A New Approach to the Phase Behavior of Oppositely Charged Polymers and Surfactants

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The complex salt (ionic surfactant + polymeric counterion) cetyltrimethylammonium polyacrylate (CTAPA) has been synthesized, and its aqueous mixtures with cetyltrimethylammonium bromide (CTABr) have been studied. These mixtures differ from conventional oppositely charged polymer/surfactant mixtures in that the conventional counterion of the polyion (usually sodium, for the polyacrylate) is absent, which simplifies the studies and their interpretation considerably. The phase diagram of the CTAPA/CTABr/water system at > 20wt % water and at 40 °C has been established, representing the first truly ternary phase diagram of an oppositely charged polymer/surfactant pair in water. The two dimensions of the phase diagram may be chosen as the water content (in weight percent) and the fraction of bromide counterions, x_{Br} (in units of charge equivalents). The phase diagram is characterized by a large hexagonal phase (at low water contents and for all values of $x_{\rm Br}$), a small cubic phase (at 55 wt % water content and for $x_{\rm Br} < 0.1$), a narrow isotropic (micellar) phase (at high water contents and for $x_{Br} > 0.9$, and a large multiphase region (at water contents >50 wt %) containing two or three of the cubic, hexagonal, or isotropic phases in coexistence. The cubic and hexagonal phases are connected to the corresponding phases that separate out from aqueous NaPA/CTABr mixtures. The maximum water uptake of the hexagonal phase is remarkably constant at ca. 50 wt % over a large CTAPA/CTABr composition range ($x_{Br} < 0.9$). The study confirms previous conclusions that the polyacrylate counterions favor a higher aggregate curvature (leading to smaller aggregates) than do the bromide counterions.

Introduction

In recent years, an increasing number of studies of oppositely charged polymer/surfactant mixtures have focused on concentrated systems. Such systems include the dry complex salts,¹⁻⁷ the concentrated "precipitates" or "coacervates" that separate out from aqueous mixtures in certain concentration intervals,⁸⁻¹⁶ and the collapsed gels that result when polyelectrolyte gels are immersed in solutions of oppositely charged surfactant.¹⁷⁻²⁴ A variety of surfactant aggregate structures (micellar, cubic, hexagonal, lamellar, et al.) have been observed in such systems, but the understanding of the various factors that determine these aggregate structures, and their miscibility with water, is still in its infancy. Apart from the characteristics of the polyion (charge density, rigidity, hydrophobicity/hydrophilicity) or the surfactant (chain length, identity of charged group), a key question concerns the effects of simply varying the concentrations of the various ionic species (the polyion, the surfactant ion, the simple counterions) contained in the mixture. To what extent may the structures and concentrations of the concentrated phase be manipulated by the choice of the initial content of surfactant, polyelectrolyte, (external salt), and water in the mixture from which phase separation occurs?

Recently, Ilekti et al.^{8,9} investigated the mixtures of sodium polyacrylate (NaPA), cetyltrimethylammonium bromide (CTABr), and water in some detail with the questions above in mind. A rich variety of structures (micellar, hexagonal, cubic) and water contents were found, depending on both the surfactant/poly-electrolyte ratio and the overall water content of the initial



Figure 1. A three-dimensional pyramid phase diagram (schematic) that fully describes the phase behavior of aqueous mixtures of a charged surfactant with an oppositely charged polyelectrolyte. See text.

mixture. Indeed, it was possible to vary both the structure and the concentration of the concentrated phase(s) simply by successively diluting a stoichiometric mixture of polyelectrolyte and surfactant with water.

If the results were interesting and promising, the studies by Ilekti et al.,^{8,9} as well as previous less-detailed studies,^{25,11} also clearly illustrated the inherent difficulty in studying the phase behavior of conventional mixtures of polyelectrolyte, surfactant, and water. Such systems are four-component systems, and their full description requires a three-dimensional phase diagram, such as the pyramid phase diagram proposed by Thalberg et al.²⁵ (Figure 1). The pyramid has water at the top and the four possible combinations of the four ions into neutral salts at the

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corners of its quadratic base. Here, as in refs 8 and 9, we have chosen to use the following terminology for the various ions and neutral salts. The *surfactant* is the salt composed by the *surfactant ion* and its (normal) *simple counterion*, whereas the *polyelectrolyte* is the salt composed by the *polyion* and its *simple counterion*. The *complex salt* is then composed by the surfactant ion and the polyion, whereas the *simple salt*, finally, is the combination of the two simple counterions from the surfactant and the polyelectrolyte.

