Soluble Complexes from Poly(ethylene oxide)-*block*-polymethacrylate Anions and *N*-Alkylpyridinium Cations

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ABSTRACT: Complexes from poly(ethylene oxide)-*b*-poly(sodium methacrylate) (PEO-*b*-PMANa) and *N*-alkylpyridinium bromides are water soluble, in marked contrast to those from poly(sodium methacrylate). These systems are studied using potentiometric titration, microcalorimetry, ζ-potential measurement, light scattering and electron microscopy. Three regions (**A**−**C**) are observed with a complex from PEO-*b*-PMANa and cetylpyridinuim bromide (C_{16}PyBr) when the composition of the mixture (Z = [C_{16}PyBr]/[COO^-]) is varied. **(A)** At $Z < 1$ C_{16}PyBr binds electrostatically to the polyion to form soluble complex with a negative ζ-potential. **(B)** The size of the complex decreases and reaches minimum (o.d. 67 nm) at $Z = 1$ when $\zeta = 0$. Those stoichiometric complexes are soluble and stable. They appear to be micelles with a core formed by C_{16}PyBr neutralized polyion chains and a shell of PEO chains. **(C)** With a further increase in Z, the surfactant cations incorporate in the particles ($\zeta > 0$). The particles formed at saturating concentrations of C_{16}PyBr are spherical and remarkably monodisperse. Overall, these systems represent a new class of lyophilic colloids that exhibit combined properties of amphiphilic block copolymers and polyelectrolyte−surfactant complexes.

Introduction

Polyelectrolyte complexes from DNA and a block ionomer containing a nonionic water soluble segment, e.g. poly(ethylene oxide) (PEO), and a polycation segment have been advanced recently for gene delivery.[1−4] In these systems the charges of the DNA are neutralized by the polycation segments while the complex remains soluble due to the effect of the PEO segments. Such systems belong to a broader class of polyelectrolyte complexes formed by block ionomers. The studies on the complexes from PEO-*b*-poly(L-lysine) cation and PEO-*b*-poly(α,*β*-aspartate) anion[5] as well as PEO-*b*-polymethacrylate anion and poly(*N*-ethyl-4-vinylpyridinium) cation[6] have suggested that they represent a *new type of chemical entity* with combined properties of amphiphilic block copolymers and polyelectrolyte complexes. Such systems are stable and soluble in aqueous solutions and can form a microphase from the neutralized polyion segments surrounded by a shell from PEO segments.[5,6] In addition, these complexes may form micelle-like aggregates with a concentration dependence resembling those characterized by a critical micelle concentration (CMC).[6] At the same time, like regular polyelectrolyte complexes, these systems are salt-sensitive since they fall apart as the salt concentration increases beyond a critical value. Furthermore, they were shown to participate in substitution reactions involving neutralized polyion segments.[6] Kataoka *et al.* have termed these systems the "*polyion complex micelles*".[5] Since these complexes do not always form micelles, we prefer another definition, the "*block ionomer complexes*" or "*BIC*".[6]

This paper reports the data on the new family of BIC that differ significantly from the complexes previously studied.[1−6] We have recently begun investigating the complexes formed between block ionomers and oppsitely charged surfactants. In such complexes, the charged head groups of the surfactants are bound to the units of the polyion segment of the block ionomer, so that the surfactant tails are grafted to this segment. This paper reports the studies on the BIC from poly(ethylene oxide)-*block*-polymethacrylate anions and *N*-alkylpyridinium cations. These BIC are similar to regular polyelectrolyte−surfactant complexes from polymethacrylate anions and *N*-alkylpyridinium cations in the sense that they also formed due to electrostatic attraction between the pyridinium groups of the surfactant and carboxylate groups of the polyion and stabilized by hydrophobic interaction of alkyl groups. However the BIC described in this paper are soluble over the whole range of the compositions of the surfactant and polyion mixtures. This includes the stoichiometric complexes, in which the charges of the polyion segments are neutralized completely. In this sense the BIC are totally different from the regular polyelectrolyte−surfactant complexes that usually are insoluble. The potentiometric titration, ζ-potential measurement, photon correlation spectroscopy, electron microscopy, and microcalorimetry techniques are used in this work to characterize the structures and transitions with these systems.

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Experimental Section

Materials. The block copolymer of *tert*-butyl methacrylate and ethylene oxide used in this study was prepared by sequential anionic polymerization generally following the previously published procedure.[7] The block lengths in copolymer were 176 for the PEO and 186 for *tert*-butyl methacrylate segments, respectively. This copolymer was hydrolyzed to obtain PEO-*b*-poly(methacrylic acid) (PEO-*b*-PMAA) as described in ref 7. The PEO-*b*-poly(sodium methacrylate) (PEO-*b*-PMANa) polymer was prepared by redissolving the acid form of the copolymer in a tetrahydrofuran−methanol mixture (95:5 v/v) and adding NaOH in methanol. The precipitate containing PEO-*b*-PMANa was filtered and washed with methanol and then redissolved in water and freeze dried. The concentration of carboxylate groups in the copolymer sample was estimated by potentiometric titration. The homopolymer poly(methacrylic acid) (PMAA) with a $\bar{P}_w = 930$ was obtained by radical polymerization.[8] Cetylpyridinium bromide monohydrate (C_{16}PyBr) and dodecylpyridinium bromide (C_{12}PyBr) were purchased from Aldrich Co. and were used without further purification.

