Poly(acrylic acid)−Cetyltrimethylammonium Bromide Interactions Studied Using Dynamic and Static Light Scattering and Time-Resolved Fluorescence Quenching

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ABSTRACT: Poly(acrylic acid) (PAA) and cetyltrimethylammonium bromide (C_{16}TAB) are found to interact strongly in aqueous solution. The properties of the system are determined mainly by the parameter β, defined as [C_{16}TAB]/[PAA]; the PAA concentration is expressed as monomers. Light scattering measurements in dilute solutions show that a single PAA chain binds several C_{16}TAB micelles to form a complex. At $\beta \approx 1$ (independent of the PAA concentration), the complex is saturated with surfactant. At higher β, free micelles coexist with the complexes. The hydrodynamic radius of the complex is smaller than ($\beta < 1$) or similar to ($\beta > 1$) the radius of the surfactant-free PAA coil. Estimates of the hydrodynamic virial coefficient show that the effective repulsion between complexes increases with β up to $\beta \approx 1$ where a dramatic change is brought about by the screening effect of free micelles. Time-resolved fluorescence quenching shows that the aggregation number of the micelles in the complex increases from 50 at $\beta = 0.35$ to 90 at $\beta = 1$. (The aggregation number for 20 mM C_{16}TAB in the absence of polymer is estimated as 107.) Pyrene lifetime measurements indicate that this change is accompanied by an increase of the apparent degree of bromide ion binding to the micelles from 50% to 95% of the value for free C_{16}TAB micelles. Furthermore, the decreasing influence of the polymer on the surfactant assembly with increasing β is supported by the variation of the intramicellar quenching rate constant. Viscosity measurements confirm that no multipolymer complexes form in the studied concentration range. pH measurements show that the degree of dissociation of the polymer acidic groups increases when the polymer binds to the micelles.

Introduction

A convenient classification of polymer/surfactant systems is offered by the presence or absence of charges on the interactants and, if present, the type of charges.[1] Most frequently studied are nonionic polymer/anionic surfactant[1−3] (P^0/S^-) and polyelectrolyte/oppositely charged surfactant[1,3,4] (P^-/S^+, P^+/S^-) systems. Early investigators noted that several cationic surfactants, in contrast to anionic surfactants, did not interact in a detectable way with nonionic polymers. An increasing number of studies show, however, that cationic surfactants do interact with several nonionic polymers, in particular with polymers having nonpolar moieties.[5−10]

The importance of strong hydrophobic interactions in the case of cationic surfactants was demonstrated by Anthony and Zana,[11] who investigated the effect of temperature on the interactions between poly(ethylene oxide) (PEO) and tetradecyltrimethylammonium bromide (C_{14}TAB). At low temperatures, where PEO is rather hydrophilic, they found no interaction with C_{14}TAB. At higher temperatures (>35 °C), however, where PEO takes on a less polar average conformation,[12] the polymer interacts strongly with the surfactant. Nevertheless, a comparison between anionic and cationic surfactants interacting with the same polymer shows that, for many common polymers, the interactions are stronger with anionic surfactants. For instance, even at low temperatures, PEO shows a strong interaction with the anionic surfactant sodium dodecyl sulfate (SDS).[2,3,13] Several explanations have been proposed to account for this difference. Witte and Engberts[14] suggested that the hydration of the interactions is important, which would favor the interaction with anionic surfactants in most cases studied. According to the models by Nagarajan[15] and Ruckenstein et al.,[16] both dealing with the effect of polymer on the effective forces between surfactant molecules at the micelle surface, the strength of the interaction increases with decreasing size of the surfactant head group. However, as discussed by Lindman and Thalberg in a recent review article,[1] this may influence the behavior in some systems but cannot be used as a general explanation. For instance, it has been reported that the interaction between ethyl(hydroxyethyl)cellulose (EHEC) and C_{16}TAB is stronger than between EHEC and SDS when formamide is the solvent, whereas the opposite is observed in aqueous solutions.[15] It was suggested that this polymer may have a charged character resulting from interactions with the solvent molecules, thus favoring interactions with an oppositely charged surfactant. On the other hand, an electrostatic repulsion between polymer and surfactant may weaken the interaction but can be compensated for by strong hydrophobic interactions.

Zana and co-workers[17] found that the binding of EHEC to micelles of C_{16}TAB (and C_{16}TAC) is accompanied by a release of surfactant counterions and a reduction of the surfactant aggregation number. The latter effect has also been reported for other systems of neutral polymers and ionic surfactants.[10,18−21] It is generally believed that polymers promote surfactant aggregation by reducing the effective interfacial tension between micelles and water (and between the polymer and water).[1] This is consistent with the observed reduced aggregation numbers for polymer-bound micelles. In the case of ionic surfactants, this can in turn

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explain the lower degree of counterion binding of the polymer-bound micelles; the area per surfactant head group increases with a decreasing aggregation number, and therefore the charge density of the micelles. Thus, an additional important driving force for the association with polymer can be the increased entropy of the counterions.

In addition to the aforementioned induction of interactions by increasing the hydrophobicity of the polymer, interactions between weakly interacting polymer/surfactant pairs can be promoted by replacing the counterion with a more "hydrophobic" (typically a less hydrated) one. This is evident from the early work by Saito et al., who investigated the effect of a large number of different counterions on the interactions between cationic surfactants and nonionic polymers.[22,23] It was shown that the effect of surfactant on the properties of different polymer solutions, studied mainly using cloud point, viscosity, and conductivity measurements, increased with increasing "hydrophobicity" of the counterions. In particular, a noninteracting system could be changed into a strongly interacting system. The interpretation is thus that an effective counterion can induce the interaction in cases, e.g., where there is a weak intrinsic repulsion between polymer and surfactant head groups or where the binding of polymer is not possible without a too large increase of the electrostatic free energy. The latter situation is expected if the polymer, upon binding, prohibits close contact between counterions and micelle charges.