Oppositely charged polymer/surfactant mixtures are generally prepared as mixtures of the surfactant with the polyelectrolyte; this defines the conventional mixing plane indicated in Figure 1. A two-dimensional map of the phase behavior of conventional mixtures can be drawn in this plane, defining one-phase, twophase, and multiphase areas. The problem with this description, however, is that the compositions of the coexisting phases in the two- or multiphase areas are not situated within the conventional mixing plane, that is, their compositions cannot be described as combinations of polyelectrolyte, surfactant, and water. This is schematically illustrated by the tie-line in Figure 1, which shows that, quite naturally, the concentrated phase that separates out is enriched in the complex salt, whereas the dilute phase (often) essentially contains only simple salt and water. Apart from the difficulties to describe the phase diagram graphically, it is clear that a full description of the pyramid is cumbersome, to say the least.

In this study, we have circumvented the problem above by a seemingly obvious strategy that, nevertheless, seems not to have been used previously. We have eliminated one of the simple ions from our mixtures. Thus, we have chosen to study *a truly ternary mixture* (neglecting the polydispersity of the polyion) of the complex salt, the surfactant, and water. This mixing plane corresponds to the front face of the pyramid in Figure 1. By performing this study, we are thus asking the question: How does the phase behavior of an ionic surfactant in water change when the counterions are changed from pure simple counterions, via mixtures of simple counterions and polyions, to pure polyions? As far as we are aware, this simple and basic question has not previously been addressed in a clean systematic study.

For this first study of the phase behavior of a ternary surfactant/complex salt/water mixture (additional studies are in progress), we have chosen CTABr as the surfactant and cetyltrimethylammonium polyacrylate (CTAPA) as the complex salt. Thus, the results here belong to the same pyramid as the mixtures of CTABr and NaPA that were studied in detail previously.^{8,9} The polyion, PA⁻, is quite hydrophilic; there is no strong hydrophobic attraction between the polyion and the surfactant aggregate, and hence the polyion–surfactant attraction is essentially electrostatic. This is evidenced because the complex CTAPA salt dissolves in water on the addition of simple salt caused by electrostatic shielding.

An interesting conclusion from the previous studies of CTABr/NaPA mixtures was that the curvature and geometry of the surfactant aggregate was influenced not only by the change from monomeric to polymeric counterions per se, but also by the chemical identity of the charged group (bromide vs carboxylate). Another objective of our study is to elucidate this specific point further. As in the previous studies, both phase compositions and phase structures have been determined, the latter by small-angle X-ray scattering (SAXS) experiments.

Materials and Methods

Materials. Poly(acrylic) acid (HPA; 2 000 g/mol), was purchased from Aldrich. This is the same product (but not the

same batch) as that used in refs 8 and 9. The batch in refs 8 and 9 was examined through size-exclusion chromatography coupled with low-angle light scattering. (See the references for experiment details.) The HPA had a number average molar mass $M_{\rm p}$ of 2800 g/mol and a weight average mass $M_{\rm w}$ of 4700 g/mol. The polymer batch used in this study was purified by dialysis for 5 days against Millipore water, followed by freeze-drying. ¹H NMR revealed a small amount of an organic impurity in the polymer, which remained even after the dialysis procedure. Two different batches of HPA both showed the presence of the impurity, which we tentatively ascribe to heterounits at the ends of the short polymer, originating from the synthesis procedure. Titration of HPA with NaOH showed that the equivalent molar mass of the polymer was 89.3 g/(mol carboxylic acid), as compared with the theoretical value of 72 g/mol for a repeating unit of HPA. Presumably, this difference is caused primarily by the impurity in the polymer. The contribution from water to the equivalent molar mass should be small. The water uptake of freeze-dried HPA exposed to ambient air was 2 wt % after 1 h and 5 wt % after several days.

