

## Effects of Polyelectrolytes on the Structures and Interactions of Surfactant Aggregates

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Aqueous solutions of sodium polyacrylate (NaPA) have been mixed with different phases of the system water–cetyltrimethylammonium bromide (CTABr). In all mixtures, the surfactant ions (CTA<sup>+</sup>) associate to form micelles. The polyions (PA<sup>−</sup>) bind to these micelles, displace their counterions, and bridge them together. The replacement of micellar counterions changes the micellar shapes. The bridging may change the distances between micelles, and cause them to separate into a concentrated phase; in this case excess water and salt are released in a dilute aqueous phase. The structures of the concentrated phases have been determined. At low water contents, the hexagonal, nematic, and micellar phases of the polymer-containing system merge with the corresponding phases of CTABr/water. At high water content, the concentrated phases that separate are closer to the hexagonal and cubic phases of cetyltrimethylammonium acetate/water.

## Introduction and Background

When a charged surfactant in a dilute solution is mixed with an oppositely charged polyelectrolyte, an associative phase separation occurs: A concentrated phase forms that is enriched in both polyions and surfactant ions.<sup>1–4</sup> In such an associative mixture, the surfactant ions occur as hydrophobically self-assembled surfactant aggregates. From the surfactant perspective, then, an added polyelectrolyte has the effect of bringing oppositely charged surfactant aggregates together into a concentrated phase, leaving a dilute aqueous solution behind. We note that the determination of structures of concentrated complex polyion–surfactant salts is currently a very active area, with several studies of the dried complex salts<sup>5–8</sup> and also of structures formed in concentrated phases<sup>9–13</sup> and polyelectrolyte gels<sup>14–18</sup> in equilibrium with dilute solutions. The purpose of the present study is to address a number of questions as to the details of this process: How far is the process of concentrating the aggregates driven (i.e., what is the equilibrium water content)? What are the ionic compositions of the separating phases? To what extent are the shapes and sizes of the surfactant aggregates altered by the phase separation process? Does any long-range order of the surfactant aggregates (i.e., mesophases) appear as a result of the phase separation?

The answers to the above questions are known to vary with the global composition of the initial mixture. In a recent study on mixtures of cetyltrimethylammonium bromide (CTABr) with the sodium salt of low-molecular-weight poly(acrylic acid) (NaPA),<sup>19</sup> we illustrated this point, and particularly the importance of the overall water content of the mixture. Since they form the background to the present study, we will recapitulate the main results of the previous study here. The focus was there on stoichiometric mixtures, containing equivalent numbers of moles of polyelectrolyte and surfactant, which were progres-

sively diluted with water. At sufficiently low water contents, a single-phase mixture was found, but on addition of water, a dilute phase eventually separated out. More added water caused a third, even more concentrated hexagonal phase to form, and then the initial phase disappeared, leaving only the hexagonal and the dilute aqueous phase. The concentration of the concentrated phases always increased with increasing amounts of water.

The sequence of events just described could only be understood by considering all four ionic species in the mixture: The *surfactant ion*, the *polyion*, and the original negative and positive *simple counterions* of the surfactant ion and the counterion, respectively. In fact, it was argued that the concentration upon dilution was best understood in terms of an alternative description of the stoichiometric mixture as a mixture of an insoluble *complex salt* (the surfactant ion + the polyion) with a soluble *simple salt* (the two oppositely charged simple ions). This is illustrated in the schematic drawings of Figure 1: In a concentrated mixture, the high concentration of simple salt screens the attraction between oppositely charged surfactant aggregates and polyions. Hence, no phase separation occurs. On dilution with water, however, the simple salt is diluted, its screening effect becomes weaker, and the attraction between the highly charged aggregates increases. This increasing attraction leads first to a phase separation (which may be viewed as a finite swelling of the mixture on adding water) and then to a contraction of the phase containing the complex salt, on addition of more water.

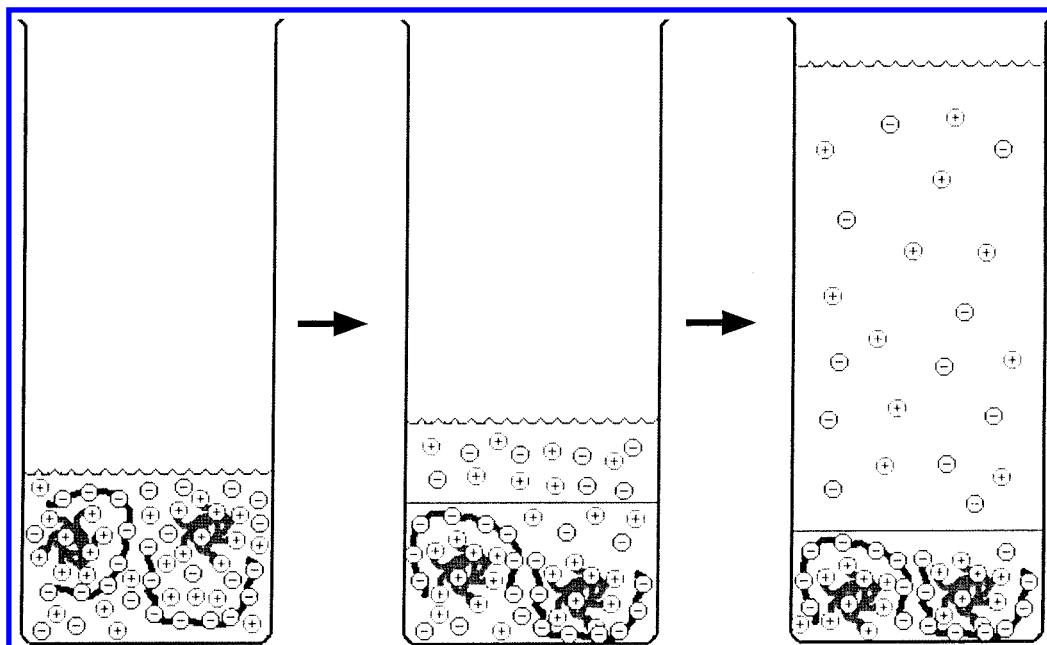
The full phase behavior of a mixture of two salts, based on four different ions and water, cannot, in general, be described in a two-dimensional phase diagram. Nevertheless, in a very simple case, such as that depicted in Figure 1, where the dilute phase only contains the simple salt (no surfactant ions or polyions), the associative phase separation would be completely describable in a ternary diagram of the components complex salt, simple salt, and water. However, the real mixtures of CTABr with NaPA turned out to be more complex than that. The full behavior would require a three-dimensional diagram,

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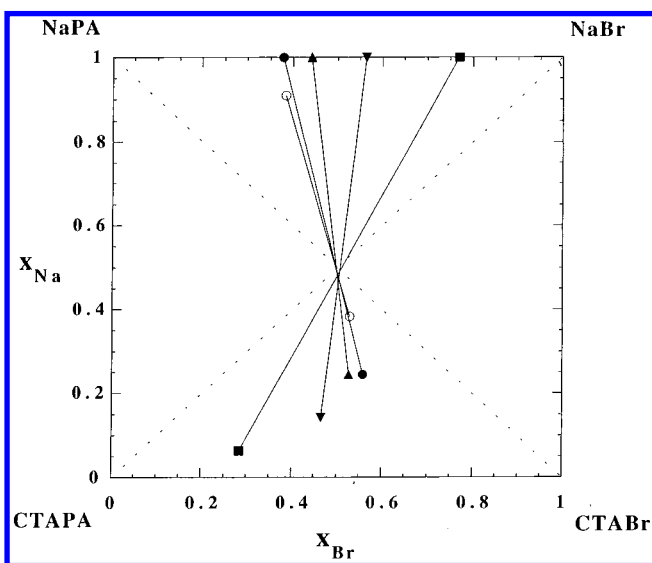
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**Figure 1.** Evolution of stoichiometric mixtures of oppositely charged polyelectrolyte and surfactant upon addition of water. Concentrated mixtures are monophasic, since the high concentration of simple counterions screens the attraction between the polyions and the surfactant aggregates. On addition of water a dilute phase, containing simple salt, eventually separates out. On progressive dilution the concentrated phase becomes more concentrated, since the concentration of screening simple salt becomes more dilute.



