = 90000$. The results suggest that f is independent of polyelectrolyte molecular weight, as expected by theory.¹ At 1.0 M PAA, shown in the inset to Figure 4, precipitation was unavoidable for $C_{12}TAB$ additions above 10 mM, consistent with the phase diagram of Lindman and Thalberg.²⁷ Hence, the range of c/c_p is necessarily quite small for high polyelectrolyte concentrations.

In principle, the data with $\eta_{sp} < 1$ should be modeled using eq 3 with a prefactor that matches the prediction of eq 4 at c^* , instead of eq 4. Since eq 3 has a weaker dependence on surfactant concentration than eq 4, this would make the viscosity predictions at high concentrations in Figures 3–5 somewhat larger. However, it is a subtle change, and the data are actually described better by the simple application of eq 4 to all data. Hence, we ignored this crossover for simplicity and compared the data below c^* with eq 4. The remarkable predictive power of the simple model suggests that the idea of neutralized monomers binding to the micelle surface in a stoichiometric fashion (Figure 2) is approximately correct.

Discussion

The aggregation number of ionic surfactant micelles formed in the presence of oppositely charged polyelectrolyte has been reported to be somewhat larger or somewhat smaller than the aggregation number of the micelles formed without polymer present (see refs 2 and 3, and the references therein). Such changes are not fully understood at present. One very nice feature of our simple model is that the predictions are insensitive to aggregation number (as long as the micelles are still roughly spherical!). Viscosity is determined by the size of the polyelectrolyte chain in solution. In our model the size of the chain, and hence the viscosity, is determined simply from the fraction of monomers associated with micelles, not the details of the micelle sizes. This simplifying feature is crucial to the general applicability of our model, because some systems of polyelectrolyte with oppositely charged surfactant have the aggregation number change with stoichiometry.⁹ Our model predicts that viscosity only depends on the molar ratio of added surfactant to polyelectrolyte monomer (c/c_p), the extent of neutralization α , and the fraction of monomers bearing an effective charge f .

A cautionary note is in order for the case of low neutralization extents for weak polyacids (and weak polybases). Fundin et al.⁹ have shown that binding to the micelle can cause more of the acid groups to dissociate, since the presence of the oppositely charged micelle favors dissociation.²⁸ Such dissociation would need to be taken into account properly for a quantitative description of the viscosity of weak polyacids and polybases as oppositely charged surfactant is added.

Given the success of our simple model in predicting the viscosity as $C_{12}TAB$ is added to aqueous solutions of PAA with various neutralization extents and chain lengths, we are encouraged to test our model against literature data. Kogej and Skerjanc^{19,20} reported the viscosity of dilute solutions of anionic polyelectrolytes as the cationic surfactant cetylpyridinium chloride ($C_{16}PC$) is added. For NaPAA ($\alpha = 1$) with $M = 10000$, we know the fraction of charged monomers will be approximately the same as that for our PAA sample with $\alpha = 0.9$ ($f = 0.23$; see Table 1). The experimental data are compared to the prediction of eq 3 with $\alpha = 1$ and $f = 0.23$ in Figure 6. The agreement is remarkable with the possible exception of the highest concentration of added surfactant. At high concentrations of added surfactant the model may well break down because often more interesting phases are formed than the simple random placement of spherical micelles that is assumed in our model. Both lamellar phases²⁹ and cubic phases of spherical micelles^{30,31} have been reported for polyelectrolyte solutions with high concentrations of added oppositely charged surfactant.

Similarly superb agreement between model and experiment is seen for the viscosity data of Kogej and Skerjanc^{19,20} when $C_{16}PC$ is added to dilute solutions of NaPSS with $M = 70000$, as shown in Figure 7. The extent of neutralization is $\alpha = 1$ for

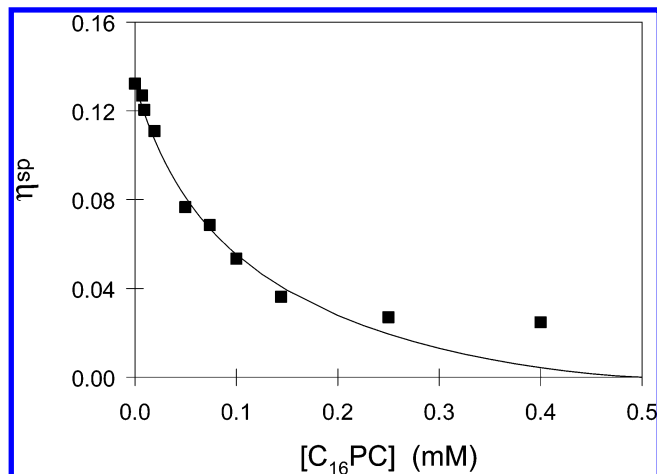


Figure 6. Specific viscosity of $c_p = 0.5$ mM NaPAA ($M = 10000$) as a function of added $C_{16}PC$ with $\alpha = 1$ (data of Kogej and Skerjanc^{19,20}) compared with the predictions of eq 3 with $f = 0.23$.