CTABr was purchased from Merck and used without further purification. The molar mass of CTABr is 364.5 g/mol. The molar mass of the bromide ion, 79.9 g/mol, is close to the molar mass per charged unit of PA. Thus, the equivalent molar masses (the molar masses per ion pair) of CTAPA and CTABr are almost the same (within 2%). The (equivalent) fraction of bromide counterions in a sample will be expressed as x_{Br} = (equivalents of bromide)/(total equivalents of bromide + polyacrylate).

The complex salt, CTAPA, was prepared by titrating the hydroxide form of the surfactant with the acid form of the polymer. The first step was to convert CTABr into CTAOH by ion exchange.²⁶ The ion-exchange resin (Dowex SBR, dry mesh 20-50, from Sigma) was charged by stirring in an excess amount of 1 M NaOH for 2 h and then rinsed with Millipore water until the pH of the water reached 7. CTABr (40 g) was then dissolved in a plastic beaker containing 200 g of the charged ion-exchange resin (a large excess of hydroxide ions) and 300 mL of Millipore water. The solution was stirred until all CTABr was dissolved. The slurry was filtered and the filtrate rinsed with Millipore water into a new batch of 200 g resin and 300 mL water, which was stirred for another 2 h. The last step was repeated once more with a third fresh batch of resin. The alkaline solution now contained CTAOH at a concentration of approximately 0.05 M. A solution of HPA (0.5 M) was titrated drop by drop into the freshly prepared solution of CTAOH under stirring. This was done immediately to avoid Hofmann elimination of the quaternary ammonium hydroxide group of the surfactant in the basic solution.²⁷ (Any possible uptake of carbon dioxide from the air should have been driven back by the addition of acid to the solution.) The pH was measured by using a standard pH electrode. A white precipitate, the complex salt was formed at the start of the titration. The titration was continued until the equivalence point was reached in the solution. The latter point was taken as the inflection point (pH = 8.6) in the pH-titration curve, as determined in a separate measurement. After equilibrating overnight, the solution with the precipitate was freeze-dried. The complex salt was then obtained as a white, hygroscopic powder, which was put to storage over a silica gel in a desiccator. Titrimetric analysis gave a bromide content below the detection limit (0.3 wt %) in the complex.

Weighing experiments indicated a weight increase of the complex salt, through water uptake, by approximately 10 wt %

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in the desiccator, and by 20 wt % after prolonged storage in air. Care was taken to minimize the exposure of the complex salt to air during sample preparation, and a water content of 10 wt % in the complex salt was assumed when calculating the sample compositions. The water uptake of the surfactant, CTABr, was less than 1 wt % in air.

Sample Preparation. Appropriate amounts of the complex salt, the surfactant and water were weighed and put in glass tubes. After mixing with a Vortex vibrator, the tubes were flame-sealed. The mixing was continued in a centrifuge during 6 h at 4 000 rpm and 40 °C. The tubes were turned end over end every 15 min. The samples were left to equilibrate in an oven at 40 °C for several weeks. This temperature was chosen to exceed the Krafft point of CTABr (23 °C); it was also the temperature chosen in the earlier studies of CTABr/NaPA/water mixtures.^{8,9}

Methods. The samples were investigated by visual inspection in normal light and between crossed polarizers to detect optically anisotropic phases (in the present case, the hexagonal phase).

SAXS measurements were performed with two different setups. At the D 43 instrument at L.U.R.E. in Orsay, France, a parallel monochromatic beam of wavelength 1.445 Å was focused with point collimation on the sample. The sample was contained in a flat cell with mica windows kept at 40 °C. The sample-to-detector distance was 395 or 377 mm. A Kratky compact small-angle system with linear collimation was used at the Lund laboratory. The X-rays were detected with a positive sensitive detector. The wavelength was 1.54 Å, and the sample-to-detector distance 277 mm. The sample cell had mica windows and was maintained at 40 °C.

The bromide content of dilute phases was determined by a titrimetric analysis. The sample was titrated with a mercuric nitrate solution with diphenyl carbazone as indicator.