Binding Isotherms. The binding isotherms of surfactants (C_{16}PyBr, C_{12}PyBr) to polyions of opposite charge were determined potentiometrically by using the following ion-selective electrode: Ag/AgCl|1 M NH_4NO_3 agar bridge|reference solution (surfactant, 2.5×10^{-4} M)|PVC membrane|sample solution|1 M NH_4NO_3 agar bridge|Ag/AgCl. The preparation of the PVC ion-selective electrode is described elsewhere.[9] The electromotive force (emf) of the cell was measured with a digital Radiometer pHM-83 pH-meter. The electrode exhibited a good Nernstian response over the range of surfactant concentrations examined. Binding isotherms were obtained by titration of 5×10^{-4} base-mol/L PEO-*b*-PMANa solutions with the solution of the corresponding surfactant. The results were corrected for the effect of the gradual decrease in the copolymer concentration as a result of the addition of the surfactant solution.

Spectrophotometry. The turbidity measurements were carried out using a Shimadzu UV160 spectrophotometer at 420 nm after equilibration of the system typically for 3 min. The data are reported as (100 − T)/100, where *T* is transmittance (%).

ζ-Potential and Sizing Measurements. The electrophoretic mobility (EPM) measurements were performed at 25 °C with an electrical field strength of 15−18 V/cm by using a "ZetaPlus" ζ-potential analyzer (Brookhaven Instrument Co.) with 15 mV solid state laser operated at a laser wavelength of 635 nm. The ζ-potential of the particles was calculated from the EPM values using the Smoluchowski equation. The effective hydrodynamic diameter was measured by photon correlation spectroscopy using the same instrument equipped with the multiangle option. All solutions were prepared using double-distilled water and were filtered repeatedly through the Millipore membrane with pore size 0.22 μM. The sizing measurements were performed at 25 °C at an angle of 90°.

Electron Microscopy. Two different procedures were used for preparing the samples for the transmission electron microscopy (TEM) studies: (1) negative staining with 1% uranyl acetate and (2) Pd/Pt shadowing. For the negative staining experiments a drop of the sample solution was allowed to settle on a Formvar precoated grid for 1 min. Excess sample was wicked away with filter paper, and a drop of staining solution was allowed to contact the sample for 1 min. The samples were analyzed using a Hitachi H-7000 microscope. For the shadowing experiments the Formvar precoated grids were used also, and the sample solutions were in contact with the grids for 5−10 min. After the excess sample was removed, the grids were air dried for 4−5 h, and Pd/Pt shadowing was performed. The samples were studied using a Phillips EM400 microscope.

Microcalorimetry. Microcalorimetric experiments were performed with an Omega isothermal titration microcalorimeter (MicroCal, Northampton, MA). PEO-*b*-PMANa was added into the sample cell. The reference cell served only as a thermal reference to the sample cell, and was filled with water.[10] Four microliter injections of a 25 mM solution of surfactant were carried out. All experiments were performed at 37.0 ± 0.1 °C, a temperature at which the surfactant solutions used for the injection are transparent.

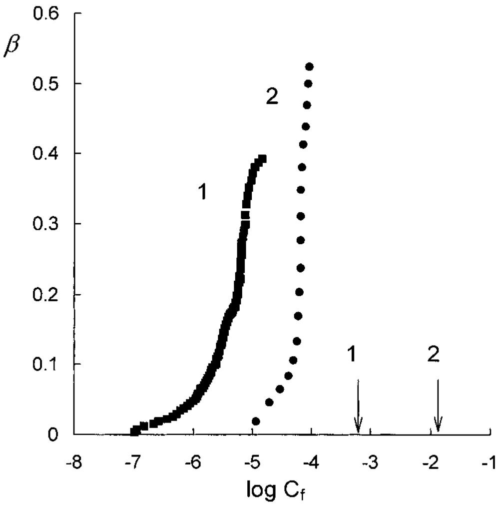

Figure 1. Binding isotherms of C_{16}PyBr (1) and C_{12}PyBr (2) to PEO-*b*-PMANa. Vertical arrows indicate the CMC for C_{16}PyBr (1) and C_{12}PyBr (2) as presented in ref 12. $C_i = 5 \times 10^{-4}$ base-mol/L, at 25 °C, pH 9.2.