**Figure 2.** Ionic compositions of the equilibrium phases in stoichiometric mixtures of CTABr with NaPA. The overall water contents in the different samples were 96 (filled squares), 90 (reverse triangles), 84 (filled triangles), 83 (filled circles), and 79 (open circles) weight percent. The concentrated phases were hexagonal mesophases in all mixtures except for the one with the lowest overall water content, where the concentrated phase was isotropic.

such as the tetragonal pyramid proposed by Thalberg and co-workers.<sup>20–23</sup> In Figure 2, we give a simplified representation which only describes the ionic compositions of the separated phases that result from an increasing dilution of stoichiometric mixtures of NaPA and CTABr with water. The data are from ref 19, but the representation in Figure 2 is novel. The abscissa in this representation gives the mole fraction (in units of equivalent charge) of simple anions out of the total anion concentration in a phase; in the present case, the quantity  $[Br^-]/([Br^-] + [PA^-])$ . The ordinate gives the corresponding composition of the mixture of cations. Note that no information on the water content of the phases is given (for this, a third dimension would be required). Hence, the diagram can be

thought to illustrate the compositions of the dried separated phases. Note that the composition of a dry mixed salt, made up from two different cationic and two different anionic species, is completely specified by the two mole fractions of the cations and the anions, respectively. This follows from the condition of electroneutrality: the total equivalent concentration of the cations must equal the total equivalent concentration of the anions. For example, a phase containing only NaBr in water would be represented by a point in the upper right-hand corner. The lines drawn between the phase composition data are tie-lines, connecting corresponding equilibrium phases. All initial mixtures in ref 19 were stoichiometric mixtures, represented by a point in the center of the diagram ( $x_{Br} = x_{Na} = 1/2$ ). Hence, all tie-lines run through this point.

The dashed diagonal line connecting the NaPA and CTABr corners represents a plane in the total phase pyramid, the plane containing all possible mixtures of NaPA, CTABr, and water. Since most studies deal with such mixtures of a conventional polyelectrolyte (polyion + simple counterion) plus a conventional ionic surfactant (surfactant ion + simple counterion), we have called this plane the *conventional mixing plane*. Conversely, the *alternative mixing plane* of complex salt, simple salt, and water is represented by the orthogonal dashed line connecting the CTAPr and NaBr corners.

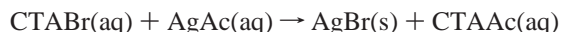
The important point that Figure 2 illustrates is that the compositions of the separating phases of the CTABr/NaPA mixtures are generally far away from either of the mixing planes. Clear trends are seen, however. First, the dilute phases, which correspond to the upper points in the diagram, are virtually void of surfactant ions, except for the biphasic mixture with the lowest overall water content. They do, however, contain a large proportion of  $PA^-$  ions. A finite  $PA^-$  content might be expected merely from the fact that the polyions used were rather short ( $M_w = 2$  kD); this would imply a certain solubility in the dilute phase. But this cannot explain the result that the  $PA^-$  ions actually dominate ( $x_{Br} < 0.5$ ) the initial dilute phases that separate out. We attributed the latter effect to the intrinsically high ‘chemical’ affinity of bromide ions to the surfactant aggregates.<sup>24–27</sup>

However, Figure 2 also shows that, as the mixtures are progressively diluted with water, the phase compositions "swing over" more and more toward the alternative mixing plane. This we interpret<sup>19</sup> in the following way: As the system becomes more and more dilute, the translational entropy per charge of the ions becomes more and more important. Hence, dilution results in a continuous ion exchange, where multivalent  $\text{PA}^-$  ions are increasingly replacing  $\text{Br}^-$  ions in the concentrated phase, since the latter ions are to an increasing degree lost to the dilute phase.

The present study is an extension of the previous study on the same mixtures (NaPA and CTABr), where we address the following points. First, to obtain a more complete picture of the phase behavior, we have extended the range of mixtures investigated, both to nonstoichiometric mixtures and to mixtures with a higher overall concentration of surfactant. To avoid the formation of solid crystals in the surfactant-rich part of the mixing range (this would unnecessarily complicate the picture), we have also raised the temperature to 40 °C, well above the Krafft temperature of CTABr.<sup>27,28</sup> Thus we have constructed a rather detailed phase map of the conventional mixing plane. As in our previous study, we have also made structural analyses (by small-angle X-ray scattering) and, in some cases, detailed composition analyses of the separated phases. One recurrent theme of the present investigation is the effect on structure and phase behavior of the exchange between the  $\text{Br}^-$  and  $\text{PA}^-$  counterions of the surfactant aggregates, as was illustrated for the stoichiometric mixtures in Figure 2. As the importance of the chemical nature of the anion is evident from our findings, we have also compared structures occurring in CTABr/NaPA/water mixture with structures in aqueous cetyltrimethylammonium acetate (CTAAc) or CTAAc/CTABr mixtures; note that the  $\text{Ac}^-$  ion may be viewed as a single repeating unit of the  $\text{PA}^-$  ion.

## Materials and Methods

**Materials.** Poly(acrylic acid) ( $M_w = 2000$  g/mole) was purchased from Aldrich. NaPA was obtained by addition of an equivalent amount of sodium hydroxide to ionize the acid functions of the polymer. The pH of the NaPA solutions was about 8. Consequently most carboxylic functions were ionized. Solutions of NaPA in 0.1 M  $\text{LiNO}_3$  were examined by size exclusion chromatography (SEC) coupled with low-angle light scattering (LALS), yielding a number average molar mass  $M_n = 2700$  g/mole and a weight average mass  $M_w = 4700$  g/mole. The polyelectrolyte concentration is expressed in weight percent (%) or in mole of monomer per liter. CTABr was purchased from Merck and used without further purification. Note that CTABr has a density of 0.9<sup>29</sup> which causes the concentrated phases to cream to the top of phase-separated samples. CTAAc was prepared through the reaction of CTABr with silver acetate:<sup>30</sup>



CTABr was mixed in aqueous solution with a stoichiometric amount of silver acetate. The reaction produced a dispersion of insoluble silver bromide while the CTAAc remained in solution. The colloids of AgBr were removed by centrifugation at 15000 rpm during 2 h. Then the bromide content of the CTAAc solution was analyzed by capillary ion analysis (CIA). The bromide ion concentration was found to be lower than 1 ppm. Accordingly, all the bromide ions of the surfactant must have been replaced by acetate counterions, indicating that the reaction

was complete. The solution was then freeze-dried in order to obtain the CTAAc powder.

**Methods.** Samples were prepared by mixing an aqueous stock solution of CTABr with a stock solution (at pH 8) of NaPA. The samples were left at 60 °C for a few hours. They were then stored at 40 °C, above the Krafft temperature of CTABr (23 °C), until the phase separation process was completed. Elemental analyses on biphasic samples were performed on each of the separating phases: (i) In the dilute phase, the sodium and bromide ions were analyzed by CIA, while the polyion was analyzed by carbon analysis and SEC. The surfactant ion was analyzed by a colorimetric two-phase titration method using sodium dodecyl sulfate as titrant, a mixture of a cationic indicator (dimidium bromide), and an anionic indicator (sulfan blue), and chloroform as the organic phase.<sup>31</sup> We verified that the presence of the polyion had no effect on the result on this titration within a 5% error margin. (ii) The concentrated phase was solubilized in water at low pH with nitric acid. The surfactant ion was analyzed with the same colorimetric method as above. The concentrations of sodium and bromide ions were determined by CIA.