Results and Discussion

Overview of the Phase Diagram. The phase diagram of the ternary system CTAPA/CTABr/water at 40 °C is presented in Figure 2. Sample compositions are given as weight percent of the components. Owing to the closely similar equivalent molar masses of CTAPA and CTABr (cf. the materials section), the total equivalent concentration of salt at a given weight percent of solids is very nearly independent of the counterion; moreover, the equivalent ratio of CTABr to CTAPA is almost equal to the mass ratio.

The phase diagram is based on analyses of almost 150 samples. It contains, in the investigated composition region (>20 wt % water) three single-phase regions, three two-phase regions, and one three-phase triangle. The dominating parts of the phase diagram are the single hexagonal phase (which extends all the way across, from pure CTAPA, via all mixing ratios, over to pure CTABr), and the large two-phase area with coexisting micellar and hexagonal phases. The other single-phase regions, the cubic phase and the micellar phase, are limited to the almost pure ion forms CTAPA and CTABr, respectively. Note that the phase diagram, being a true ternary phase diagram, contains explicit tie lines connecting coexisting compositions of the single-phase regions.

Below, we will discuss in some detail the trends that are observed as the compositions of the mixtures are varied along different paths in the phase diagram.

The Binary Mixtures. As is well-known, CTABr is highly water soluble, forming a micellar or a hexagonal phase at high or low water contents, respectively.²⁸ By contrast, as expected, CTAPA only takes up a limited amount of water. The maximum



Figure 2. Experimental phase diagram of the complex salt CTAPA, the surfactant CTABr, and water at 40 °C. The mixing plane corresponds to the front face of the pyramid in Figure 1.



Figure 3. SAXS spectrum of the hexagonal phase containing 60 wt % CTAPA and 40 wt % water at 40 °C. Relative locations of visible peaks: 1, $3^{1/2}$, $4^{1/2}$.

water content is ca. 55 wt % of the total mass, corresponding to 25 water molecules per ion pair of CTAPA. Further added water ends up as a separate phase of essentially pure water (cf. the biphasic area on the water-CTAPA axis in Figure 2).

Below 55 wt % water, different structures of CTAPA are found, depending on the water content. The dry complex salt is a white and hygroscopic powder. It readily absorbs humidity from air up to 20 wt % water (5 water molecules per ion pair of CTAPA). SAXS measurements on a sample that contained ca. 10 wt % water indicated a mixture of lamellar structures. Previous investigators have also found a lamellar structure for dry CTAPA.^{6,14,29} A detailed investigation of the dry or verywater-poor systems is beyond the scope of this investigation.

At water contents between ca. 30 and 50 wt %, the CTAPA/ water mixtures are translucent, solidlike, and birefringent. The SAXS measurements show hexagonal patterns (Figure 3), and this region may thus be identified as a hexagonal single-phase region. At about 50 wt % of water, a sharp transition occurs;



Figure 4. SAXS spectrum of the cubic phase containing 45 wt % CTAPA and 55 wt % water at 40 °C. Relative locations of peaks (with invisible peaks of the *Pm3n* structure given in parentheses): (1), $2^{1/2}$, $4^{1/2}$, $5^{1/2}$, $6^{1/2}$, $8^{1/2}$, $10^{1/2}$, $12^{1/2}$, $(13^{1/2})$, $14^{1/2}$, $16^{1/2}$, $17^{1/2}$, $(18^{1/2})$, $20^{1/2}$, $21^{1/2}$.

the samples become optically isotropic and the SAXS spectra show a cubic structure of the *Pm3n* type (Figure 4). This cubic structure is composed of slightly elongated globular micelles in a body-centered cubic arrangement.³⁰ The same structure was previously observed for the concentrated phase that separates out from aqueous CTABr/NaPA mixtures at very high dilution.⁸ The resolution of the spectrum is much better in the present study, and 12 of the spectral lines can be identified (Figure 4).

