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Fluorescence and Conductivity Studies of Polyelectrolyte-Induced Aggregation of Alkyltrimethylammonium Bromides[†]

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Micelle formation of alkyltrimethylammonium surfactants (C_nTMAB) in aqueous sodium poly-(styrenesulfonate) (NaPSS) solutions was studied by fluorescence and conductivity measurements at 25 °C. The dependence of the aggregation phenomena on the chain length of the surfactant (n = 12, 14, 16, 18) and on the ionic strength of solutions was investigated. The critical aggregation concentration (cac) decreases with increasing hydrophobicity of the surfactant but remains approximately unchanged for C_{16}TMAB and C_{18}TMAB. The cac values are considerably lower than the critical micellization concentration (cmc) values for the same surfactant. The decrease is in the range from about three orders of magnitude for C_{12}EDMAB in water to approximately 10 times for C_{18}TMAB in 0.01 M NaBr. Furthermore, the cac for C_{12}EDMAB and C_{14}TMAB in NaPSS was found to increase slightly with increasing NaBr concentration but much less than, for instance, in sodium poly(acrylate) solutions. No significant effect of NaBr on cac values for C_{16}TMAB and C_{18}TMAB was found. The relatively weak dependence of cac on the surfactant chain length and on the simple salt concentration can be explained by the formation of a very stable aggregate between the polyelectrolyte and the amphiphile via the inclusion of aromatic side groups on the polymer chain into the surface of the micelle-like surfactant aggregate. Measurements of electrolytic conductivity showed that the mobility of the surfactant ions is greatly reduced in the presence of oppositely charged polyion. The surfactant preferentially forms the complex with the polyelectrolyte. When the complexation is complete free micelles appear in the system at the apparent critical micellization concentration (cmc*), which is therefore slightly higher in polyelectrolyte solutions than the ordinary cmc in pure surfactant solutions.

Introduction

In past years the interactions between polyelectrolytes and ionic surfactants with opposite charge have received much attention experimentally[1−18] and theoretically.[19−21] The strong association of the surfactant and polymer ion

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was attributed to the mutual action of electrostatic and hydrophobic forces between surfactant ions and polyion and between the hydrocarbon chains of bound amphiphilic ions, respectively. The polymer charge density parameter, determined by the average linear charge separation on the polymer backbone, is one of the decisive factors governing the binding process. Recently, influence of the hydrophobic character of the polyelectrolyte chain itself was recognized also.[4,11,15]

The experimental effort in this field was first devoted to the determination of binding isotherms,[1−6] enthalpies of binding,[6,7] and various thermodynamic[6,8] and transport properties[9] in solutions of a polyelectrolyte with added surfactants. Recently, spectroscopic techniques also have become very successful in investigating phenomena that occur in polyelectrolyte−surfactant systems.[10−18] All investigations indicated that many similarities exist between binding of surfactants to polyions and micelle formation in polymer-free solutions. In aqueous solutions without a polymer, surfactants are known to self-aggregate into micelles at a well-defined critical micellization concentration (cmc). Likewise, in the presence of a polymer micelle-like aggregates start to form along the polymer chain at a critical aggregation concentration (cac). cac is thus an analog of cmc but in solutions of surfactants with added polymeric component. A characteristic feature of this parameter is that it is always lower than the cmc of the corresponding surfactant. The lower cac is particularly pronounced in solutions of polyelectrolytes with opposite charge to the surfactant, with high linear charge densities, and when the polyelectrolyte has a flexible backbone. Furthermore, cac depends on the surfactant hydrocarbon chain length and on the ionic strength of solutions. As

mentioned before, other specific effects, e.g., hydrophobicity of the polymer, have to be considered.

Alkyltrimethylammonium salts (C$_n$TMAX) are very commonly studied cationic surfactants. The aggregation of these surfactants was studied in solutions of various anionic polyelectrolytes,[10−17] but the reports on micelle behavior in the presence of sodium(polystyrenesulfonate), NaPSS, are relatively few,[2,3,10,12,13,15] especially with regard to the dependence of cac on the hydrophobic chain length of the amphiphile and the ionic strength of solutions. The water soluble NaPSS is interesting because it has some hydrophobic character due to the aromatic side groups (benzenesulfonate groups) attached to the polymer backbone.