At first sight it seems possible that sufficiently strong interactions between surfactant and counterion could reduce the interactions with polymers. However, the results reported by Saito and others[10,24] show that this is not the case. Indeed, the results indicate that the effect of salt is always to promote surfactant assembly in the presence of neutral polymers as well as in pure surfactant solutions. Furthermore, the addition of simple salt has been found to give the same relative reduction of the critical aggregation concentration (cac) in the presence of polymer as of the critical micelle concentration (cmc) in polymer-free solution.[25] Arguments based on specific interactions between surfactant counterions and polymer were used by Treiner and Nguyen[24] to explain why the cac's for copper dodecyl sulfate ($Cu(DS)_2$) in solutions of PEO and poly(vinylpyrrolidone) (PVP) are almost identical, or in fact lower with PEO at polymer concentrations above 0.8%, whereas it is well documented that SDS interacts much more strongly with PVP than with PEO.[3] In the same system, they found that the surfactant concentration where free micelles started to form in equilibrium with the polymer-bound micelles decreased with increasing polymer concentration. This is opposite to the general observations.[3]

Kiefer and co-workers[26] recently found that the interaction between C_{14}TAB and partially neutralized PAA in very dilute aqueous solutions (0.5 mM PAA, expressed as the concentration of monomers) increased with a decreasing degree of ionization of the polymer. This is somewhat surprising as the cac in oppositely charged polyelectrolyte/ionic surfactant mixtures[4] is generally much lower than in neutral polymer/ionic surfactant mixtures. It has also been found by others that the cac increases with decreasing linear charge density of the polymer.[27,28] The effect reported by Kiefer et al., evident from measurements with a surfactant-sensitive electrode, suggests that hydrophobic interaction between PAA and C_{14}TAB becomes increasingly important as the degree of ionization of PAA is reduced and seems to be able to compensate for the weaker electrostatic stabilization of the surfactant aggregates. It should be pointed out that for the fully ionized poly(acrylic acid) the interaction with the surfactant is most likely purely electrostatic,[29−31] and the aggregation numbers of C_nTAB ($n = 12-16$) have been found to be the same as in polyelectrolyte-free solutions.[31,32] Surprisingly, the slope of the cooperative part of the binding isotherms reported by Kiefer et al. increased with decreasing ionization of PAA. In this respect, the behavior resembles the binding of C_{12}TAB to hydrophobic alternating copolymers of maleic acid[33,34] but is different from that observed with hydrophilic polyions.[27,28] To throw more light on these findings, we investigate the related system of C_{16}TAB with weakly ionized PAA in aqueous solution and compare with the results for interactions with fully charged polyacrylate and neutral polymer/charged surfactant systems.

The approach in this paper is mainly to follow the changes as surfactant is added to solutions of fixed PAA concentration. The outline, briefly, is as follows. First the pH is measured to check if the polymer becomes further ionized when interacting with the surfactant. This is followed by a light scattering investigation where the dimensions and the mutual interaction between the polymer/surfactant complexes, both in the absence and in the presence of equilibrium free micelles, are studied at different concentrations and stoichiometries. Finally, the polymer/surfactant aggregates are examined using time-resolved fluorescence measurements, giving surfactant aggregation numbers and estimates of the degree of micelle ionization. Some of the results are complemented with viscosity measurements. All experiments were made at C_{16}TAB concentrations well above the cmc. As the cac is even lower, the main part of the surfactant is always distributed in aggregates.

Experimental Section

Poly(acrylic acid), $M_w = 9 \times 10^4$, was a 25% solution from the Aldrich Chemical Co. C_{16}TAB from Merck was used without further purification. Milli-Q grade water from a Millipore apparatus was used for sample preparation. After reaching equilibrium, the solutions used in light scattering experiments were filtered through 0.2 μm Sartorius Minisart N filters into cylindrical 15 mm diameter glass light scattering cells. To estimate the original concentration of the PAA, aliquots were diluted with a 1 M NaBr solution and titrated against standard NaOH (Merck) to the phenolphthalein end point. For fluorescence measurements, pyrene (Analytical grade) from Serva and *N*-cetylpyridinium chloride (C_{16}PC) from Merck were used as supplied.

Polyelectrolyte−Surfactant Solutions. Solutions containing 0.1% w/w PAA (14 mM) with 20 mM NaBr were mixed with C_{16}TAB to obtain different surfactant/polymer molar ratios. Stirring was thereafter continued for at least 24 h to attain equilibrium. The mixtures were diluted and filtered into the glass light scattering cells. For static light scattering measurements, the solutions were dialyzed using cellophane membranes (2.5 nm pore size) from Union Carbide Corp. (Chicago). The C_{16}TAB concentration was the same on both sides of the membrane, so that only the PAA concentration changes when the stock solutions were diluted with the dialysate. For the fluorescence measurements, a stock solution was prepared by adding solid NaBr and aqueous PAA to a solution containing C_{16}TAB and pyrene (the fluorescent probe). After mixing, an aqueous solution of C_{16}PC (the quencher) was added to a portion of the stock solution. The two stock solutions were separately diluted with a PAA/NaBr solution to yield different C_{16}TAB to PAA ratios. The initial solution

of C_{16}TAB and pyrene was prepared in the following way. An appropriate volume of a standard solution of pyrene in ethanol was transferred to a flask. The ethanol was evaporated by a mild flow of nitrogen, and an aqueous C_{16}TAB solution was added. The solution was stirred overnight before use.

Dynamic Light Scattering (DLS). The technique and apparatus used are described elsewhere.[35] An ALV 5000 wide-band multi-τ, digital autocorrelator from ALV-Langen, Germany, was employed to determine the relaxation time. This instrument has a monitoring capacity of up to 9 decades in delay time. The measured time−intensity correlation function is related to the electric field correlation function by the Siegert relation:

$$g^{(2)}(t) = B(1 + \beta|g^{(1)}(t)|^2) \quad (1)$$

where B is a baseline and β is a factor accounting for deviations from ideal correlation, for instance fluctuations in the scattering volume. In a continuous distribution corresponding to an infinite range of particle sizes, the inverse Laplace transform (ILT) may be used:[36]

$$g^{(1)}(t) = \int_0^\infty A(\tau) \exp(-t/\tau)\mathrm{d}\tau \quad (2)$$

ILT was performed by using a constrained regularization routine, REPES, developed by Jakes,[37] to obtain the distribution of decay times. This program is similar in many respects to CONTIN by Provencher,[38] but directly minimizes the sum of squared differences between the experimental and calculated intensity−intensity correlation functions, $g^{(2)}(t)$, using nonlinear programming and allows selection of the parameter P (probability to reject), which determines the degree of smoothing. The analysis of data, encompassing 288 exponentially spaced grid points and a grid density of 12 per decade, can be rapidly performed on an IBM AT desk-top computer. Relaxation time distributions are given in the form $\tau A(\tau)$ versus $\log \tau$, providing an equal-area representation. Diffusion coefficients were calculated from the ILT moments as

$$D = (\Gamma/q^2)_{q\to 0} \quad (3)$$

where q is the magnitude of the scattering vector.