The stability range of the cubic phase in the binary CTAPA/ water mixture is quite narrow. In our experiments, an increase of the water content beyond 55 wt % resulted in samples that were initially whitish, but after prolonged storage (for months) at 40 °C separated into a clear cubic top phase and a low-viscous aqueous bottom phase. (The density of aqueous CTAPA is lower than the density of water.⁸) The solubility of the complex salt in water was not determined, but in all probability it is very low. The most dilute mixture that we prepared (1 wt % of CTAPA in water) was clearly still biphasic. The concentrated phases from several samples in the biphasic region were investigated by SAXS, giving spectra identical (within experimental error) with the one shown in Figure 4.

Addition of CTABr to CTAPA/Water Mixtures. The most striking effect of adding CTABr to CTAPA/water mixtures is that the cubic phase rapidly disappears. The pure cubic phase extends only to $x_{Br} = 0.06$; a larger fraction of bromide counterions leads to the formation of a hexagonal phase. Evidently, (cf. also below) the curvature of the surfactant aggregate decreases when polyacrylate counterions are replaced by bromide counterions. This decrease in curvature induces a transition from essentially globular to cylindrical surfactant aggregates. The difference between the two counterions may be attributed to the fact that bromide ions bind "chemically" to cationic surfactant aggregates, whereas carboxylate ions, such as the simple acetate ion, remain fully dissociated.³¹ The hexagonal and the cubic phases coexist up to a bromide fraction of 0.20-0.30, and at high water contents, a three-phase coexistence exists between these two phases and excess water. At still higher bromide fractions, the large two-phase area of hexagonal/micellar coexistence appears.

Samples from all multiphase areas were checked visually, and their multiphase nature was confirmed by SAXS analyses, showing superposed cubic/hexagonal structures in the cubic/ hexagonal two-phase area and in the three-phase area. We did not succeed in separating the cubic and hexagonal phases macroscopically; hence, they could not be analyzed separately.

The limited extension of the cubic phase is a striking feature: replacing a small amount of PA by Br results in the formation of a new, hexagonal, phase, which is enriched in Br. A similar behavior was observed in previous work on the phase behavior of stoichiometric CTABr/NaPA mixtures with increasing amounts of added water.⁸ The authors found that an increasing total water content led to a decreasing bromide content of the surfactant-rich phase, and that the latter was hexagonal down to very low bromide fractions (e.g., $x_{Br} = 0.28$). This result agrees with the phase diagram in Figure 2, where the phase in equilibrium with the dilute phase is hexagonal down to a bromide fraction of 0.20–0.30. In the CTABr/NaPA mixtures, the cubic structure of the surfactant-rich phase developed only when the bromide fraction had decreased further (e.g., at a total water content of 99 wt %).

Addition of CTAPA to CTABr/Water Mixtures. We saw above that small additions of CTABr sufficed to make one of the structures, the cubic phase, disappear. Similarly strong effects are seen at the other end of the phase diagram, when small amounts of CTAPA are added to aqueous CTABr. The appearance of the phase diagram makes it convenient to consider the effects of added CTAPA separately for three different concentration regions of aqueous CTABr, corresponding to the micellar phase, the dilute hexagonal phase, and the intermediately concentrated hexagonal phase.

The *micellar phase* is only stable down to a bromide fraction of $x_{Br} \approx 0.90$. At a larger fraction of CTAPA, a concentrated hexagonal phase, enriched in CTAPA, separates out from the mixture.

When a few percent of CTAPA are added to a dilute hexagonal phase of CTABr in water (up to ca. 35 wt % surfactant), the sample is transformed into a monophasic micellar solution. As a result, the micellar phase extends to higher concentrations when polyacrylate counterions are present. A similar effect of adding NaPA to aqueous CTABr was observed in ref 9 and was explained in terms of the effect of short-range counterion-surfactant interactions on the curvature of the surfactant aggregate. Polyacrylate, just as the corresponding simple acetate counterion, favors a higher curvature, and brings about a tendency toward spherical or finite aggregates. Bromide, on the other hand, gives a lower curvature and more extended, rodlike aggregates. The hexagonal-to-micellar transition induced by replacing bromide in CTABr with polyacrylate thus mirrors the cubic-to-hexagonal transition that occurs when the polyacrylate ions in CTAPA are replaced by bromide (cf. above).