Results and Discussion

Potentiometric Study of the Binding Equilibrium. One of the most convenient methods to study the binding of surfactant ions to the polymers is the potentiometric titration using an ion-selective membrane electrode.[11] The potentiometric results are usually represented in the form of binding isotherms, i.e. the fraction of occupied binding sites, β, vs the logarithm of the concentration of the free surfactant, C_f.[11] The parameter β is defined as

$$\beta = (C_t - C_f)/C_i \tag{1}$$

where C_t is the total concentration of added surfactant, C_f is determined using the calibration curves (i.e., linear plots of "emf vs log C_t" determined in the absence of polymer and C_t < CMC), and C_i is the concentration of ionic groups of the block ionomer. This technique was used to study the interaction between the *N*-alkylpyridinium bromides (C_{16}PyBr and C_{12}PyBr) and PEO-*b*-PMANa (the study was performed at pH 9.2 when all carboxyl groups of the block ionomer were ionized). Figure 1 shows the binding isotherms of C_{16}PyBr and C_{12}PyBr to the block ionomer. These isotherms have a typical sigmoidal shape which is an indication of cooperative binding of a surfactant to a polyion. As is also clear from Figure 1, the onset of the binding (also termed "critical association concentration" or "CAC") is observed at the surfactant concentration that is about 3 orders of magnitude lower than the corresponding CMC. For instance, the binding of C_{16}PyBr to the block ionomer (Figure 1, curve 1) starts in the range of C_{16}PyBr concentration from 10^{-7} M to 5×10^{-7} M, whereas the CMC[12] of C_{16}PyBr is 6×10^{-4} M. The CAC of C_{12}PyBr (Figure 1, curve 2) is observed at about 10^{-5} M, while the CMC[12] is 1.5×10^{-2} M. This behavior is very similar to that observed for the interaction of the *N*-alkylpyridinium salts and homopolymer PMANa (data not shown). As a result of this interaction, the polyelectrolyte−surfactant complexes are formed.[11] In such complexes the surfactant head groups are electro-

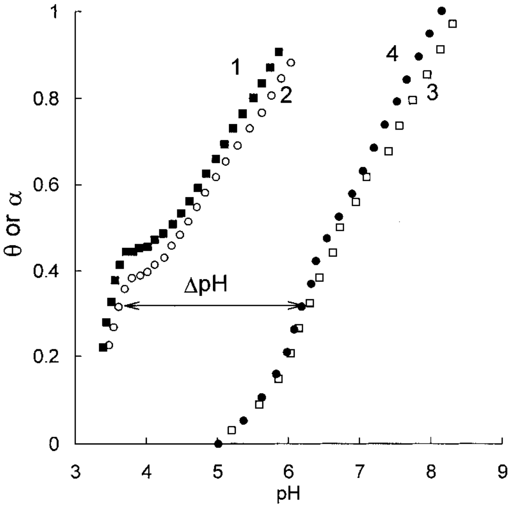

Figure 2. Dependencies of the degree of conversion (θ) in the polyion coupling reactions (■, ○) and degree of ionization (α) of polyacid samples (□, ●) for the following systems: C_{16}PyBr/PEO-*b*-PMAA (curve 1, ■); C_{16}PyBr/PMAA (curve 2, ○); PEO-*b*-PMAA (curve 3, □); and PMAA (curve 4, ●). The pH shift, ΔpH, between the θ−pH and α−pH dependencies is shown for the PMAA complex as an example.

statically bound to the polyion units, while the surfactant hydrophobic tails segregate to form micelle-like clusters. The cooperative stabilization of these clusters as a result of interaction between the surfactant and the polyion is a reason for the shift of the onset of the binding toward lower concentrations of the surfactant compared to the respective CMC.[11,13]

The interaction between a cationic surfactant (S^+) and a polyacid represents an ion exchange reaction resulting in the release of the protons in accordance with the following scheme:

$$(|-\mathrm{COOH})_n + n\mathrm{S}^+ \rightleftharpoons [|-\mathrm{COO}^-\mathrm{S}^+]_n + n\mathrm{H}^+ \qquad \text{(I)}$$

The equilibrium of this reaction at different pH can be studied by potentiometric titration.[14] The alkali titration curves were obtained for the mixtures of C_{16}PyBr with (1) PEO-*b*-PMAA and (2) PMAA. In both cases the total concentration of the surfactant was equal to the concentration of the ionizable groups of the polyacid. The degree of conversion, θ, in the ion exchange reaction (eq I) was determined from the original titration curves. For a weak polyacid, θ at a given pH is expressed in a good approximation as[14]

$$\theta = (m_b/V + [H+] - \sqrt{K_a C_o})/C_o \qquad (2)$$

where m_b is the number of moles of the added base, V is the current volume of the reaction system, K_a is the characteristic dissociation constant, and C_o is the base-molar concentration of the polyacid.