Static Light Scattering (SLS). The angular dependence of the integrated intensity was measured using the DLS equipment described above. The light source is a helium−neon laser with the wavelength 633 nm. Toluene (Rayleigh ratio 13.59×10^{-6} cm^{-1})[39] was used in the calibration. The apparent radii of gyration for the polymer and for the complexes were calculated at a PAA concentration of 0.1% within the Guinier range $qR_g \ll 1$. In measurements made on solutions with an excess of C_{16}TAB, the ILT of the DLS data are characterized by bimodal relaxation time distributions. The relative amplitudes of the fast and slow modes describe the intensity scattered from free micelles and the complex, respectively. R_g for the PAA−C_{16}TAB complex was determined from the angular dependence of the scattered intensity of the slow mode, according to the Zimm theory.[40] In the dialysis experiments, the solution inside the semipermeable membrane contained a stock solution of both PAA and C_{16}TAB in 20 mM NaBr. The outer solution consisted of 20 mM NaBr and the same concentration of C_{16}TAB as inside to prevent precipitation of the PAA−C_{16}TAB complex in the stock solution arising from dilution of surfactant through the membrane (see the results section).

Time-Resolved Fluorescence Quenching (TRFQ). The fluorescence decay data were collected with the single-photon-counting technique. A detailed description of the experimental technique and equipment used is given elsewhere.[41] All measurements were performed at 25 °C in equilibrium with or in the absence of air. The fluorescence was monitored at 395 nm following excitation at 320 nm.

Evaluation of TRFQ Data. For each sample, decay curves were recorded without and in the presence of quencher (C_{16}PC). The pyrene lifetime, τ_0, was estimated by fitting the unquenched curve to a single-exponential function. The quenched curves were fitted to a function proposed by Infelta et al.[42] describing the time evolution of the fluorescence signal, $F(t)$, from a probe situated in small uniform micelles:

$$F(t) = A_1 \exp[-A_2 t + A_3\{\exp(-A_4 t) - 1\}] \quad (4)$$

In the case of stationary probe and quencher, a Poissonian distribution of the quencher implies the simple interpretation[43]

$$A_1 = F(0) \quad (4a)$$

$$A_2 = 1/\tau_0 \quad (4b)$$

$$A_3 = \langle n \rangle \quad (4c)$$

$$A_4 = k_q \quad (4d)$$

where xk_q is the quenching frequency in micelles containing x quenchers. k_q should be considered as a quasi-first-order rate constant, independent of the number of quenchers per micelle, but generally decreasing with the size of the micelles.[44] $\langle n \rangle$ is the average number of quenchers in a micelle. In the fitting procedure, A_2 was kept fixed equal to $1/\tau_0$.

Equations 4 have been extensively used[45,46] to analyze fluorescence data both in pure surfactant and in polymer/surfactant solutions, and it is well established that it is one of the most convenient methods to estimate surfactant aggregation numbers.[47] In particular, it allows the estimation of aggregation numbers of polymer-bound micelles, as the presence of the polymer, as such, does not affect the measurements.

The surfactant aggregation number (the number of surfactant monomers per micelle), N_s, was calculated from[31]

$$N_s = \langle n \rangle / X \quad (5)$$

where X, the mole fraction of quencher in micelles, was approximated with the total mole fraction of C_{16}PC in the solution (calculated on a surfactant only basis). Even at the lowest C_{16}TAB concentration used (25 mM), this approximation is excellent; the cac is expected to be lower than the cmc (=0.8 mM)[48] for pure C_{16}TAB.

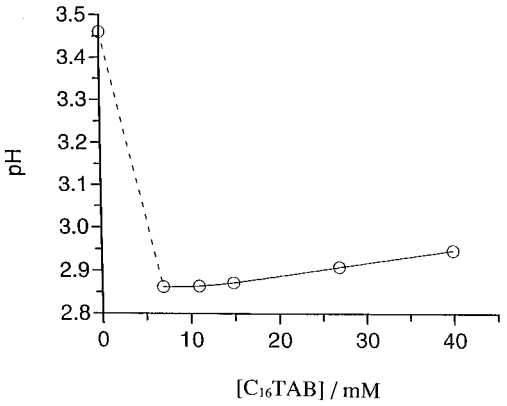

Figure 1. Dependence of pH on the C_{16}TAB concentration in a 14 mM PAA solution containing 20 mM NaBr. The initial part is shown dashed owing to the lack of data in this range.

Results and Discussion

pH Measurements. Figure 1 depicts the change in pH with increasing C_{16}TAB concentration at a constant PAA concentration of 0.1% (w/w) (14 mM) in 20 mM NaBr. From the pH in the surfactant-free solution, the degree of ionization, α, of the polymer is calculated as 0.026. The addition of small amounts of C_{16}TAB resulted in phase separation. This behavior is expected upon addition of an oppositely charged surfactant to a weakly charged polymer.[49] At a somewhat higher surfactant concentration, redissolution is observed, ac-

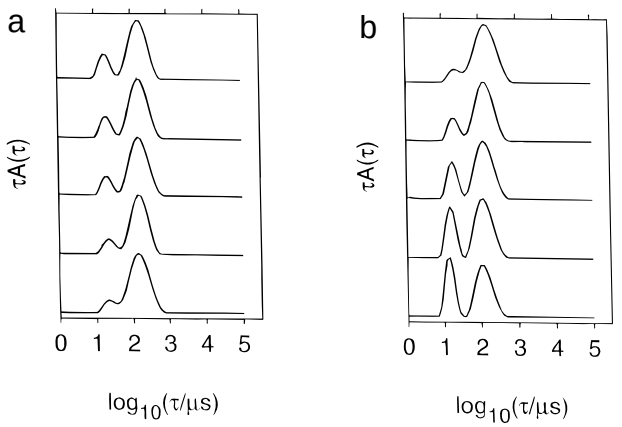

Figure 2. (a) Relaxation time distributions where the PAA concentrations are 5.6, 7.0, 8.3, 11, and 14 mM from the top. C_{16}TAB concentration is constant at 20 mM. Temperature 25 °C and scattering angle 90°. (b) Relaxation time distributions for $\beta = 1.4$. The PAA concentrations are 14, 28, 42, 56, and 70 mM from the top. Scattering angle = 90°.