For hexagonal CTABr samples at intermediate concentrations (35-50 wt %), the successive replacement of bromide counterions with polyacrylate eventually results in a phase separation into a concentrated (50 wt %) hexagonal phase and a more dilute micellar phase. This part of the wide hexagonal/micellar twophase region is the most difficult region to investigate in the entire phase diagram. The reasons for this are the following. First, both of the coexisting phases are quite concentrated in this region. As a result, the development of a macroscopic phase separation is very slow. Another consequence of the concentrated viscous phases is a possibility that a shear-induced orientation of the micellar phase, as a result of the introduction of the sample into the sample cell, could persist for a very long time. Whereas some of the micellar phases in this region showed an anisotropic two-dimensional diffraction pattern, which could indicate a nematic phase, we cannot exclude that this anisotropy was actually caused by such shear-induced ordering.



Figure 5. Values of q_1 , the first hexagonal peak in the SAXS spectrum, for a series of aqueous CTAPA/CTABr samples at 60 wt % water and with different bromide contents. Samples at $x_{Br} < 0.9$ are biphasic (hexagonal + micellar).

A second reason for the difficulties to analyze biphasic micellar/hexagonal samples at high bromide contents is that a density inversion occurs somewhere in this region. As we have pointed out above, the mass per unit volume of CTAPA/water mixtures decreases with increasing CTAPA content, whereas the reverse is true for aqueous CTABr. Thus, with mixed counterions an intermediate situation must exist in which the less concentrated (micellar) phase has exactly the same density as the more concentrated (hexagonal) phase. In the region of density inversion, centrifugation obviously does not help to achieve a macroscopic phase separation.

To illustrate the transitions occurring in this bromide-rich region at 50–65 wt % water, we investigated by SAXS a series of samples with different Br/PA ratios, including pure CTABr, at a constant water content of 60 wt %. The results are shown in Figure 5. As Figure 5 shows, the *q* value of the first hexagonal peak stays at about 0.11 Å⁻¹ in the single-phase hexagonal region (at high Br contents), then it suddenly jumps to ca. 0.14 Å⁻¹ as the two-phase region is entered (approximately $x_{Br} \approx 0.90$). Within the two-phase region, nothing much happens to the hexagonal spacing as the bromide content is lowered further. This result is in accordance with the phase diagram in Figure 2, which shows that the maximum water content of the hexagonal phase is constant across a wide range of compositions.

The Hexagonal Phase. The hexagonal phase is the only single phase that extends across the phase diagram, regardless of the PA/Br ratio. At a fixed water content, the characteristic dimensions of the hexagonal phase vary only weakly with the nature of the counterion. The radius of the cylindrical aggregates, R, was calculated from the first diffraction line, q_1 , of the hexagonal spectrum and the volume fraction, f_s , of surfactant ions (assuming a specific volume of 1 cm³/g) by the following set of equations.

$$a = \frac{2}{\sqrt{3}} \frac{2\pi}{q} \tag{1}$$

$$R = a\sqrt{\frac{\phi_s}{2\pi}\sqrt{3}} \tag{2}$$

At 35 wt % water *R* increases slightly, from 16 to 20 Å, as the counterion is exchanged from polyacrylate to bromide. This effect is in line with the findings in ref 9, and it is consistent with the general trend that the carboxylate group of polyacrylate induces a higher curvature of the aggregates than bromide.

Addition of Water to the Hexagonal Phase. We will end our tour around the phase diagram by considering the effect of adding water to the hexagonal phase at different ratios of the counterions. We have already noted the transition to a cubic phase at low bromide contents. What remains to be discussed in more detail is the transition from the pure hexagonal phase into hexagonal-micellar coexistence. At high bromide contents, the behavior is that of the regular hexagonal phase of CTABr. A repulsion occurs between the surfactant aggregates, and the hexagonal phase therefore swells continuously when water is added. Eventually (at 70 wt % water) the long-range order is lost, and across a narrow two-phase region a transition occurs to an isotropic micellar phase. By contrast, when water is added to a hexagonal phase containing a sufficient (small) fraction of polyacrylate counterions, a maximum water content exists above which the hexagonal phase refuses to swell. Further added water ends up in a more dilute micellar phase. Clearly, the polyacrylate counterions give rise to an attractive force that keeps the surfactant aggregates together. This attraction may have two causes: polymer bridging, or an electrostatic attraction between surfactant aggregates with polyions condensed on their surfaces.