Figure 2 presents the dependence of θ on pH for the reaction of C_{16}PyBr with PEO-*b*-PMAA (curve 1) and PMAA (curve 2). The ionization degrees, α, for the individual polyacids are also presented in this figure (curves 3 and 4). As is seen from Figure 2 the θ values increased sharply over a narrow interval of pH with both PEO-*b*-PMAA and PMAA systems. This suggests a cooperative interaction between the cationic surfactant and polyacids, which is also consistent with the results of titration using an ion-selective electrode. The nonmonotonous character of the θ on pH curves with both PEO-*b*-PMAA and PMAA systems is possibly attributed to the cooperative transition of the intramolecular clusters of H-bonded PMAA units and/or H-complexes between PMAA and PEO segments[15] into the polyelectrolyte−surfactant complexes. The θ−pH curves observed with PEO-*b*-PMAA (curve 1) and PMAA (curve 2) were shifted to lower pH compared to α−pH curves of the corresponding polyacids (curves 3 and 4). The pH difference, ΔpH(α), between θ−pH and α−pH curves at each $\theta = \alpha$ is a *differential* measure of a free energy of cooperative stabilization of the complex[16] , assuming that in the case of BIC formation all alkali is consumed for neutralization of protons released in reaction

$$\Delta\Delta G^*_{\mathrm{st}}(\alpha) = 2.303RT\Delta\mathrm{pH}(\alpha) \qquad (3)$$

where $\Delta\Delta G^*_{\mathrm{st}}(\alpha)$ is the difference of free energies of ionization of the polyacid in the presence and absence of the cationic surfactant. For example, at $\theta = \alpha = 0.3$ the $\Delta\Delta G^*_{\mathrm{st}}(\alpha)$ values are −3.7 and −3.4 kcal·mol^{-1} for the PEO-*b*-PMAA and PMAA complexes, respectively. It is noteworthy, that the difference between the θ−pH curves for the C_{16}PyBr/PEO-*b*-PMAA and C_{16}PyBr/PMAA systems (curves 1 and 2) is much less significant than that previously reported for the complexes of poly(*N*-ethyl-4-vinylpyridinium) cation with the same polyacids.[6] Importantly, $\Delta\Delta G^*_{\mathrm{st}}(\alpha)$ observed with the polycation/PEO-*b*-PMAA complex was about −3.3 kcal·mol^{-1} ($\theta = \alpha = 0.3$) which is close to that for the C_{16}PyBr/PEO-*b*-PMAA complex. These were the complexes formed by the PMAA homopolymer that revealed a significant dependence on the nature of the cationic component (surfactant vs polycation). For example, $\Delta\Delta G^*_{\mathrm{st}}(\alpha)$ for the polycation/PMAA system at $\theta = \alpha = 0.3$ was only −2.0 kcal·mol^{-1} (compared to −3.4 kcal·mol^{-1} observed for the C_{16}PyBr/PMAA complex). It was suggested that some steric difficulties related to the precipitation of the polycation/PMAA complex were hindering the binding of the polyions.[6] These effects were not observed with the polycation/PEO-*b*-PMAA complexes that were soluble. It is possible that the similarity in the behavior of C_{16}PyBr/PMAA and C_{16}PyBr/PEO-*b*-PMAA systems is explained by the absence of the steric difficulties to the binding of the low molecular mass cationic surfactant. Overall, the potentiometric studies suggested that binding of cationic surfactants to block ionomers of the opposite charge is similar to that observed with a regular polyelectrolyte−surfactant complex. However, some major peculiarities in the solution behavior of the BIC were observed that make these systems very different from regular polyelectrolyte−surfactant complexes.

Solubility of the C_{16}PyBr/PEO-*b*-PMANa System. Figure 3 represents the data on the turbidity of the C_{16}PyBr/PEO-*b*-PMANa and C_{16}PyBr/PMANa systems as a function of the composition of the mixture, Z. The composition of the mixture was expressed as a ratio of the C_{16}PyBr concentration to the concentration of ionic groups of the corresponding polyanion:

$$Z = C_t/C_i \qquad (4)$$

Since the study was performed at pH 9.2, C_i equaled the base-molar concentration of the methacrylic acid units in the system. As seen from Figure 3, the C_{16}PyBr/PEO-*b*-PMANa mixture is practically transparent or slightly opalescent for all values of Z (curve 1). In contrast, the C_{16}PyBr/PMANa system phase separates under comparable conditions (curve 2). It is well-known that the products of interaction between

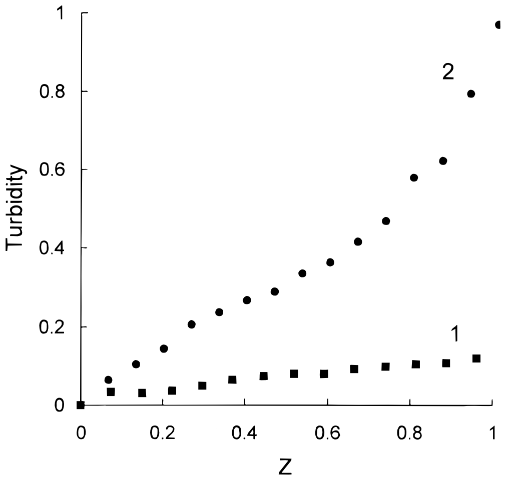

Figure 3. Turbidity in the C_{16}PyBr/PEO-*b*-PMANa (curve 1) and C_{16}PyBr/PMANa (curve 2) systems as a function of the composition of the mixture. $C_i = 1.08 \times 10^{-3}$ base-mol/L, at 25 °C, pH 9.2.