companied by a considerable drop in pH (corresponding to approximately 1 mM H^+). Further addition of surfactant produces a very small increase in pH. Thus, the initial binding of highly charged micelles to PAA is followed by a release of a fraction of the protons. However, as α is increased to about 0.1, no further ionization occurs even in a large excess of surfactant. At this point, an optimum in the interaction energy between the polymer and the surfactant is probably reached, with favorable contributions from both electrostatic and hydrophobic interactions.[3] The binding isotherms reported by Kiefer et al.[26] for C_{14}TAB show that the cac increases if α is increased above 0.1, which was the lowest degree of ionization in their study, except for a sample containing an excess of HBr (α ≈ 0). In the latter case, the cac was again higher (more than one order of magnitude) than at α = 0.1, indicating the existence of a minimum in the cac as a function of α.

Dynamic Light Scattering Results. Parts a and b of Figure 2 show representative relaxation time distributions obtained by ILT for the PAA−C_{16}TAB system at different compositions. NaBr (20 mM) was present in all samples. Two diffusive modes can be observed; their q^2 dependence was checked in the angular range 45−135°. The fast mode corresponds to free C_{16}TAB micelles and the slow mode to single-chain polymer/surfactant complexes, as concluded from the estimated infinite dilution hydrodynamic radii (see below). Although not shown by Figure 2a,b, the fast mode is present only at C_{16}TAB-to-PAA molar concentration ratios (from now on denoted β) above 1. Thus, at a certain value of β, further binding of surfactant to the polymer is no longer favored, and free micelles appear if a sufficient amount of surfactant is added. The appearance of free micelles marks the transition into region III in the type of "phase diagram" introduced by Jones,[50] completely in accordance with previous results on nonionic polymer/ionic surfactant systems.[3]

In Figure 2a the solutions are diluted with respect to PAA, starting at 14 mM (0.1%), at a fixed C_{16}TAB concentration of 20 mM (β increases from 1.4 to 3.6). As expected, both modes are always present and the amplitude of the fast mode increases relative to that of the slow mode upon dilution of the polymer and thereby the complex. However, the relaxation times for both modes are almost constant (see below). In contrast, results from measurements at $\beta = 1.4$ (fixed) (Figure 2b) show that upon dilution the amplitude of the fast mode decreases relative to that of the slow mode. This can be due to (i) weaker scattering from the free micelles relative to the scattering from the complexes due to a decreased ion binding to the former as the concentration (and the aggregation number) decreases, (ii) stronger scattering from the complexes at lower concentrations, and (iii) a larger maximum degree of surfactant binding to each polymer at lower PAA concentrations. The latter explanation is supported by the relatively large effect, but such a behavior is generally not observed in P^0/S^- or P^0/S^+ systems.[3]

Diffusion coefficients, D, were calculated from the relaxation rates of the slow mode using eq 3. For all PAA concentrations, D first increases as C_{16}TAB is added (i.e., increasing β) but then decreases abruptly within a narrow concentration range ($\beta \approx 1$). This reflects the changes in size (or rather the self-diffusion coefficient) of the complex with β as well as the thermodynamic interactions. In principle, the two contributions can be separated from each other from the concentration dependence of D using the relationship applicable to dilute solutions

$$D = D_0(1 + k_D C) \tag{6}$$

where D_0 is the value of D extrapolated to zero concentration and k_D is the hydrodynamic virial coefficient. Strictly, for this to be allowed, the stoichiometry of the complexes and the interactions with the solvent must not change upon dilution. The latter requirement is clearly not fulfilled when $\beta > 1$ since the concentraton of free micelles is not kept constant. However, in this qualitative study, we neglect this and use the values of D and D_0 estimated from families of relaxation time distributions like those in Figure 2b (i.e., each corresponding to a given β) to calculate, in turn, the dependence of k_D on β. The result is shown in Figure 3a, where a dramatic change at $\beta \approx 1$ is obvious. To understand this behavior, we note that k_D can be interpreted as[36]

$$k_D = 2B_2M - k_f - 2\nu_2 \tag{7}$$

where B_2 is the second virial coefficient, related to the pair potential between complexes in the present solvent, k_f describes the concentration dependence of the friction coefficient, and ν_2 is the partial specific volume of the complex. Thus, k_D first increases with β due to the charging up of the complex as more and more surfactant binds; both the larger dimensions of the complexes and the higher net charge will tend to increase the magnitude of B_2. When free micelles are present, the interaction between complexes is strongly screened as monitored by the drop in k_D at $\beta \approx 1$. Note that, as the "solvent" changes from a simple electrolyte solution to an ionic micellar solution, B_2 should decrease and k_f increase. No such drop is observed in the system of PAA with the nonionic surfactant $C_{12}E_8$ (dodecyl octa[oxyethylene]glycol).[51] A further increase in β has only a small effect on k_D since the stoichiometry of the complex and the properties of the "solvent" change less.

When the equilibrium free concentration of surfactant exceeds the cmc, there is no further binding of surfactant to the polymer. If the cooperativity in the binding is low, this may occur before the polymer/surfactant complex is saturated.[52] Then the value of β corresponding to the onset of free micelle formation would be dependent on the polymer concentration. In the present