Remarkably, the phase diagram shows that the maximum water uptake of the hexagonal phase is almost constant at about 50 wt % across a large range of Br/PA ratios in the middle of the phase diagram. This indicates that the minimum in the interaction potential is located at approximately the same distance between the surfactant aggregates for all counterion compositions below $x_{Br} = 0.90$. We believe that the underlying reason for this is that the polyion-bridging attraction is short-ranged. As the proportion of polymeric counterions is decreased, the depth of the potential minimum may be strongly affected, but not its position. At sufficiently low proportions of polymeric counterions, however, the minimum disappears, and the interaction force becomes repulsive. Evidently, this is what happens in the experiments above $x_{Br} = 0.90$.

A final feature to note regarding the hexagonal-micellar coexistence is the direction of the tie lines, showing that the bromide fraction is always higher in the micellar phase than in the coexisting hexagonal phase. (As pointed out above, the minimum bromide content of the micellar phase is rather constant at $x_{\rm Br} \approx 0.90$.) This is, of course, entirely expected; the monomeric counterions are enriched in the more dilute phase.

Concluding Remarks

In this work we have demonstrated that the study of the phase behavior of oppositely charged polymer–surfactant systems is simplified immensely if one of the simple ions is eliminated from the mixture. The strategy involves preparing the complex polyion–surfactant ion salt and studying its binary mixtures with water, and ternary mixtures including, in addition, either the surfactant or the polyelectrolyte. Here, we have chosen to study mixtures with the surfactant, addressing the question as to the effects on the surfactant phase behavior of gradually exchanging the counterions from 100% polymeric to 100% monomeric. We note several interesting results of our study.

• Surfactant mesophases with polymeric counterions have a limited swelling in water. This reveals the presence of an attractive force that keeps the surfactant aggregates together. An interesting problem for future research is to discover the nature of this force, and the balance of forces that determines the maximum swelling.

• The ternary CTABr/CTAPA/water phase diagram contains both of the mesophases (cubic and hexagonal) that have previously been found to separate out from dilute CTABr/NaPA/ water mixtures. The stability of those phases, with respect to the PA/Br ratio and the overall water content, has been clarified. The cubic structure exists essentially for pure CTAPA at its maximum water content. The marginal stability of this structure with respect to changes in either water or bromide content is intriguing. A single hexagonal phase has been shown to extend through all possible mixing ratios of polyacrylate and bromide counterions. This result confirms that the hexagonal phase separating from CTABr/NaPA mixtures in water is connected to the "normal" hexagonal phase of CTABr, as speculated in ref 8.

• The micellar phase of CTABr can only accept a limited "contamination" with polymeric counterions before a hexagonal phase separates out. This is a consequence of the same attractive forces that limit the maximum water uptake of the hexagonal phase, that is, the bridging of the surfactant aggregates by the polyions.

• The importance of short-range interactions between the counterions and the surfactant aggregates has been confirmed and clarified by this study, as well as the previous conclusion⁹ that the polyacrylate counterion favors a higher aggregate curvature than does the bromide counterion. The latter conclusion is supported by (*i*) the cubic-to-hexagonal transition as PA⁻ is replaced by Br⁻, (*ii*) the hexagonal-to-micellar transition as Br⁻ (in the dilute hexagonal region) is replaced by PA⁻, and (*iii*) the decreased radius of the rodlike micelles in the hexagonal phase as Br⁻ is replaced by PA⁻.

Further studies of other ternary mixtures involving the complex salt, CTAPA, are in progress in our laboratory. These include aqueous mixtures with the polyelectrolyte (the CTAPA/NaPA/water system) and mixtures with the acetate (Ac) salt of the surfactant (the CTAPA/CTAAc/water system). The former mixtures correspond to another face of the phase pyramid in Figure 1. The mixtures with CTAAc are of special interest because the acetate ion may be viewed as one repeating unit of polyacrylate. Experiments with longer polyacrylates are also in progress.

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