The concentrations of the various species are related by the electroneutrality condition and by the known total weight of the concentrated phase, consequently the set of equations available to calculate them is overdetermined. For the calculations, we used only the most reliable measurements, in the following way. The polyion and water contents in the concentrated phase were calculated from the sodium, surfactant ion and bromide analyses, using the electroneutrality condition and the known total weight of the concentrated phase. Then, from the initial quantities, the amount left in the dilute phase was calculated. The carbon analysis made on the dilute phase and the dried content of the concentrated phase supported these calculations.

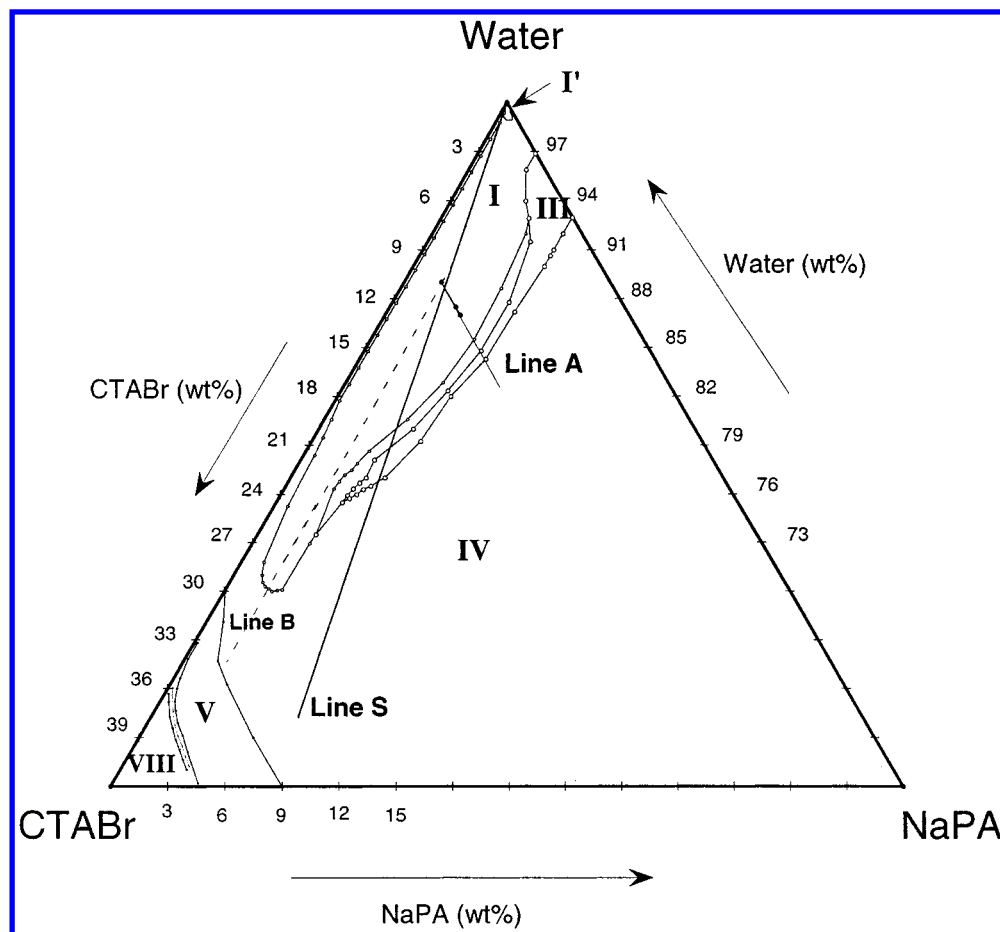
Small-angle X-ray scattering measurements were performed on the D43 instrument at LURE. A parallel monochromatic beam of wavelength 1.445 Å was focused with point collimation on the sample, which was contained in a flat cell with mica windows. The sample cell was maintained at 40 °C. The detector was an image plate located at 37.1 cm from the sample. With this setup the scattering vectors ranged from 0.03 to 0.4 Å<sup>-1</sup>.

## Results

### Phase Map of Aqueous Mixtures of NaPA and CTABr.

An overview of the phase separation behavior is presented in Figure 3, which is a map of the phase behavior encountered in the conventional mixing plane of the initial components. Thus, the global compositions of the mixtures are given in terms of the weight fractions of surfactant (surfactant ion + original bromide counterion), polyelectrolyte (polyion + original sodium counterion), and water. In this map, we indicate the mixtures that remain single phase, the ones that separate into two or three phases, and the nature of the phase(s) appearing in each mixture. The stoichiometric line (line S) indicates mixtures with equivalent concentrations of all ions.

The top corner of the diagram contains samples made from dilute micellar solutions of CTABr with dilute NaPA solutions. In this range, most samples separated into a dilute aqueous phase and a concentrated mesophase. The two-phase region is the droplet-shaped domain indicated as region I in Figure 3. Since the concentrated phase collected on the top of the tube, we will refer to it as the cream (phase). Note that region I extends nearly all the way to the surfactant/water axis (the addition of minute amounts of polyelectrolyte, e.g., 1% w/w, caused phase separa-



**Figure 3.** General phase map at 40 °C. The phase separation patterns are as follows. Region I: concentrated hexagonal mesophase and dilute aqueous phase. Region I': concentrated cubic phase and dilute aqueous phase. Region II: concentrated hexagonal mesophase, micellar phase, and dilute aqueous phase. Region III: micellar phase and dilute aqueous phase. Region IV: single micellar phase. Region V: micellar phase and nematic phase. Region VI: single nematic phase. Region VII: nematic phase and hexagonal mesophase. Region VIII: single hexagonal mesophase.

tion) and to the polyelectrolyte/water axis (the addition of minute amounts of surfactant caused phase separation). According to X-ray scattering experiments (presented below), the concentrated phase was a hexagonal mesophase over most of region I. There was also, at very high dilutions, a smaller region, noted I', where the concentrated phase was a cubic phase.

At higher concentrations of CTABr or NaPA, the mixtures changed from a two- or three-phase state to a single-phase state. This change occurred in two different ways, depending on the path followed through the mixing plane.

The effects of higher polyelectrolyte concentrations were investigated by making series of samples at fixed CTABr concentrations (either 3%, 6%, 9%, 12%) where water was progressively replaced with NaPA (Line "A" in figure n°3 corresponds to 9% CTABr). In each series the sequence of phase separation processes was the same. First, the addition of polyacrylate, even in very small amounts, caused the separation of a mesophase from a dilute aqueous phase. This two-phase region extended past the stoichiometry line, up to NaPA concentrations of about 5%. Then (region II), a third phase appeared between the cream and the aqueous phase; this phase was a micellar phase with a concentration intermediate between the cream (upper phase) and the dilute aqueous solution (lower phase). Upon further additions, the mesophase vanished (region III), and finally the dilute aqueous phase vanished as well (region IV).