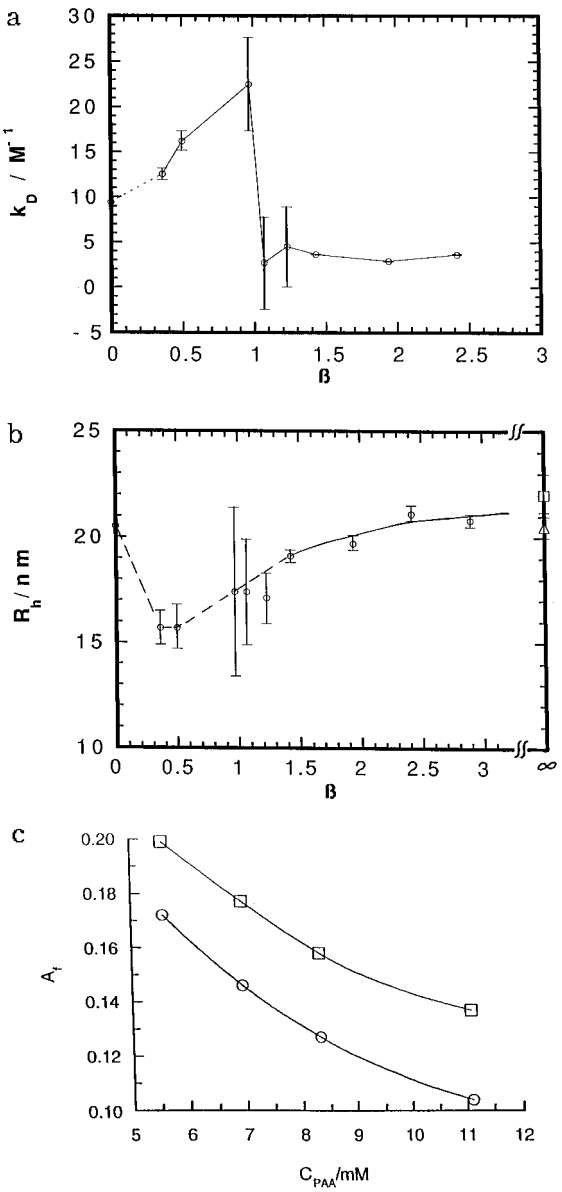

Figure 3. (a) Hydrodynamic virial coefficient, k_D, of the complex as a function of β at 25 °C. (b) Hydrodynamic radius, R_h, of the complex as a function of β. R_h calculated from D_0 values estimated at infinite dilution of the complex at fixed β (25 °C) (circles) and infinite dilution of the polymer at finite C_{16}TAB concentrations, 25 °C (square), 35 °C (triangle). (c) Relative amplitude for the fast relaxation mode, A_f, corresponding to unbound C_{16}TAB micelles, as a function of PAA concentration at 20 mM C_{16}TAB. Measurements at 25 °C (circles) and at 35 °C (squares).

system, however, the formation of free micelles as probed by the drop in the apparent diffusion coefficient, D, starts at $\beta \approx 1$ in the full range of PAA concentrations studied. We may thus conclude that at $\beta \approx 1$ the complex is truly saturated.

Using the Stokes−Einstein equation

$$R_h = \frac{k_B T}{6\pi\eta_0 D_0} \tag{8}$$

where η_0 is the viscosity of the solvent, the hydrodynamic radii (R_h), for the free micelles and the PAA/C_{16}TAB complexes were calculated using the estimated values of D_0. For the free C_{16}TAB micelles corresponding to the fast mode in Figure 2a, R_h was obtained as 3.4 nm, which is close to the value estimated in polymer-free solutions. Figure 3b illustrates the change in R_h for the complex as a function of β. Upon binding of micelles, the polymer coil initially shrinks. Subsequently, as more micelles are formed at each chain, the coil expands, reaching at higher β's a radius close to the radius of the initial PAA coil. This behavior is similar to that observed earlier in P^0/S^- systems using other techniques.[3] The radius of the complex at the lowest studied β is about 75% of the value for the initial PAA coil despite the fact that the net charge per polymer is larger. However, a fraction of the charge due to the surfactant is compensated for by the release of protons. The effect shows that the interaction between PAA and C_{16}TAB is strong.

At β close to 1, a small change in the composition favoring the formation of free micelles has a large effect on the complex−complex interactions and hence the magnitudes of k_D and D_0. This is expected to be responsible for the large uncertainty in the estimates of these parameter when β is close to 1; see Figure 3a,b.

Indicated in Figure 3b is also the hydrodynamic radius for the complex estimated in the limit as β goes to infinity, i.e., obtained from extrapolation to zero PAA concentration at fixed C_{16}TAB concentration. Here we used data from Figure 2a and the corresponding sets of data obtained at 15, 17, 27, and 33 mM C_{16}TAB (temperatures: 25 and 35 °C). In the small range of concentrations studied, no pronounced dependence on the C_{16}TAB concentration was found. The size of the complex determined at infinite dilution of the complex at finite surfactant concentrations is slightly larger than that obtained for $\beta > 1$ at infinite dilution of both the complex and the free micelles. By considering the larger electrostatic screening expected at finite C_{16}TAB concentrations, this may seem strange. It should be emphasized, however, that the latter estimates (finite β) do not correspond to infinite dilution of the complex in a true sense. For instance, in the case of $\beta = 2.9$, the free concentration of C_{16}TAB was approximately 26 mM in the most dilute sample measured (totally 40 mM C_{16}TAB). Thus, the estimated value of D_0, obtained by extrapolating to zero PAA (and C_{16}TAB) concentration, is clearly influenced by the presence of free C_{16}TAB.

Figure 3c shows the effect of temperature on the amplitude, A_f, for the fast mode relative to the amplitude for the slow mode measured at different PAA concentrations. The concentration of C_{16}TAB was kept fixed at 20 mM. (The results at 25 °C correspond to the relaxation time distributions in Figure 2a.) The relatively larger scattering from the micelles at the higher temperature can be explained by a larger number of free micelles. However, it is difficult to judge from the present set of data if the change is due to a release of bound surfactant or due to a smaller aggregation number (e.g., a larger number of scattering micelles) at an unchanged β. The aggregation number for C_nTAB is generally found to decrease with increasing temperature.[53,54]

Static Light Scattering Results. In order to investigate the complexes at *finite* concentrations in equilibrium with free micelles ($\beta > 1$), the apparent radius of gyration, R_g, was determined from the q^2 dependence of the inverse Rayleigh ratio. The apparent R_g for the PAA coil in the absence of surfactant was determined as 27 nm and for the PAA−C_{16}TAB complex as 44, 31, and 28 nm at β equal to 1.0, 1.2, and 1.4, respectively, at a PAA concentration of 14 mM. The inverse Rayleigh ratio was linear in q^2 over the entire