polyelectrolytes and surfactants of opposite charge, including PMANa and C_{16}PyBr, are water insoluble.[17] At $0 < Z < 1$ disproportionation is observed, so that the stoichiometric polyelectrolyte−surfactant complex precipitates and an excess of free polyelectrolyte chains remain in solution. At $Z = 1$ all polyelectrolyte chains incorporate into the stoichiometric complex and precipitate. The facts that (1) the C_{16}PyBr/PEO-*b*-PMANa system is soluble in all range $0 < Z \leq 1$ and (2) surfactant cations bind to polyanion segments of the block ionomer, i.e. the complex forms (as seen from the potentiometric titration), suggest a major difference in the structure and behavior between the block ionomer− and regular polyelectrolyte−surfactant complexes.

ζ-Potential and Size of the Particles. The solubility of the complexes from C_{16}PyBr and PEO-*b*-PMANa permitted their characterization using the laser microelectrophoresis technique and photon correlation spectroscopy. The data on the ζ-potential (ζ) and effective diameter (D_e) of the species of the complex as a function of Z are presented in Figure 4. The increase in the amount of the C_{16}PyBr added to the block ionomer at $0 < Z \leq 1$ resulted in the increase of ζ indicating a decrease in the net negative charge of the particles (Figure 1a). This behavior is evidently explained by the neutralization of the polyanion segments of the block ionomer incorporated in the complex by the surfactant cations. Importantly, at $Z = 1$, ζ-values reached 0, suggesting that the charges were neutralized completely. This result was consistent with the assumption that at $Z = 1$ all surfactant cations added to the system formed salt bonds with the carboxylate groups of the PEO-*b*-PMANa and that the complex was stoichiometric. Binding of the surfactant to the block ionomer at $0 < Z \leq 1$ also led to a decrease in the particle size. This was explained by the probable condensation of the polyion segments of the block ionomer in the complex as a result of the charge neutralization. Indeed a minimum effective diameter (≈67 nm) was observed at $Z = 1$, when the particles were electroneutral. Consequent measurements with these samples showed that the ζ-potential and sizes are the particles remained unchanged for at least several days. Since these systems are stable in solution and their sizes are close to that of the block copolymer micelles (e.g., polystyrene-*b*-PEO[18] or sodium polyacrylate-*b*-polystyrene[19]), it is reasonable to assume that they are micelle-like aggregates with a core of polyanion segments neutralized by surfactant cations, and a shell of PEO segments. When Z crossed 1 the ζ-potential became positive (Figure 4a), and the size of the particles began increasing (Figure 4b). Still, the system was practically transparent, and no aggregation was observed over the course of several days. The change in the sign of ζ at $Z > 1$ was consistent with incorporation of the excess of cationic surfactant into the particles of the stoichiometric complex. It is likely that the aliphatic tails of the surfactant were inserting into the hydrophobic core of the complex with the ionic head groups localizing in the surface area. Both the ζ-potential and the effective diameter of the particles practically leveled-off ($\zeta \approx 17$ mV and $D_e \approx 93$ nm) at $Z \approx 3$. On the basis of these data, one can assume that above this point further incorporation of surfactant ions in the complex was hindered, e.g. by electrostatic repulsion. If this hypothesis is true, then the excess of the surfactant that did not incorporate into the complex remained in the solution.

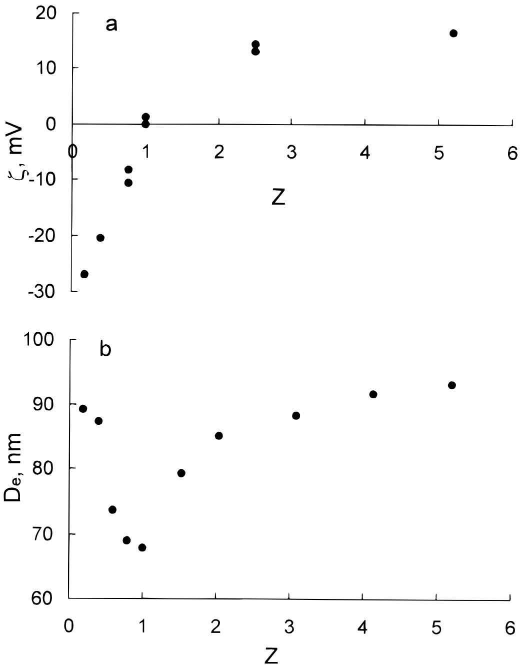

Figure 4. (a) ζ-Potential and (b) effective diameter of particles formed in the C_{16}PyBr/PEO-*b*-PMANa mixture at various Z. $C_i = 8 \times 10^{-4}$ base-mol/L; 25 °C, pH 9.2.