In the present contribution we investigate the aggregation phenomena of alkyltrimethylammonium bromides, C$_n$TMAB, with four different chain lengths (n = 12, 14, 16, 18) in dilute NaPSS solutions without added NaBr and in 0.01 M and 0.1 M NaBr solutions. Because the concentration range investigated is often low in most systems the applicability of various methods is limited. Here, we use fluorescence emission spectroscopy[18] to determine the cmc and cac values and the total degree of binding of each surfactant to the polyion. We put emphasis on cac values determined with pyrene as a fluorescence probe.[18] Solubilization of this aromatic photochemical probe within the self-assembled surfactant aggregates offers a very sensitive way to study the onset of cooperative association between polyelectrolyte and surface active agent. In addition, we characterize the system by conductivity measurements in order to determine how the mobility of surfactant ions is influenced by complexation with the polyion.

Experimental Section

Materials. NaPSS, with a molecular weight of about 70 000 g/mol and degree of sulfonation 1.0, supplied by Polysciences, Inc. (Warrington, PA) was purified by the procedure described in the literature.[22] The surfactants dodecylethyldimethylammonium bromide (C$_{12}$EDMAB), tetradecyltrimethylammonium bromide (C$_{14}$TMAB), hexadecyltrimethylammonium bromide (C$_{16}$TMAB), and octadecyltrimethylammonium bromide (C$_{18}$-TMAB) were all from Fluka and were recrystallized four times from acetone and vacuum-dried at 50 °C. In the text, the abbreviations C$_{12}$, C$_{14}$, C$_{16}$, and C$_{18}$ are used for these substances. The fluorescence probes, pyrene (Aldrich), 8-anilino-1-naphthalenesulfonic acid, ammonium salt (ANS), and biphenyl (both from Fluka) were used as received. Sodium bromide, NaBr (Kemika, Zagreb), was analytical grade and was used as received. Tripledistilled water was used for preparing all of the solutions.

Sample Preparation. A constant concentration of NaPSS, equal to 5 × 10^{-4} monomol/kg solution, was used in all experiments. Surfactant stock solutions were prepared by weighing the dried substances. Freshly prepared ANS stock solution was added to solvent and to solutions of polyelectrolyte and surfactant prior to measurements. Biphenyl was used for the determination of cmc values of pure surfactants and was also added prior to measurements to solvent and to pure surfactant stock solutions. For fluorescence measurements with pyrene, the pyrene-saturated solvent was prepared in the following way: pyrene was first dissolved in a small amount of methanol. The solvent was evaporated and the probe was redissolved in water or aqueous NaBr. The solvent with pyrene was allowed to stand for 1 day to ensure saturation and was filtered prior to preparation of solutions. With the pyrene-saturated solvent, 5 × 10^{-4} M NaPSS solution was prepared which was then used for the preparation of surfactant stock solutions. This was to ensure that the concentration of the

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polyelectrolyte was constant throughout the measurements. Surfactant solutions were left to equilibrate for 24 h.

Fluorescence Emission Spectroscopy. Biphenyl, ANS, and pyrene fluorescence spectra were recorded on a Perkin-Elmer model LS-50 luminescence spectrometer with a water-thermostated cell holder at 25 °C. A 1 cm path quartz cuvette was used. The instrument was controlled from a personal computer using Perkin-Elmer Fluorescence Data Manager software.

In all cases the titration technique was used to vary the concentration of surfactants. The cmc values of pure surfactants were determined by monitoring the fluorescence from biphenyl at 290 nm as a function of surfactant concentration. ANS fluorescence intensity at 483 nm was followed in polyelectrolyte−surfactant systems to obtain the total degree of coverage of the polyion with surfactant ions. Excitation and emission slit widths for recording the spectra from biphenyl and ANS were set to 5.0 nm, the scan rate was 240 nm min^{-1}, and two scans were accumulated for each run. The emission spectra of these two probes were not corrected. Finally, the vibrational fine structure of the fluorescence bands from pyrene was investigated to determine the cac values of polyelectrolyte−surfactant solutions. The emission spectra of pyrene were recorded from 350 to 500 nm after excitation at 330 nm. The excitation and emission spectral widths for pyrene were 2.5 nm and the scan rate was 240 nm min^{-1}. Nine scans were accumulated for each run and spectra were fully corrected before the ratio of the intensities of the first and third vibrational peaks, I_1/I_3, respectively, was calculated. These two peaks appeared at approximately 373 and 384 nm.