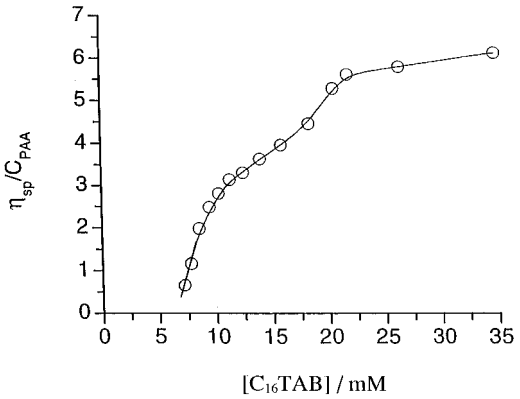

Figure 4. Reduced viscosity, η_{sp}/C_{PAA}, as a function of C_{16}TAB concentration at 14 mM PAA. Temperature = 25 °C.

range studied. The relatively large difference between R_g at $\beta = 1.0$ (approximately no free micelles present) and $\beta = 1.2$ suggests that the complex shrinks or changes shape considerably as free micelles form. We believe that this is due to the electrostatic screening, not a transfer of polymer-bound surfactant to free micelles; the addition of salt to neutral polymer/ionic surfactant solutions is generally found to favor the state of polymer-bound surfactant.[3] This is supported by the drop in k_D in Figure 3a, also suggesting that the relative difference in electrostatic screening between $\beta = 1.2$ and 1.4 is expected to be smaller than between $\beta = 1.0$ and 1.2. With support from the above discussion on the interpretation of the R_h values in Figure 3b, the R_g values reported here suggest an interpretation of R_h as close to the upper limit of the error bars indicated in Figure 3b. There is no reason, however, to expect a local maximum at $\beta \approx 1$ in Figure 3b, unless the estimated R_h values are influenced by the screening from free C_{16}TAB micelles.

In a study of dilute polyelectrolyte complex solutions, Dautzenberg et al.[55] emphasized that the shape of the scattering curve is determined by four parameters: particle size, particle shape, and internal structure of the particles, and the polydispersity of the scattering system, making extrapolation to zero angle equivocal for aggregated structures. Indeed, the contribution to the scattered light from large particles dominates in the low angular range since the probing length, $1/q$, is comparable to their size. Thus, the presence of higher order complexes would increase the value of R_g. Dubin et al.,[56] who studied the interaction between the polycation poly(diethyldiallylammonium chloride) (PDMDAAC) and anionic/nonionic mixed micelles of SDS and Triton X-100, found that above a certain concentration of the polyelectrolyte (0.1 g L^{-1}) there is an equilibrium between intrapolymer and interpolymer complexes. A very important difference, however, compared with the system studied here is that the composition of their samples was close to the two-phase region of the phase diagram typical for oppositely charged polyelectrolyte surfactant systems.[57] This type of association is driven by the electrostatic interactions.[49] For the dilute PAA−C_{16}TAB solutions studied here, very little influence from multichain complexes is expected. An important argument is that the surfactant is in excess, which means that the polymers do not need to share micelles.

Viscosity Results. Figure 4 shows the dependence of the reduced viscosity (η_{sp}/C) on surfactant concentration at 14 mM PAA in 20 mM NaBr. The initial rapid increase in viscosity with increasing surfactant concentration and the subsequent slower increase around the equimolar point support the interpretation of the light scattering results as a coil expansion and increasing intercomplex repulsion for $\beta < 1$. The changes at C_{16}TAB concentrations above 14 mM can be explained by the appearance of free micelles, e.g., a combination of viscosity enhancement (more colloids in the system) and viscosity reduction (electrostatic screening) effects. The absence of a maximum suggests that no cross-linking of polymer molecules takes place at intermediate micelle concentrations, as observed in systems where the polymer interacts hydrophobically with micelles.[1] The tendency for cross-links to be formed in the present system is expected to be largest in semidilute PAA solutions at low β, i.e., when the polymers overlap and the number of micelles per polymer is low.

Results from TRFQ. Aggregation Numbers. Figure 5a shows how the C_{16}TAB aggregation number, N_s, increases with the C_{16}TAB concentration in 70 mM (0.5%) PAA solutions. For comparison, N_s was determined as 107 in a polymer-free 20.0 mM C_{16}TAB solution, without added salt. It is clear that the micelles present in the complex with the polymer (low C_{16}TAB concentrations) are smaller than the free micelles. This is a well-known phenomenon in mixtures of surfactants and neutral polymers.[17−19,21]

In agreement with the light scattering results, the change in N_s with the C_{16}TAB concentration reveals two aggregation regimes. At low C_{16}TAB concentrations, where no free micelles can be detected by light scattering, N_s increases more strongly with increasing C_{16}TAB concentration than what is expected for polymer-free solutions of the surfactant, where the dependence is more similar to that observed in Figure 5a in the range where free micelles are present ($\beta > 1$).

At the concentration where free micelles first appear, N_s is still smaller than in polymer-free solutions of C_{16}TAB. Thus, if the free micelles coexisting with polymer-bound micelles have the same aggregation number as those in polymer-free solutions, there are two populations of micelles contributing to the observed average aggregation number. Note that N_s obtained from TRFQ is related primarily to the concentration of hydrophobic domains in the solution, not to the activity or to properties related to the physical size of the micelles.

The dependence for $\beta < 1$ points to the importance of the amount of polymer bound per micellized surfactant and shows that the polymer interacts intimately with the micelles. As discussed in the Introduction, a major driving force for the interaction is the reduction of the interfacial free energy. A small aggregation number is consistent with a large area per surfactant available for polymer binding. This situation is thus favorable at low β. Increasing β will reduce the amount of polymer available per surfactant and the surfactant molecules adapt by moving their head groups closer together, e.g., by increasing N_s. This in turn is expected to increase the electrostatic free energy and reduce the entropy of the counterions (see below). A simple calculation of the area per head group shows a decrease from 75 to 65 Å^2 as the aggregation number increases from 55 to 87, indicating a considerable increase of the surface charge density. The free micelle value ($N_s = 107$) corresponds to 62 Å^2. In the calculations, we assume that the micelles are spherical with a volume of the hydrocarbon core equal to the volume per surfactant tail (458 Å^3)[58] times N_s.