The behavior at higher surfactant concentrations was investigated in two ways. First, the polyelectrolyte/surfactant ratio

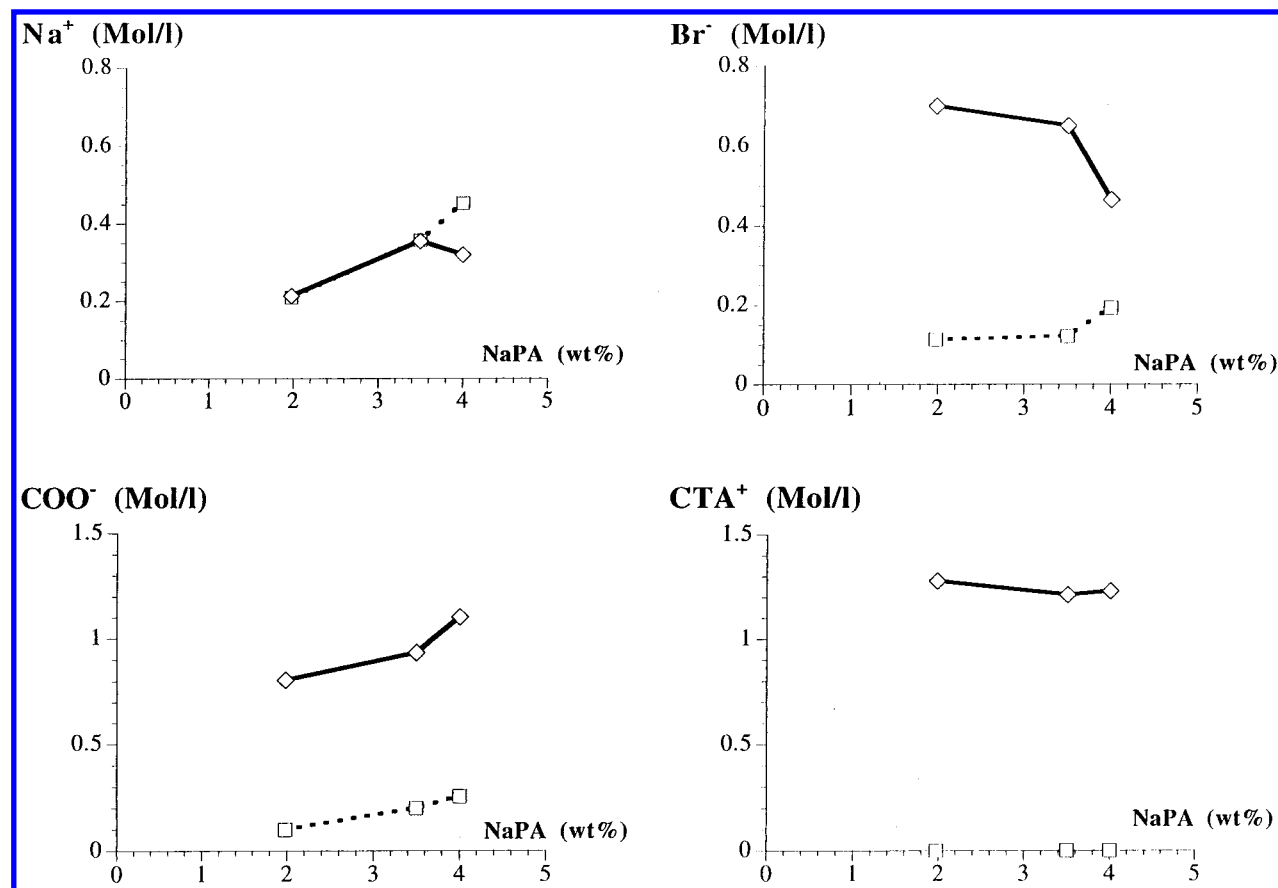
was changed at a constant high concentration (24%) of the surfactant. Here, it was found that the phase separation occurred only at limited and less-than-stoichiometric concentrations of polyelectrolyte (up to 3%). Larger additions of NaPA at this high surfactant concentration did not cause phase separation. Second, the surfactant concentration was increased at a fixed NaPA concentration (2%) along Line "B" (Figure 3). Here it was found that the compositions of the separating phases (mesophase and solution phase) merged when the surfactant concentration reached 27%. At higher CTABr concentrations, there was a region where the samples remained monophasic.

Finally, for CTABr concentrations exceeding 30%, the binary CTABr/water system forms a hexagonal mesophase,<sup>28,32</sup> (or a nematic phase at temperatures below  $T = 40$  °C). At sufficiently high CTABr concentrations, the added polyelectrolyte was incorporated into the hexagonal phase and did not cause any phase changes (region VIII). However, at intermediate CTABr concentrations (30–37%), the addition of NaPA caused the system to return to the micellar solution (region V). The complete sequence of structures is:

hexagonal  $\rightarrow$  hexagonal + nematic  $\rightarrow$   
nematic  $\rightarrow$  nematic + micellar  $\rightarrow$  micellar

This tour of the phase map shows two opposite behaviors of the ternary mixtures. Additions of NaPA to dilute micellar solutions of CTABr caused the separation of a hexagonal mesophase from a dilute aqueous solution. Addition of NaPA to hexagonal phases of CTABr caused a series of phase changes





**Figure 4.** Ionic compositions of the separating phases of mixtures along line A in Figure 3. Vertical scales: concentrations of ionic species, in mol/L. Horizontal scales: amount of added NaPA, in wt %. In all graphs, the data from the concentrated phase are the diamonds, and the data from the dilute aqueous phase are the squares. The overall content of CTABr is 9% in all samples.

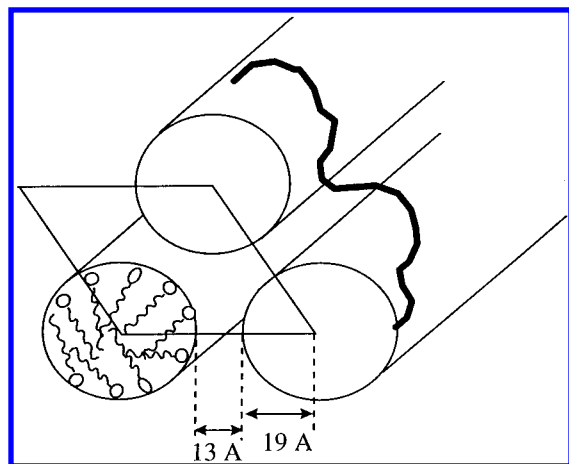
that return a concentrated micellar solution phase. This conflict comes from the representation of the system in the conventional mixing plane, since the phases that separate out generally have compositions outside this plane;<sup>19</sup> cf. also Figure 2. In fact, samples with remote overall compositions may produce, through phase separation, some phases that are related (e.g., hexagonal phases are obtained from samples made with either low or high CTABr concentrations). Experiments that determine the compositions and structures of the separating phases are required in order to understand these points. These experiments are reported next, for three series of samples that show apparently conflicting behaviors. These series of samples can be considered to be made by addition of NaPA to three different reference states of pure CTABr in water: dilute micellar solutions, concentrated micellar solutions, or hexagonal liquid crystalline solutions.

**Reference State = Dilute Micellar Solution.** These experiments were performed with samples prepared in the upper part of region I, near the water corner, where a concentrated mesophase separates from a dilute aqueous phase.

**Ionic Compositions of the Separating Phases.** The compositions of the separating phases are presented in Figure 4 for a series of samples (line A in Figure 3) made by increasing the NaPA content (2 to 4%) at a constant CTABr content (9%). The phase compositions have a number of remarkable features. First, in line with the results in Figure 2, there are no surfactant ions in the dilute solution phase. The latter phase contains only simple salt and NaPA. The concentrated phase contains all the surfactant ions, most of the polyions, and also some of the Br<sup>-</sup> counterions that originally came with the surfactant ions, plus some of the Na<sup>+</sup> counterions that came with the polyions.