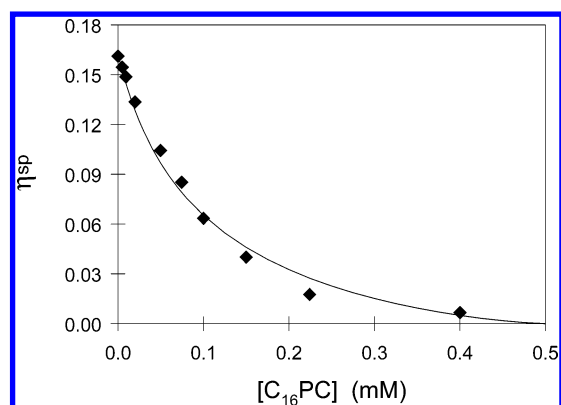


Figure 7. Specific viscosity of $c_p = 0.5$ mM NaPSS ($M = 70000$) as a function of added $C_{16}PC$ with $\alpha = 1$ (data of Kogej and Skerjanc^{19,20}) compared with the predictions of eq 3 with $f = 0.21$, determined by osmotic pressure measurements of Essafi³² for higher molecular weight NaPSS.

this strongly charged polyelectrolyte, and $f = 0.21$ has been measured by membrane osmometry.³²

The model can be tested further into the semidilute regime (as evidenced by higher viscosities with no added surfactant) using the data of Asnacios et al.^{15–18} This group studied the viscosity of very high molecular weight copolymers of acrylamide and sodium 2-acrylamido-2-methylpropanesulfonate. They report the solution viscosity of two such polymers as functions of added $C_{12}TAB$, and the data are presented in Figure 8. However, for these copolymers the fraction of charged monomers has not been independently determined. The data for the copolymer with 25% charged monomers ($\alpha = 0.25$) are best fit to eq 4 using $f = 0.15$. The fact that the observed f is significantly lower than α even though α is small is not the expectation from counterion condensation theory³³ but is quite consistent with experimental observations on weakly charged polyelectrolytes.²³

However, the viscosity data for the copolymer with 10% charged monomers cannot be described by eq 4 with any reasonable value of the fraction of charged monomers. The model prediction for this polymer using eq 4 with $f = 0.1$ grossly underpredicts the data. Indeed, the data for the 10% charged copolymer actually cross the data for the 25% charged copolymer! This pronounced underprediction indicates that one of the assumptions of our model is incorrect for this system. Weakly charged polyelectrolytes do not have condensed counterions

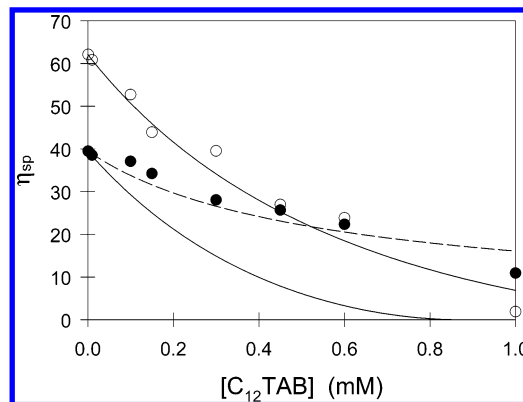


Figure 8. (Open circles) Specific viscosity of a $c_p = 6.8$ mM random copolymer of 75% acrylamide and 25% sodium 2-acrylamido-2-methylpropanesulfonate ($\alpha = 0.25$, $M = 2800000$) as a function of added $C_{12}TAB$ (data of Asnacios et al.^{15–18}) compared with the predictions of eq 4 with $f = 0.15$. (Filled circles) Specific viscosity of a $c_p = 8.6$ mM random copolymer of 90% acrylamide and 10% sodium 2-acrylamido-2-methylpropanesulfonate ($\alpha = 0.1$, $M = 2200000$) as a function of added $C_{12}TAB$ (data of Asnacios et al.^{17,18}) compared with the predictions of eq 4 with $f = 0.1$.

because once the charge spacing along the chain is larger than the Bjerrum length, the electrostatic repulsion is insufficient to cause condensation.³³ Without condensed counterions to release when the surfactant binds, there should not be any micelle formation occurring in the range of data in Figure 8, for the 10% charged copolymer. The dashed curve in Figure 8 is the viscosity prediction of eq 6, the Dobrynin scaling model¹

$$\frac{\eta_{sp}(c)}{\eta_{sp}(0)} = \left[1 + \frac{2c}{fc_p} \right]^{-3/4} \quad c^* < c < c_e \quad (6)$$

assuming no surfactant binding to the polyelectrolyte and no micelle formation (so that the added surfactant simply acts as an added monovalent salt). The fact that eq 6 describes the data for the 10% charged copolymer strongly suggests that this copolymer does not bind surfactant until more surfactant is added. Figure 9 shows viscosity data for the same 10% charged copolymer comparing added salt with added $C_{12}TAB$. The dashed line is the prediction of eq 6, and it compares very nicely with both the viscosity with added salt (open symbols) and the viscosity with added surfactant below the CAC. Above the CAC, the viscosity data are compared with eq 7.