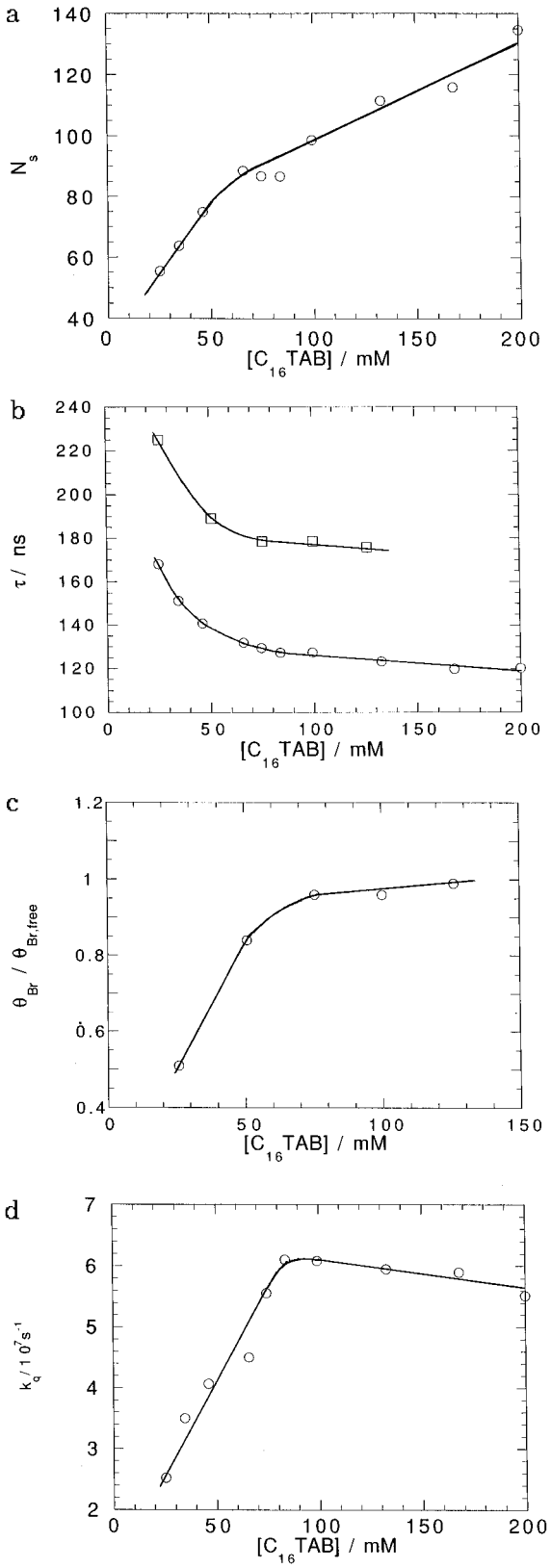

Figure 5. (a) C_{16}TAB aggregation number, N_s, as a function of C_{16}TAB concentration in 70 mM PAA solutions. Temperature = 25 °C. (b) Pyrene lifetime, τ, as a function of C_{16}TAB concentration measured in equilibrium with air (circles) and in deoxygenated solutions (squares). The PAA concentration is 70 mM. Temperature = 25 °C. (c) Degree of counterion (Br^-) binding to C_{16}TAB micelles in the presence of 70 mM PAA relative to that in polymer-free solutions, $\theta_{Br}/\theta_{Br,free}$, as a function of C_{16}TAB concentration. (d) Intramicellar quasi-first-order quenching rate constant, k_q, for the quenching of pyrene with CPC as a function of C_{16}TAB concentration. The PAA concentration is 70 mM. Temperature = 25 °C.

By considering also the interaction between micelles at the same polymer chain, it is easy to see that the described scenario must change the standard chemical potential of the bound surfactants ($\mu°$) and thus the equilibrium free concentration of surfactant above the cac. The slope of the surfactant binding isotherm is expected to be determined by (i) the gradual change of the electrostatic and interfacial free energy contributions (i.e., $\mu°$) and (ii) the magnitude of the aggregation number. Contributions i and ii are necessarily interrelated. Gilányi and Wolfram[52] derived a law of mass action model (taking into account also the binding of counterions) by assuming a single aggregation number for the polymer-bound micelles to describe the first contribution. The model was applied to the binding of SDS to poly(vinyl alcohol), PEO, and PVP. From the slope of a plot of log(C_{compl}) as a function of log(surfactant activity) they obtained aggregation numbers smaller than for SDS micelles in polymer-free solutions. Here C_{compl} stands for the concentration of complexes, which should increase linearly with the amount of bound surfactant at constant aggregation number. Later its was shown[14,18,19] that the aggregation numbers in these systems increase with increasing amount of bound surfactant, starting at values smaller than those estimated from the isotherms and at higher surfactant concentrations approaching the values for free SDS micelles. (The same trend is observed in the present study.) Thus, in the limit as C_{compl} (or β) goes to zero, the slope in a plot of log(C_{compl}) as a function of log(surfactant activity) (or, in the presence of excess added salt, log(free surfactant concentration)) should correspond to N_s of the first micelles formed. This method is not to be recommended, however, as a law of mass action model cannot account for changes in $\mu°$. This is clear from a recent study of the association of C_nTAB with anionic polyelectrolytes of high linear charge density.[28] Even in systems where N_s was independent of β, the analysis of binding data with a law of mass action model (assuming a single value of N_s) resulted in aggregation numbers considerably lower than what was found in the experiments. Nevertheless, a comparison between different polyelectrolytes showed that the apparent cooperativity increased with N_s.

Interestingly, Kiefer et al. (see Introduction) reported that the binding of C_{14}TAB to partially ionized PAA is more cooperative at $\alpha = 0.1$ than at higher α's despite the fact that the aggregation numbers are similar at different α's (as confirmed by a fluorescence study from the same laboratory[59]). An increasing cooperativity with decreasing linear charge density of the polymer has also been reported by others.[33,34] The behavior appears to be general when the modification leading to a lower charge density also makes the polymer backbone become more hydrophobic. In the light of the discussion above, an explanation should involve the dependence of $\mu°$ on β. Thus, the change in the free energy per surfactant monomer of forming, say, five micelles at the same polymer chain from the free energy of forming one is thus smaller in the case of a weakly charged polyion than in the case of a highly charged one. The short-range nature of the interaction between micelles and polymer in the former case as opposed to the long-range electrostatic interactions in the latter may be of importance. Another aspect is the difference in the distribution of counterions and their influence on the micelle−micelle interactions. As will be discussed in the next section, the surfactant aggregation at a non-

ionic or weakly charged polymer involves the binding of surfactant counterions and resembles the self-assembly of ionic surfactants in polymer-free solutions or, rather, the assembly of ionic surfactant in the presence of a medium-chain alcohol. In contrast, micellization at a highly charged polyion shows some resemblance with an ion-exchange process where surfactant ions replace ions trapped in the field of the polyion.[60] The surfactant counterions are less important but instead the strength of the interaction relies on the possibility of the polyelectrolyte to act as a counterion to the micelles.[32] In fact, at low concentrations of salt, the release of polyion counterions will contribute to a reduction of the cooperativity.[28]