Since the surfactant aggregates in the concentrated phase have lost some of their original Br<sup>-</sup> counterions, and acquired some polymeric counterions in exchange, *the phase separation process can also be described as an ion-exchange process*. It is instructive to examine how extensive this ion exchange has been for samples made at the stoichiometric ratio, i.e., the samples at 2% NaPA in Figure 4. Since the dilute phase contains no surfactant aggregates, the ionic concentrations in the dilute phase tell us simply which ions have been released from the concentrated phase by the ion-exchange process. According to these concentrations, and to the relative volumes of the separating phases, the dilute phase contains 36% of the original Br<sup>-</sup> counterions, which have been displaced from the surfaces of the surfactant aggregates by PA<sup>-</sup> polyions. Thus, the exchange is substantial but incomplete. It is notable that the ion exchange is not totally in favor of the polyions. This must be largely a consequence of the well-known affinity of Br<sup>-</sup> for surfactant surfaces—already referred to in the Introduction—which is much stronger than that of COO<sup>-</sup>.<sup>24–27</sup>

As the NaPA content is increased beyond stoichiometry in Figure 4, the surfactant ion concentration stays quite constant in the concentrated phase and remains zero in the dilute phase. In contrast, the other positive ion, Na<sup>+</sup>, is distributed almost uniformly throughout the entire system: the concentration increases linearly with the total NaPA content and is virtually the same in both phases. The interesting question is then how the anion distribution changes as the NaPA content is increased in this two-phase system, which features an extreme partitioning of CTA<sup>+</sup> and a uniformly increasing “background” concentration of Na<sup>+</sup>. The data show that the increase in the PA<sup>-</sup> concentration is stronger than proportional to the overall NaPA



**Figure 5.** Schematic picture of the structure of the hexagonal phase made by addition of NaPA to a dilute micellar solution of CTABr. This structure was obtained for all samples made with overall CTABr content between 3% and 24%, and NaPA content corresponding to compositions within region I of the phase map. The volume fraction of surfactant in the mesophase was  $\phi_s = 52\%$ .

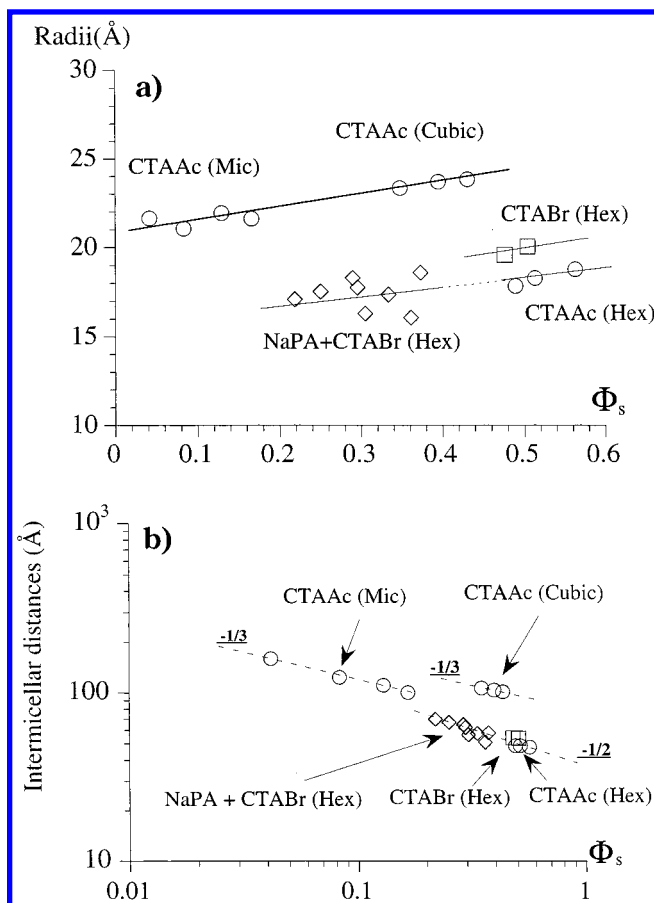
content in the dilute phase, and correspondingly weaker in the concentrated phase. This means that the added polyions (beyond stoichiometry) are distributed more evenly than the polyions in the stoichiometric mixture. The data further show that the  $\text{Br}^-$  concentration changes rather slowly—at least initially—in both phases. Evidently, the  $\text{Br}^-$  counterions are hard to dislodge from the surfaces of the surfactant aggregates: even with a 2-fold excess of polyions in the sample, the concentrated phase has less than an equivalent ratio of polyions to surfactant ions.

**Structures of the Mesophases.** The X-ray spectra from the concentrated phase of the same samples gave 2 or 3 diffraction lines at locations  $q_1, q_2, q_3$  that were characteristic of a hexagonal mesophase (spacings in the ratios 1,  $\sqrt{3}$ ,  $\sqrt{4}$ ).<sup>29</sup> The lattice parameter  $a$ , the micelle radius  $R$ , the micellar separation  $h$ , and the surface area per surfactant ion  $A$  were calculated from the values of the spacing  $q_1$ , the volume fraction of surfactant ions  $\phi_s$ , the mass per surfactant ion  $M$ , and its density  $\rho$  ( $1 \text{ g/cm}^3$ ):

$$a = (2/\sqrt{3}) (2\pi/q_1); R = a [\phi_s \sqrt{3/2\pi}]^{1/2}; h = a - 2R; A = (2M/R\rho) \quad (1)$$

The lattice parameter  $a$  was in the range 50–60 Å, which is the range for the parameters of the hexagonal phase of pure CTABr in water. The constant surfactant ion concentration shown in Figure 4 corresponds to a volume fraction  $\phi_s$  of 52% surfactant ions in the mesophase, which is also in the range of the values for the hexagonal phase of pure CTABr. Therefore it was assumed that the structure of the hexagonal mesophase in the surfactant + polyelectrolyte system was the same as that for the surfactant alone, i.e., cylindrical aggregates of surfactant ions, packed on a hexagonal lattice and separated by an aqueous medium containing the polyions and other ions. In the following, these surfactant ion aggregates will be called micelles.

All samples with the same value of  $\phi_s$  have the same peak positions. The geometrical parameters of their structures were calculated from the peak positions and from the value of  $\phi_s$ . A picture of the hexagonal phase is shown in Figure 5. A comparison with the hexagonal phases of the binary systems CTABr/water and CTAAc/water is shown in Figure 6. The cylinder radii in the polyelectrolyte containing system are the same as in the hexagonal phase of CTAAc/water and slightly

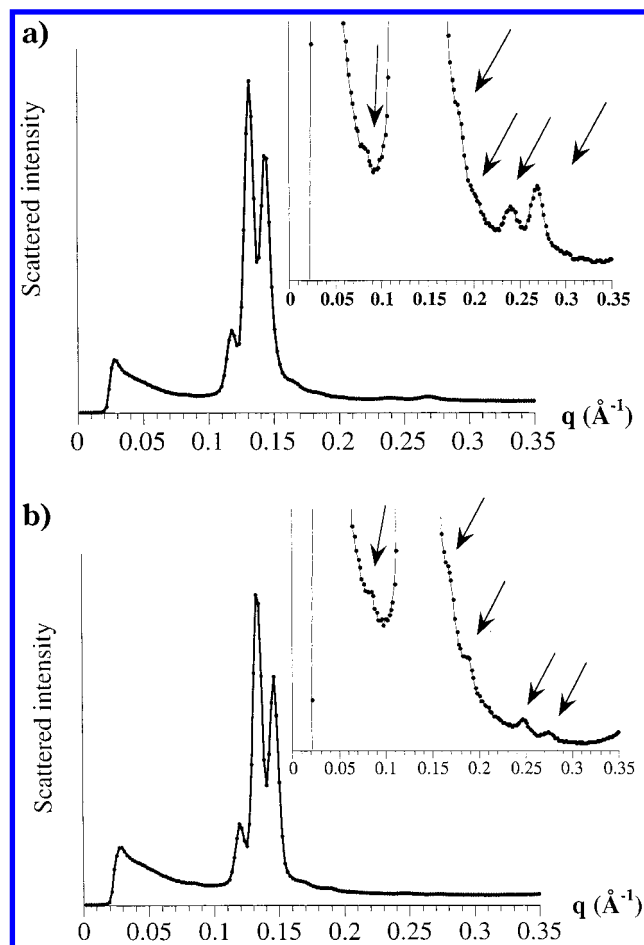


**Figure 6.** Micellar radii (a) and intermicellar distances (b), vs the volume fraction  $\phi_s$  of surfactant ions in the various mesophase. The symbols for both figures correspond to the systems indicated in (a). The data for the ternary system NaPA/CTABr/Water are taken along line B of Figure 3. The numbers  $-1/3$  and  $-1/2$  indicate the slopes of the lines in the log–log plot.