$$\frac{\eta_{sp}(c)}{\eta_{sp}(0)} = \left[1 - \delta \left(\frac{c - c_{cac}}{\alpha c_p} \right) \right] \left[1 + \frac{2c}{fc_p \left[1 - \delta \left(\frac{c - c_{cac}}{\alpha c_p} \right) \right]} \right]^{-3/4} \quad c^* < c_p < c_e \quad \text{and} \quad c > c_{cac} \quad (7)$$

The critical aggregation concentration is c_{cac} , and the fraction of micelle headgroups associated with polyelectrolyte is δ . Our simple ideas discussed earlier expect δ to be unity, and the prediction of eq 7 with $\delta = 1$ and $c_{cac} = 0.7$ mM is shown as the solid curve. Since this prediction does not describe the data, we are forced to use δ as an adjustable parameter. The dotted curve is the prediction of eq 7 with $\delta = 0.15$ and $c_{cac} = 0.5$ mM. The gradual decrease of viscosity beyond the CAC suggests that only 15% of the micelle headgroups are bound to polyelectrolyte.

Conclusion

Polyelectrolyte solution viscosity decreases rapidly as oppositely charged surfactant is added. The combination of direct

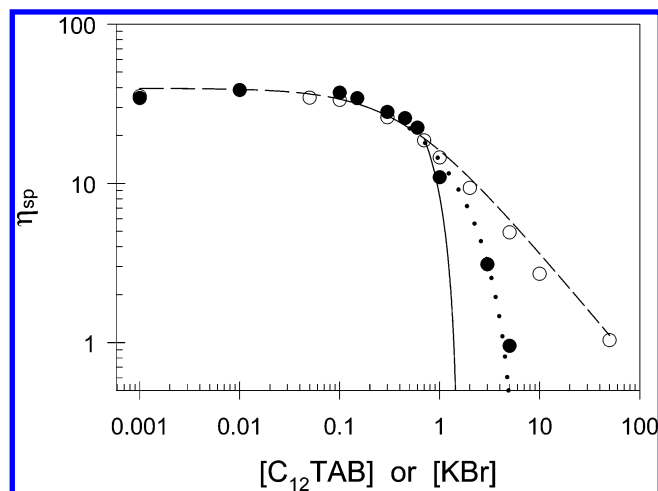


Figure 9. Specific viscosity data of Asnacios et al.^{17,18} for a $c_p = 8.6$ mM random copolymer of 90% acrylamide and 10% sodium 2-acrylamido-2-methylpropanesulfonate ($\alpha = 0.1$, $M = 2200000$) as a function of added salt (KBr, open circles) and added $C_{12}TAB$ (filled circles). The dashed curve is the prediction of eq 6 for added salt. The solid curve is the prediction of eq 7 with $\delta = 1$, $f = 0.1$, and $c_{cac} = 0.7$ mM. The dotted curve is the prediction of eq 7 with $\delta = 0.15$, $f = 0.1$, and $c_{cac} = 0.5$ mM, suggesting that only 15% of the micelle headgroups are associated with the polyelectrolyte.

Coulomb attraction and release of counterions creates strong binding between these species. This strong interaction makes the associations start at low surfactant concentrations (small CAC) and causes precipitation at high surfactant concentrations. In the presence of the polyelectrolyte, the surfactant we have studied forms spherical micelles that are roughly the same size as the micelles formed without polyelectrolyte.

The polyelectrolyte wraps around the exterior of the micelle. The amount of chain involved in this wrapping decreases with extent of neutralization, making strongly charged polyelectrolytes have the weakest reduction in viscosity. In addition to the effective reduction in chain length, counterions are released from the polyelectrolyte when the surfactant binds. The polyelectrolyte stabilizes the strong charge at the micelle surface, so no surfactant counterions condense. The surfactant counterions, together with the counterions released from the polyelectrolyte, act to screen the Coulomb interactions, just as added salt would. This screening further lowers the solution viscosity. Using the simple scaling model of polyelectrolytes, the viscosity reductions arising from both of these effects can be quantitatively predicted. The only parameter used in this model can be independently determined using an ion-selective electrode for the polyelectrolyte's counterion, leaving no adjustable parameters. We expect that this model provides a universal description of viscosity for any oppositely charged polyelectrolyte/surfactant systems having spherical micelles.

Solution viscosity is an extremely precise and sensitive measure of the polyelectrolyte coil size in solution. At a given polyelectrolyte concentration and chain length, the Dobrynin scaling theory predicts the specific viscosity is proportional to the *sixth* power of the end-to-end distance of the chain R in unentangled semidilute solution:

$$\eta_{sp} \approx \frac{c_p^2 R^6}{N^2} \quad c^* < c_p < c_e \quad (8)$$

Hence, while other measurement methods can directly measure the coil size, viscosity measurement is the preferred method for quantifying changes in coil size in unentangled semidilute polyelectrolyte solutions.

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