Conductivity. The specific conductance of solutions, κ, was measured at 25 °C with an ISKRA model MA 5964 conductivity meter using a Metrohm cell with a cell constant 0.095 cm^{-1}. The measurements were performed in aqueous solutions without added NaBr for pure surfactant and in polyelectrolyte−surfactant solutions at the same constant NaPSS concentration as in fluorescence experiments. The concentration of surfactant was changed by a titration technique.

Results and Discussion

The system C$_n$TMAB/NaPSS was characterized by fluorescence and conductivity measurements. Fluorescence measurements were performed in water, 0.01 M NaBr, and 0.1 M NaBr, whereas conductivity measurements were carried out only in aqueous solutions without added NaBr. First, we discuss the steady-state fluorescence experiments.

Fluorescence. The total degree of coverage, expressed as[10] β, of the polyelectrolyte chain with surfactant ions was obtained from plots of I/I_0, the fluorescence intensities of ANS in pure NaPSS solutions, I_0, and in NaPSS solutions with various surfactant concentrations, I, respectively. It is well known[10] that in polar media ANS shows a weak flourescence peak at 520 nm, whereas in a nonpolar environment the fluorescence shifts to around 483 nm with a concomitant increase in quantum yield. In this way ANS offers a sensitive method for the detection of free surfactant in solution. An example of an I/I_0 vs concentration plot is shown in Figure 1 for aqueous polyelectrolyte solutions of all four surfactants. As we can see, the fluorescence intensity of ANS at 483 nm shows a low and nearly constant value until a threshold surfactant concentration is reached. Above this point, I/I_0 starts to increase sharply. By comparison with results obtained for pure surfactant solutions below the cmc[10] (here, fluorescence intensity of ANS gradually increases with increasing surfactant monomer concentration), we can conclude that this increase is due to the presence of unbound surfactant in solution. Therefore, at this point the total binding of surfactant to the polyion is complete and free detergent appears in solution. This is accompanied by a decreased polarity of environment and as a consequence the fluorescence intensity of ANS increases.

Table 1. Critical Micellization Concentrations (cmc; Pure C_nTMAB Solutions), Free Energy of Micellization ($\overline{\Delta G_m^{\circ}}$), Apparent Critical Micellization Concentrations (cmc*; in the Presence of 5×10^{-4} M NaPSS), Critical Aggregation Concentrations (cac), Free Energy of Binding (ΔG_b°), and the Degree of Binding (β) of C_nTMAB in the presence of 5×10^{-4} M NaPSS

surfactant	c_{NaBr}/M	cmc $\times 10^3$	$-\overline{\Delta G_m^{\circ}}$/kJ mol^{-1}	cmc* $\times 10^3$	cac $\times 10^6$	$-\overline{\Delta G_b^{\circ}}$/kJ mol^{-1}	β
C_{12}	0	14.0[a]	10.6		7.7	29.2	0.60[a]
		14.5[b]		14.8[b]			0.60[b]
		14.2[c]		14.5[c]			0.60[c]
	0.01	11.0[a]	11.2		10	28.5	0.57[a]
	0.1	3.66[a]	13.9		15	27.5	0.50[a]
C_{14}	0	3.78[a]	13.9		4.4	30.6	0.59[a]
		3.9[b]		4.2[b]			0.60[b]
		3.7[c]		4.0[c]			0.60[c]
	0.01	1.55[a]	16.0		4.8	30.4	0.60[a]
	0.1	0.33[a]	19.9		5.7	29.9	0.50[a]
C_{16}	0	0.95[a]	17.3		2.5	32.0	0.60[a]
		0.94[b]		1.25[b]			0.62[b]
		0.90[c]		1.20[c]			0.60[c]
	0.01	0.14[a]	22.0		2.5	32.0	0.60[a]
	0.1	0.034[a]	25.5		2.5	32.0	0.50[a]
C_{18}	0	0.21[a]	21.0		2.2	33.3	0.61[a]
		0.23[b]		0.51[b]			0.56[b]
		0.22[c]		0.50[c]			0.56[c]
	0.01	0.018[a]	27.1		2.4	32.1	0.73[a]
	0.1	−			2.2	33.3	−