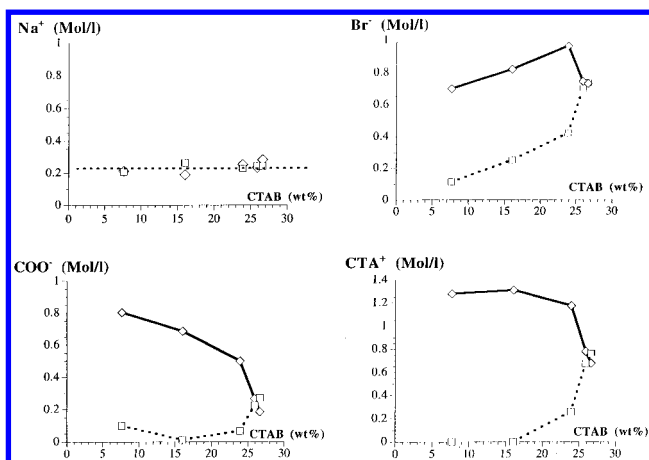
shorter than in CTABr/water. Finally the structure remains practically the same when excess polyelectrolyte is added, along line A of Figure 3.

For samples made with very large additions of water (Region I'), the X-ray diffraction patterns show a different set of diffraction lines, which cannot be indexed on a two-dimensional hexagonal lattice (Figure 7). Similar diffraction patterns were obtained in the binary system CTAAc/water (see below). In the latter case, the signal/noise ratio was higher, and additional weak lines were observed. Taking these weak lines into account, the spectra could be indexed with a cubic symmetry ( $Pm\bar{3}n$ ).<sup>33</sup> With the same assignment, the mesophase of the NaPA/CTABr/water system at high dilution was found to have the same symmetry, with a lattice parameter of 107 Å.<sup>34</sup>

**Reference State = Concentrated Micellar Solution.** The characteristic feature of concentrated micellar solutions (approximately 25–30% CTABr) is that their phase behavior becomes less sensitive to added NaPA: As the surfactant concentration increases, the two-phase area shrinks to finally vanish completely; cf. Figure 3. We have followed this evolution from biphasic (hexagonal + isotropic) to monophasic (isotropic) samples along a composition line B in Figure 3 that follows the narrow “tongue” of region I that extends into region IV. Here, the polyelectrolyte content has been kept constant while the surfactant content has been increased. The phase compositions of these samples are given in Figure 8. Below, say, 24% CTABr, most of both the surfactant ion and the polyion go to the concentrated phase. The surfactant ion concentration of the

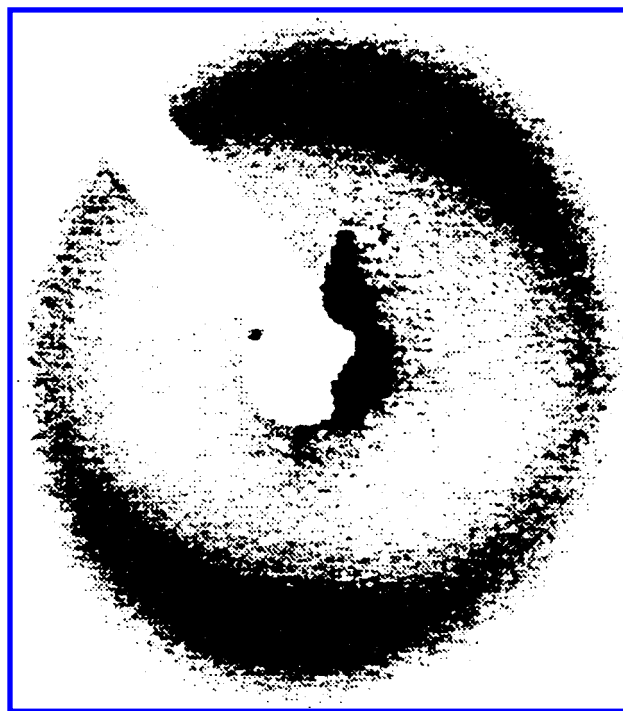


**Figure 7.** Diffraction spectra of the cubic phases obtained (a) at very high water content in the system CTABr/NaPA/water (0.046% CTABr and 0.012% NaPA) (b) at intermediate water content in the binary system CTAAC/water (56% of CTAAC).



**Figure 8.** Ionic compositions of the separating phases in mixtures along line B of Figure 3. Vertical scales: concentrations of ionic species, in mol/L. Horizontal scales: total amount of CTABr in the sample, in wt %. In all graphs, the data from the concentrated phase are the diamonds, and the data from the dilute aqueous phase are the squares. The overall content of NaPA is about 2% in all samples.

concentrated phase stays roughly constant, while the  $\text{Br}^-$  concentration increases and the  $\text{PA}^-$  concentration decreases. The latter variation is trivial; the anion composition must change since CTABr is continuously added to the concentrated phase. However, as the concentrated single-phase area is approached (above ca. 24% of CTABr), the phase compositions change rather dramatically and become almost equal. The concentrated



**Figure 9.** Diffraction pattern of a nematic phase obtained for 37.8% of CTABr and 4.3% of NaPA at 40 °C.

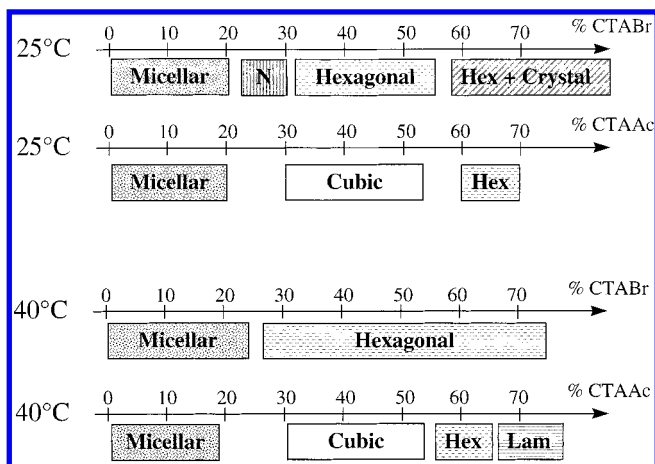
phase swells with water, while increasing amounts of the complex salt are dissolved in the dilute phase.

The same evolution is seen in the structures: along line B of Figure 3, the concentrated phase remains a hexagonal array of cylindrical aggregates, and the cylinder radii remain constant at  $R = 17 \pm 1 \text{ \AA}$  (Figure 6). However the size of the unit cell increases, and the cylinders move farther apart, as the overall CTABr concentration is increased. Near the phase boundary (overall CTABr content 26.6%) the separating phases are a swollen hexagonal phase and a micellar phase that have nearly the same repeat distance and the same micellar radius. This is consistent with the pattern of phase separation where the hexagonal phase and the micellar phase merge together.