Electron Microscopy Characterization. The morphology of the complexes formed in the C_{16}PyBr/PEO-*b*-PMANa mixture was investigated by electron microscopy technique in a wide range of Z. Typical micrographs are presented in the Figures 5 and 6. A spherical shape of the particles observed for all compositions of the mixture is noteworthy. In some cases, conglomerates of the spheres were observed, which were probably formed during evaporation of the solvent. The sizes of the isolated micelles calculated from electron microscopy data were in a very good agreement with the photon correlation spectroscopy data reported above. At $0 < Z \leq 1$ the particles were fairly monodisperse. The size of the particles appeared to be at a minimum (from 40 to 65 nm) at $Z = 1$. At $Z = 2.5$ something resembling two different populations of spherical particles was observed: (1) smaller spheres, similar to these observed at $Z = 1$, and (2) larger spheres (from 75 to 100 nm). In contrast, at $Z = 5$ the particles were remarkably

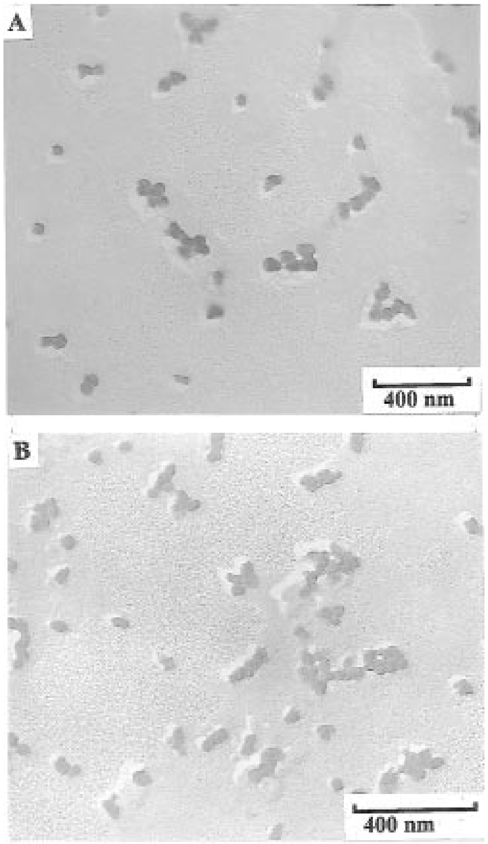

Figure 5. TEM micrographs of the complexes between C_{16}PyBr and PEO-*b*-PMANa at (A) $Z = 0.6$ and (B) $Z = 1.0$. The micrographs were obtained using Pd/Pt shadowing.

monodisperse and had an average diameter of about 85 nm.

Microcalorimetry. The interaction between C_{16}PyBr and PEO-*b*-PMANa was investigated using microcalorimetry. In these experiments a 25 mM solution of C_{16}PyBr was injected into the sample cell with or without the block ionomer. Figure 7a shows the microcalorimetric titration curves, i.e. the dependency of the enthalpy vs the final concentration of C_{16}PyBr in the sample cell, C_t. The curve obtained for C_{16}PyBr alone (curve 1) had a sigmoidal shape typical for the micelle-forming surfactants.[20] When C_t was less than the CMC the enthalpy, ΔH_1, was a sum of the enthalpies of micelle dilution and micellization (with a negative sign since the micelles were deaggregated):

$$\Delta H_1 = \Delta H_{\text{dilution}} - \Delta H_{\text{micellization}} \tag{5}$$

In contrast, at $C_t >$ CMC the enthalpy accounted for the dilution only, since the deaggregation of the micelles did not occur. (Dilution enthalpy was insignificant in the experiment presented, i.e. $\Delta H_1 = \Delta H_{\text{dilution}} \approx 0$.) Therefore, a sharp decrease in the enthalpy was observed when the CMC was crossed. The titration curve obtained when PEO-*b*-PMANa was present in the solution was more complex due to the effects of interaction of C_{16}PyBr with the block ionomer (curve 2). To discriminate these processes, the difference of the enthalpy with (curve 2) and without (curve 1) the block ionomer was calculated. The result is presented in Figure 7b as the dependence of the cumulative enthalpy on Z. (The scales of Z and C_t axes in Figure 7 are adjusted, so that the C_{16}PyBr concentration in Figure 7b can be determined by comparing with the C_t axis in Figure 7a.) At $C_t <$ CMC the net enthalpy, ΔH_2, determined in the presence of the block ionomer includes the components accounting for the micelle dilution and deaggregation, as well as the transfer of the C_{16}PyBr unimers from aqueous surroundings into the complex:

$$\Delta H_2 = \Delta H_{\text{dilution}} - \Delta H_{\text{micellization}} + \Delta H_{\text{c,unimer}} \tag{6}$$

Therefore the cumulative enthalpy under these conditions ($C_t <$ CMC) was a measure of the enthalpy of interaction of C_{16}PyBr with the PEO-*b*-PMANa-based complex:

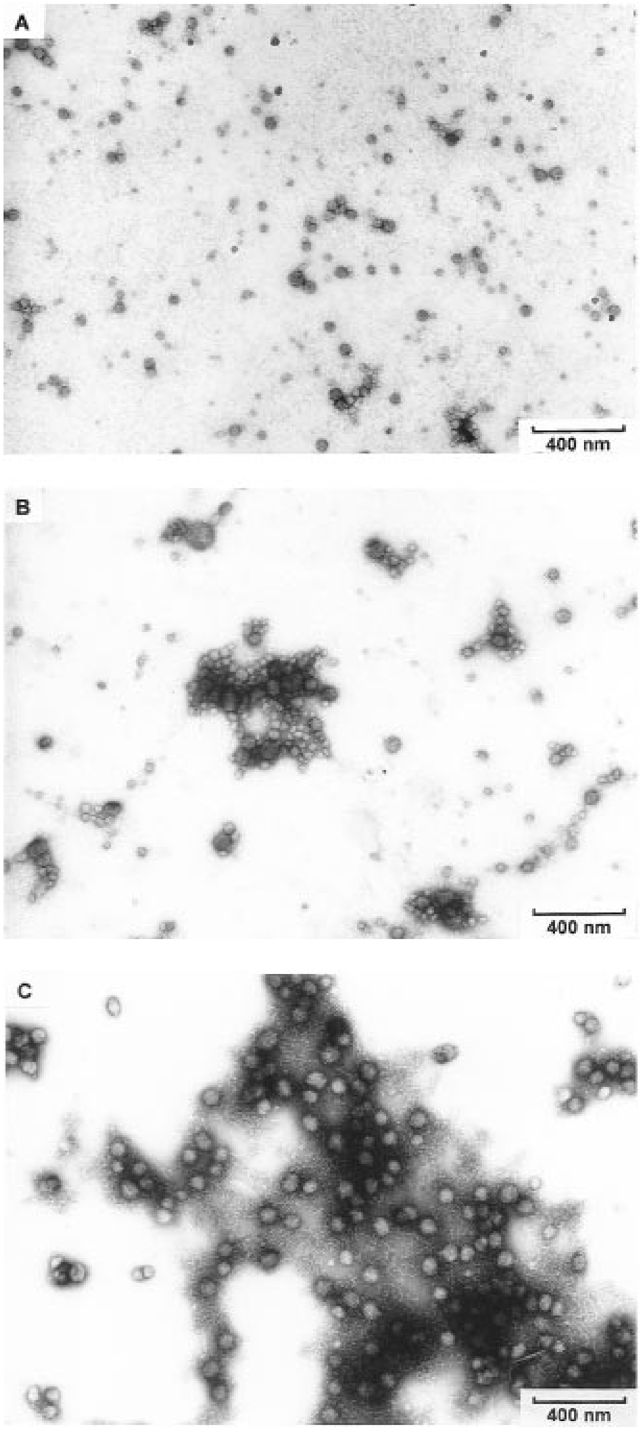

Figure 6. TEM micrographs of the complexes between C_{16}PyBr and PEO-*b*-PMANa at (A) $Z = 1.0$, (B) $Z = 2.5$, and (C) $Z = 5$. The micrographs were obtained using negative staining (uranyl acetate).

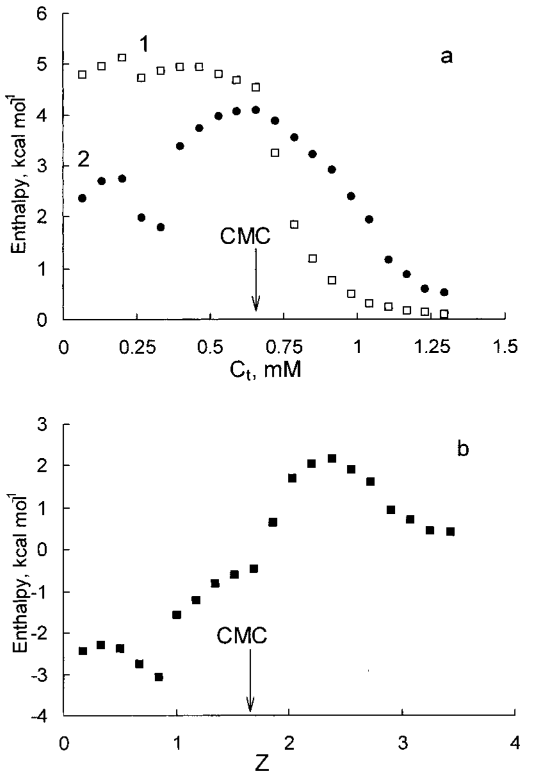

Figure 7. (a) Microcalorimetric titration curves of $C_{16}PyBr$ obtained without (curve 1) and with (curve 2) 4×10^{-4} base-mol/L PEO-*b*-PMANa in the sample cell. (b) Dependence of the cumulative enthalpy on *Z* for the $C_{16}PyBr$/PEO-*b*-PMANa system. A vertical arrow indicates the CMC for $C_{16}PyBr$. Other conditions are 37 °C, pH 9.2.