Pyrene Lifetimes. Due to a reduction of the surface charge density of the micelles as the aggregation number decreases, the counterion binding to the micelles is expected to decrease. As bromide ions are effective quenchers of pyrene fluorescence, this will affect the fluorescence lifetime but not the other quenching parameters.[61] Oxygen dissolved in the aqueous phase is also an effective quencher, and a more effective protection of pyrene from oxygen quenching as the polymer covers the micelle surface is expected to increase the lifetime. In Figure 5b the lifetime (τ), estimated in equilibrium with air, is given as a function of the C_{16}TAB concentration. The lifetime decreases from a value close to that found in C_{16}TAC micelles (177 ns)[41] to the lifetime in free C_{16}TAB micelles (123 ns). (Chloride ions are very inefficient quenchers of pyrene.) To separate the contribution from bromide quenching from the quenching by oxygen, the lifetimes in deoxygenated samples were estimated. Figure 5b shows that the main effect persists. Thus, the bromide quenching changes considerably with β.

The deactivation constant, k ($=1/\tau$), is given by[41]

$$k = k_0 + k_{ox}[O_2] + k_{Br}\theta_{Br} \qquad (9)$$

where k_0 is the unquenched deactivation constant, k_{OX} the second-order quenching constant for oxygen quenching, and k_{Br} the pseudo-first-order constant for bromide quenching. $[O_2]$ is the concentration of oxygen, the θ_{Br} is the bromide counterion degree of binding to the micelle defined as the number of "bound" bromide ions per micellized surfactant. The differences between the k values estimated in equilibrium with air and in degassed samples, respectively, give the contribution from oxygen quenching. A calculation using the data in Figure 5b shows that, the oxygen quenching increases somewhat as the concentration of C_{16}TAB increases: $k_{OX}[O_2]$ changes from about 2×10^6 to 2.5×10^6 s^{-1}, which is close to the value in free C_{16}TAB micelles, where $k_{OX}[O_2]$ is equal to 2.4×10^6 s^{-1}. Compared to the changes caused by the bromide quenching, however, oxygen quenching gives only a small contribution.

By assuming that k_0 is the same as in free C_{16}TAC micelles (2.97×10^6 s^{-1}),[41] it is possible from eq 9 to estimate the degree of bromide ion binding to the polymer-bound micelles, θ_{Br}, relative to that of free C_{16}TAB micelles, $\theta_{Br,free}$. In Figure 5c the ratios $\theta_{Br}/\theta_{Br,free}$ have been calculated from the lifetimes in deoxygenated solutions ($[O_2] = 0$) using the relationship

$$\frac{(k - k_0)_{pol}}{(k - k_0)_{free}} = \frac{\theta_{Br}}{\theta_{Br,free}} \qquad (10)$$

where the indices "pol" and "free" indicate the presence and absence of polymer, respectively. It is assumed that k_{Br} has the same value for polymer-bound and free micelles. From the given data, $k_{Br}\theta_{Br}$ was estimated as 2.7×10^6 s^{-1} for free micelles. At the lowest C_{16}TAB concentration (26 mM), the counterion binding appears to be about 50% lower than for free micelles.

In free micelles pyrene is most likely distributed in or close to the micelle surface.[62] One may argue that the decreased bromide ion quenching as the polymer crowds the micelle surface could be due to a hindered access of the probe. However, the weak dependence of the oxygen quenching on β gives no such indication.

The suggested change in the counterion binding is similar to the results given in a recent report on the interaction between C_{16}TAB/C and the neutral polymer ethyl(hydroxyethyl)cellulose (EHEC).[17] From self-diffusion experiments it was shown that the micellar degree of ionization at 5 mM C_{16}TAC and 25 °C increased from about 0.3 in the absence of polymer to 0.6 at 0.5% EHEC.

Quenching Rate Constants. Another effect reported in TRFQ studies of polymer/surfactant complexes is the slow intramicellar quenching rates. The effect seems to be quite general. Both in solutions of polyions[41,63,64] and neutral polymers,[17−19,41] k_q is smaller in the polymer-bound micelles, even when the micelles are smaller than the corresponding free micelles. Generally, k_q should decrease with an increasing size of the micelles and with decreasing mobility of the probe and the quencher in the micelles.

Figure 5d shows the change in k_q with C_{16}TAB concentration. For $\beta < 1$, the latter effect dominates in this system; as the amount of polymer associated with each micelle increases, the effect on k_q increases despite the decrease of the aggregation number. Quenching occurs close to the micellar surface since the active part of the quencher, the pyridinium group, is charged and cannot enter the micellar core. The quencher (and the probe) may thus have a restricted mobility as imposed by the presence of the polymer at the micellar surface.

When free micelles appear in the system, k_q decreases slightly with surfactant concentration. The largest value is still much smaller than in the polymer-free system, where k_q was determined as 9.7×10^6 s^{-1}. This is expected since the observed value represents an average from polymer-bound and free micelles. In free micelles k_q decreases strongly with the size of the micelles (with R^{-2} as suggested by Van der Auwerer et al.[44]).

Conclusions

The presence of PAA strongly influences the micellization of C_{16}TAB in aqueous solution. Each polymer chain gathers together several micelles (and a fraction of their counterions) to form complexes stabilized by hydrophobic and electrostatic interactions. An optimal situation is realized through (1) an increased degree of dissociation of the polymer acidic groups and (2) an adjustment of the surfactant aggregation number and the degree of counterion binding as dictated by the value of β. At $\beta = 0.5$ the hydrodynamic radius of the complex is 75% smaller than the surfactant-free PAA coil. At higher β the coil expands and the size approaches the size of the initial coil. For $\beta > 1$ the complex is saturated with surfactant and free micelles coexist with the complex. The free micelles have a strong effect on the intercomplex interactions (they essentially reduce the complex−complex correlation).

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