**Reference State = Hexagonal Mesophase.** These experiments were performed with samples in regions V to VIII of the phase map, also close to the water/surfactant axis. The main set of samples was made with a constant polyelectrolyte content (2%) and with surfactant contents ranging from 30% to 39%. As indicated in Figure 3, the samples with CTABr concentrations below 32% gave a single micellar phase, instead of the pure hexagonal phase of the NaPA-free system. At higher CTABr concentrations (33 to 36%), the samples separated into two viscous fluid phases, of which the top phase was birefringent. X-ray diffraction spectra of the birefringent phase (Figure 9) were typical of oriented nematic phases as they demonstrate anisotropy but no long-range order (diffuse lines). At the highest concentrations (CTABr > 37%), X-ray diffraction spectra gave the sharp lines characteristic of a hexagonal phase.

Over this range of CTABr contents, the variation of lattice parameters was continuous, in line with the CTABr content, and the values of this parameter were in the continuation of the values for the stoichiometric samples and for the hexagonal phase of the CTABr/water system (Figure 6b). Additional experiments with different polyelectrolyte contents indicated that a very small amount of polyelectrolyte is sufficient to cause the transition to the micellar phase (at 31% CTABr) or to nematic + micellar (at 34% CTABr).

The compositions of the separating phases were measured



**Figure 10.** Sequence of phases in the binary systems CTAAC/water and CTABr/water,<sup>2</sup> at 25 °C (top) and at 40 °C (bottom).

for one composition in the nematic + micellar two-phase region. Both phases had similar compositions, but the nematic phase had more Br<sup>-</sup> and the micellar phase more PA<sup>-</sup>. This was consistent with the idea that the polyions causes the micelles to change from cylindrical shape (hexagonal phase) to elongated but finite (nematic phase) and to even less elongated (micellar phase).

**Mesophases of CTAAC and Water.** To better understand the structures that are formed when polycarboxylate ions bind to CTA<sup>+</sup> micelles and displace Br<sup>-</sup> counterions, we have also studied the structures of the binary system CTAAC/water where all the counterions of CTABr have been replaced with the monocarboxylate ion, Ac<sup>-</sup>, that corresponds to a repeating unit of PA<sup>-</sup>.

X-ray diffraction experiments were performed for CTAAC concentrations below 70 wt %, and at two temperatures (25 and 40 °C). The spectra were characteristic of mesophases rather than solid crystalline phases (the Krafft temperature of CTAAC must be much below that of CTABr). Four types of diffraction patterns were obtained: micellar (single broad line), cubic (sharp lines at relative locations 1 (not seen),  $\sqrt{2}$ ,  $\sqrt{4}$ ,  $\sqrt{5}$ ,  $\sqrt{6}$ ,  $\sqrt{8}$ ,  $\sqrt{10}$ ,  $\sqrt{12}$ ,...), hexagonal (1,  $\sqrt{3}$ ,  $\sqrt{4}$ ,  $\sqrt{7}$ ), and lamellar (1, 2). The corresponding sequences of phases at both temperatures are shown in Figure 10. The locations of the phase boundaries are quite different from those obtained with CTABr: instead of forming a hexagonal phase at surfactant concentrations above 37%, CTAAC forms a cubic phase over a surprisingly large range of surfactant concentrations, between 25 and 56%. The hexagonal phase is not formed until the surfactant concentration reaches 60%. At higher temperatures (40 °C) a lamellar phase appears at high concentration (70%).

In the spectra of the cubic phase, we obtained about 10 lines, but not the first diffraction order, which is presumably too weak and too close to the beam to be observed. Assuming that the first order is not seen, the next 8 lines are consistent with the extinctions expected for a cubic structure of the *Pm3n* type. Beyond the eighth line, a few lines are missing, but the few lines that are observed are still consistent with the *Pm3n* structure. This structure has already been observed for cubic phases of micelles, also located next to an isotropic micellar phase and before the hexagonal phase.<sup>34</sup> It has a body-centered cubic unit cell, with large micelles at the apexes and center of a cube, and pairs of smaller anisotropic micelles at the centers of the faces. With the assignment of diffraction lines, the first line of the

experimental spectrum is the 110 diffraction order, and the position of this line gives a lattice parameter (edge of the cube) of 107 Å.

The structural parameters of the micellar and cubic phases are consistent with those expected for the packing of globular micelles. In the micellar phase, the intermicellar distance varies with volume fraction  $\phi_s$  of surfactant ions with the exponent  $-1/3$  expected for the three-dimensional swelling of a phase of globular micelles (Figure 6). The micelle radius calculated from this variation is 21 Å, which is somewhat shorter than the length of the extended surfactant chain, as is usually the case for micellar radii. In the cubic phase, this variation is continued, and the micellar radius calculated from the measured lattice parameter is 23 Å quite close to the length of the extended surfactant chain (24 Å).

Thus the nature of surfactant aggregates in CTABr/water and CTAAC/water are quite different: In the former, elongated micelles are formed already at low surfactant concentrations, near the cmc, and at higher concentrations they are packed in a hexagonal phase. In the latter, globular micelles are formed at low concentrations, and at higher concentrations they are packed in a cubic phase. These differences are related to different curvatures of the surfactant/water interfaces; cf. the Discussion section below.

**CTABr/CTAAC Mixtures.** The structural results presented so far show some correspondence between the phases of the ternary system NaPA/CTABr/water and some phases of the binary systems CTABr/water and/or CTAAC/water. The structure of the hexagonal phase of the ternary system is intermediate between the hexagonal phases of the two binary systems, and the structure of the cubic phase of the ternary system is quite close to that of CTAAC/water (indeed the line positions and relative line intensities are nearly identical, as shown in Figure 7). This may be consistent with the idea that polymeric PA<sup>-</sup> and monomeric Ac<sup>-</sup> counterions produce similar effects. To test this idea quantitatively, we made samples with mixtures of CTAAC and CTABr, and compared their structures with those of samples with mixtures of NaPA and CTABr.

Samples were prepared by mixing CTABr and CTAAC with a water content of 50%, which is in the range of water content of the cubic mesophase. We found hexagonal phases when the mole fraction of Ac<sup>-</sup> counterions was 70% of the total or less, and cubic phases at 87% and above. This is consistent with our observations in the NaPA/CTABr/water system, in which the cubic phase is found near the water corner of the composition map, where the ion exchange is nearly complete (cf. also Figure 2), and the hexagonal phase at higher contents in surfactant, where the ion exchange is incomplete.

Thus, these experiments confirm the idea that the sequence of the phases in the ternary systems is determined by the extent of the counterion exchange, and of course by the water content: at the same water content, and at the same extent of counterion exchange, we find identical phases with monomeric (Ac<sup>-</sup>) and polymeric (PA<sup>-</sup>) counterions. We still have to explain, of course, what determines the water content, and what determines the extent of ion exchange.

## Discussion

In this study, we have investigated the phases and structures that are formed when NaPA is added to various phases of the CTABr/water system. We have found a quite complex behavior: In the small part of the composition map that we have explored (Figure 3), there are at least 3 single-phase regions and at least 6 different two- or three-phase regions. This phase



behavior reflects the variety of structures that are formed in such mixtures. We have determined these structures, and found that they match classical structures formed in binary surfactant/water systems, with certain choices of water content and counterions.

Of course, this correspondence does not explain why a particular structure forms at a particular composition. For instance, when the composition map is crossed at fixed polyelectrolyte composition (2%), from low surfactant concentration to high surfactant concentration, the succession of phases that is observed may seem, at first sight, rather strange and not at all what simple arguments based on water content and curvature would seem to indicate. Thus, we need to find some way to rationalize this unusual behavior.

A good starting point for such a rationalization is the self-association of the surfactant ions. In every sample, we have found that all the surfactant ions are contained in one or more concentrated phases, where they associate to form large aggregates ("micelles"), either globular or cylindrical. This makes sense, since the hydrophobic free energy between two surfactant chains is, by far, the largest interaction energy in the system.