$$\Delta H_2 - \Delta H_1 = \Delta H_{c,unimer} \qquad (7)$$

It is seen therefore from the Figure 7b that at $Z < 1$ the interaction enthalpy was negative (≈ -2 kcal·mol^{-1}); i.e., the process was exothermic. The same value was obtained for the enthalpy of $C_{16}PyBr$ binding to homopolymer PMANa at $Z \leq 0.2$. In contrast, the interaction of $C_{12}PyBr$ with the PEO-*b*-PMANa system was weakly endothermic: $\Delta H_{c,unimer} \approx 0.3$ kcal·mol^{-1} (data not shown). As a first approximation, at $Z < 1$ the enthalpy of interaction of ionic surfactant with the polyion of opposite charge includes the contributions from electrostatic interactions of the charged groups and aggregation of the surfactant molecules. It is known that the electrostatic component is usually positive and small.[21] The surfactant aggregation can have a significant negative impact if it involves the crystallization of aliphatic tails of the surfactant.[22,23] However, crystallization is observed only with sufficiently long hydrocarbon tails, e.g. C_{16} and longer. Therefore, the exothermic effect during interaction of $C_{16}PyBr$ and PEO-*b*-PMANa can be explained by the contribution of the crystallization of the cetyl groups of the surfactant. In contrast, the crystallization did not occur in the case of $C_{12}PyBr$, and the driving force for the formation of the $C_{12}PyBr$/PEO-*b*-PMANa complex appeared to be exclusively entropic. At $Z > 1$ and $C_t <$ CMC the $\Delta H_{c,unimer}$ calculated for the $C_{16}PyBr$/PEO-*b*-PMANa system increased and reached -0.5 to -0.3 kcal·mol^{-1} just before the CMC. It is known from the ζ-potential measurements that positively charged particles containing an excess of the surfactant cations are formed under these conditions. Therefore the increase in $\Delta H_{c,unimer}$ was probably explained by the endothermic contribution of the electrostatic repulsion of the cationic groups in the complex.[24] The nonmonotonous dependency of the cumulative enthalpy at $C_t >$ CMC is explained by the micellization of the surfactant in the absence of the block ionomer (compare with Figure 7a, curve 1). Under these conditions, eqs 5−7 are not correct. However, it is reasonable to assume that at sufficiently high C_t and *Z*, the particles of the $C_{16}PyBr$/PEO-*b*-PMANa complex are in equilibrium with the surfactant micelles. Overall, the results of the microcalorimetry study are consistent with the assumption that at $Z < 1$ the binding of the cationic surfactants to the block ionomer is similar to that observed with the homopolymer polyion. However, the block ionomer complex remains in solution while the regular polyelectrolyte−surfactant complex precipitates. The transition in $\Delta H_{c,unimer}$ observed at $Z > 1$ ($C_t <$ CMC) indicates that a different type of complex is formed that is also consistent with the result of the ζ-potential measurements, sizing, and TEM experiments.

Conclusion

A very unusual self-assembly behavior is described in this paper involving the mixtures of poly(ethylene oxide)-*block*-polymethacrylate anions and *N*-alkylpyridinium cations. Like the regular polyelectrolyte−surfactant complexes, the BIC are formed due to electrostatic attraction between the surfactant head groups and the ionic units of the polyion segments and hydrophobic interaction of alkyl groups. However, they remain soluble for the whole range of compositions of the mixture. The solubility of the stoichiometric complexes, in which the charges of the polyion segments are neutralized completely, is remarkable. This behavior is unique for regular polyelectrolyte−surfactant complexes that are usually water-insoluble. In addition, when a saturating excess of the surfactant is added to the solution of the stoichiometric BIC, a special type of particle is formed that is positively charged and remarkably monodisperse. These systems apparently represent 1:1 electrostatic complexes incorporating some excess of surfactant cations. The detailed structure of these species is worth investigating. While free *N*-alkylpyridinium cations form small spherical micelles in aqueous solutions, in the presence of polyanions (e.g. cross-linked polyacrylate anion) they self-assemble into lamellae structures, which are very similar to those from phospholipids.[23] It is very probable therefore that the complexes studied in this work comprise the lamellae elements. One way to picture such structures is vesicles composed of closed lamellae from polymethacrylate anion-bound surfactant and PEO chains "grafted" to the lamellae. The validation of this hypothesis is underway in our laboratory. Overall, this work strongly suggests that complexes from block ionomers and oppositely charged surfactants represent a new class of lyophilic colloids, which exhibit combined properties of amphiphilic block copolymers and polyelectrolyte complexes.

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(13) As a first approximation the stabilization free energy, ΔG_{st}, can be estimated as a difference of the free energy of surfactant association with the block ionomer (RT ln CAC) and free energy of micellization (RT ln CMC): $\Delta G_{st} = RT \ln \mathrm{CAC} - RT \ln \mathrm{CMC}$. The ΔG_{st} values obtained for C_{16}PyBr and C_{12}PyBr using the binding isotherms are −4.6 and −4.2 kcal·mol^{-1} respectively.

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$$\Delta G_{\mathrm{total}} = \int_0^{\alpha_1} \Delta\Delta G^*_{\mathrm{st}}(\alpha)\, d\alpha = 2.303\, RT \int_0^{\alpha_1} \Delta \mathrm{pH}(\alpha)\, d\alpha$$

See ref 6 for derivation.

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