Then, the problems of phase behavior and structure can be analyzed according to two questions: how do polyions modify the sizes and shapes of these micelles, and how do they modify their separations. Upon addition of NaPA to CTABr/water, we have observed three types of effects: situations where the CTA<sup>+</sup> micelles retain the same shapes as in CTABr/water, but their distances are collapsed (region I), situations where the distances remain the same, but the shapes are changed (regions IV, V, and VI), and situations where both distances and shapes are changed (formation of a cubic phase). We now examine these three situations successively, then we discuss how the polyions can produce such effects.

**Effect on Distances.** When polyions are added to dilute micellar solutions, where the micelles are far apart, their effect is to pull all the micelles together in a concentrated phase, leaving behind a dilute phase containing water and salt. Therefore, in the presence of polyions, the micelles attract each other. There are two possible mechanisms for this attraction.<sup>35</sup> (a) The polyions bind to the micelles, compensate their charge, and bridge them together.<sup>36</sup> This effect is similar to the bridging flocculation of colloidal particles.<sup>37,38</sup> (b) The polyions bind to the micelles, compensate their charge, and cause an electrostatic attraction between them. This attractive force may be the same as the attraction caused by ionic correlations between charged surfaces. These two mechanisms cannot be distinguished in the present conditions where the concentrated phases are always formed from micelles that are packed together at very short distances. In the following, both mechanisms will be called "polyion bridging".

This bridging may explain a strange feature of the composition map, namely that samples located in the dilute region (region I) may phase separate to produce a hexagonal phase that is structurally similar to hexagonal phases made by samples located in the concentrated region (region VIII), even though the two regions are not connected in the phase map of Figure 3. The obvious question is whether these two hexagonal phases are part of the same thermodynamic phase. Examination of the compositions reveals that they have similar water contents, but differ by the extent of ion exchange. In region I, a substantial fraction of the Br<sup>-</sup> have been displaced by PA<sup>-</sup>, and a dilute aqueous phase has been expelled; in region VIII, all Br<sup>-</sup> have been kept, and a small amount of PA<sup>-</sup> has been incorporated into the phase. Accordingly, a hexagonal phase can be obtained

either with strong bridging, under conditions of excess water, or by simply adding NaPA at compositions where the system is already concentrated due to a restricted amount of water. Note that the composition of the hexagonal phase formed in region I lies outside the conventional mixing plane of Figure 3. Thus, it is expected that a continuous path exists between these hexagonal phases: the amount of water must be fixed at a value that corresponds to hexagonal phases, and then Br<sup>-</sup> can be exchanged progressively by polyions.

**Effect on Shapes.** When polyions are added to concentrated surfactant phases, they cause a succession of phase changes according to the sequence hexagonal → nematic → micellar. In this sequence, the surfactant concentration remains fixed, therefore the distances between micelles also remain the same, and only their shapes can vary: long cylindrical micelles may become shorter, or more flexible. The mechanism through which polyions cause these effects may be a change in the local curvatures of the surfactant/water interfaces. Indeed, it is likely that the replacement of Br<sup>-</sup> counterions of the surfactant by a PA<sup>-</sup> polyion can change the local curvature of the interface. It will be argued below that this change is to a stronger curvature. A local change to a stronger curvature may alter the shapes in two ways: (a) The principal curvature that is associated with the cylinder radius will increase, and the cylinder will become thinner. (b) Both principal curvatures become equal and the cylinder may terminate with a polyion capping the end.

In the concentrated phases of NaPA/CTABr/water, it appears that both effects operate to some extent. Evidence for mechanism (a) is found in the values of the cylinder radii of the hexagonal phases containing NaPA, that are smaller than those of the CTABr/water mixtures system, and close to those the CTAAC/water system (Figure 6). Evidence for (b) is found at high CTABr content where the addition of NaPA causes the hexagonal phase (rigid-cylindrical micelles) to be replaced by a nematic or micellar phase (short or flexible micelles).

**Effect on Shapes and Distances.** When polyions are added to very dilute micellar solutions of CTABr, they cause the separation of a concentrated cubic phase from a dilute aqueous solution (Region I' in Figure 3). The structure of this cubic phase appears to be the same as that of the cubic phase of the binary system CTAAC/water. This latter phase is located between a micellar phase and a hexagonal phase, therefore it is presumably made of globular micelles positioned on a cubic lattice. We therefore assume that the cubic phase of the ternary system CTABr/NaPA/water is also made of globular micelles positioned on a cubic lattice. Accordingly, the addition of polyions to a solution of CTABr has caused a shape change (the cylindrical micelles become globular) and a change in distances (they are brought close together).

The change in distances is caused by bridging, as in the case of region I. The correspondence with the cubic phase of CTAAC/water indicates that the change of shape is caused by the replacement of most Br<sup>-</sup> counterions by the COO<sup>-</sup> from the polyions. Thus, the occurrence of a cubic phase at this location of the composition map is caused by the very strong ion exchange that results from the large addition of water: the large volume of water extracts all Br<sup>-</sup>, and only the COO<sup>-</sup> from the polyions remain bound to the micelles (cf. Figure 2). At lower amounts of water, the ion exchange is incomplete; enough Br<sup>-</sup> remain to cause the micelles to be cylindrical, but nevertheless the polyion bridging causes the micelles to condense in a concentrated hexagonal phase. Thus the strange sequence from cubic to hexagonal is explained in this way.

**How Can Polyions Cause These Effects?** So far we have

argued that the exchange of bromide ions for polyions causes changes in the curvature of surfactant/water interfaces, and in the separation of the surfactant aggregates. In this section we examine the mechanisms through which the polyions may cause these changes. One way to do this is to picture the succession of events that occur when polyions are mixed with oppositely charged micelles. (1) We may picture a polyion as an object that carries a very high concentration of carboxylates. (2) Because the polyion carries this high negative charge, it can bind to a micelle surface and replace monovalent counterions. This exchange is most efficient at low overall ion concentrations, where the translational entropy of the monovalent ions is important. (3) After micelles have adsorbed polyions, they may have attractive interactions with each other through polyion bridging. This will cause the formation of a concentrated phase, where the distances between micelles will be determined by the configurations of the polyions. (4) The structures of the concentrated phases formed with polyions are close to those formed, at the same water content, by surfactant ions with the corresponding monovalent counterions. Thus, the connectedness of the polyion might not influence the counterion distribution in a concentrated mesophase, presumably because the counterion concentration in the mesophase is at least as high as that generated by the polyion. (5) Conversely, we find that the replacement of  $\text{Br}^-$  counterions by carboxylates causes structural changes (a hexagonal mesophase may be replaced with a cubic phase or with a concentrated micellar phase). This is consistent with the well-known fact that micelles with  $\text{Br}^-$  counterions tend to be cylindrical, whereas micelles with  $\text{Ac}^-$  or  $\text{Cl}^-$  counterions tend to be globular.<sup>23</sup> It is a consequence of a more nonuniform counterion concentration profile in the case of  $\text{Br}^-$ , as compared with  $\text{COO}^-$ . Indeed,  $\text{Br}^-$  tend to form ion pairs with positively charged micellar surfaces, whereas  $\text{Cl}^-$  and  $\text{Ac}^-$  ions do not.<sup>24,25</sup> At high concentrations, the affinity of the bromide ions to the surfactant aggregates prevents the exchange, and then the phase retains the structure of the pure CTABr/water mesophase.

## Conclusion

When polyions are added to oppositely charged surfactant aggregates (micelles ...), they bind and displace their counterions. This has two consequences. It may cause a change in the shapes of the micelles, if the ion exchange modifies the distribution of counterions near the micellar surface. It may cause a change in their distances if the micelles are initially far apart, and can be pulled together by polyion bridges. The system then builds the phase that corresponds to the water content that is imposed by the bridging, and to the curvature that is imposed by the ion exchange.

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