[a] From fluorimetry. [b] From κ vs c curves. [c] From Λ vs $\sqrt{c}$ curves. [d] cmc, cmc*, and cac in mol/kg solution.
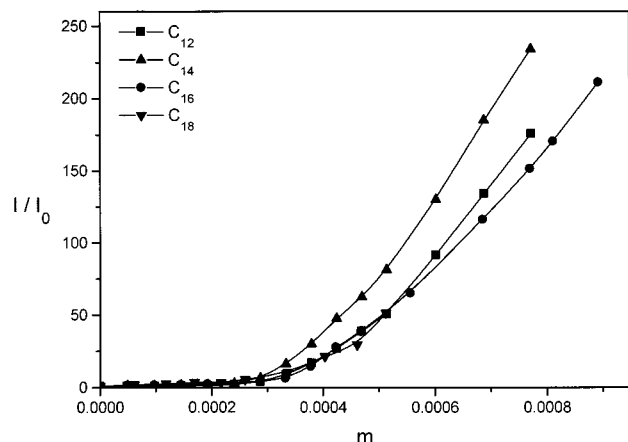

Figure 1. The dependence of fluorescence intensity of ANS on C_nTMAB concentration (m in mol/kg solution) in aqueous polyelectrolyte solutions ($c_{NaBr} = 0$). Polyelectrolyte concentration, $m_{NaPSS} = 5 \times 10^{-4}$ M.

Parameter β was calculated from the expression

$$\beta = \frac{m_S}{m_P} \qquad (1)$$

as the ratio of the total surfactant concentration at this point, denoted by m_S, to the polyelectrolyte concentration, m_P. The concentration of free surfactant was not taken into account but as it is seen from the very low intensity of ANS there is almost no free detergent below this threshold concentration. The obtained values are collected in Table 1. The value of β for C_{18} in 0.1 M NaBr was not determined because ANS caused heavy precipitation in this case. For the same reason β for C_{18} in 0.01 M NaBr might be too high. The total degree of coverage of the polyion with surfactant ions is to a first approximation independent of the chain length and it is approximately 60% in water, slightly less in 0.01 M NaBr, and approximately 50% in 0.1 M NaBr. If we take into account, that our values for β do not consider the concentration of free surfactant, the agreement with results obtained with surfactant ion-selective electrode for the binding of C_{12}-TMAB to NaPSS at 30 °C in the presence of NaCl is satisfactory.[2]
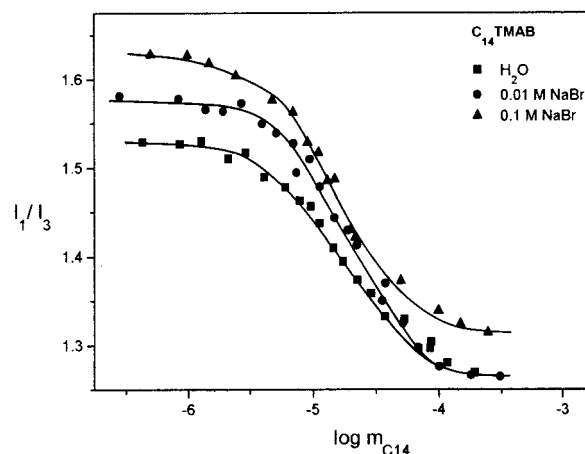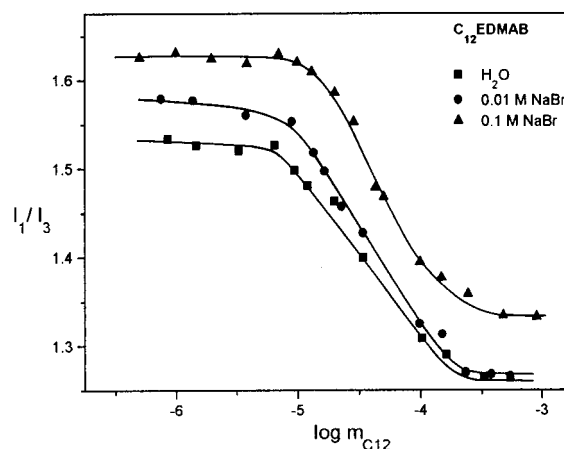
Figure 2. I_1/I_3 ratio of the fluorescence of pyrene in solutions of C_{12} and C_{14} surfactants in water, in 0.01 M NaBr, and in 0.1 M NaBr in the presence of 5×10^{-4} M NaPSS.

The experimental curves obtained with pyrene are shown in Figures 2 and 3 as the ratio I_1/I_3 vs the logarithm of surfactant concentration. It is well known that changes in I_1/I_3 reflect micelle or other similar aggregate formation.[18] All curves plotted in Figures 2 and 3 show a characteristic shape. At first, the ratio is approximately
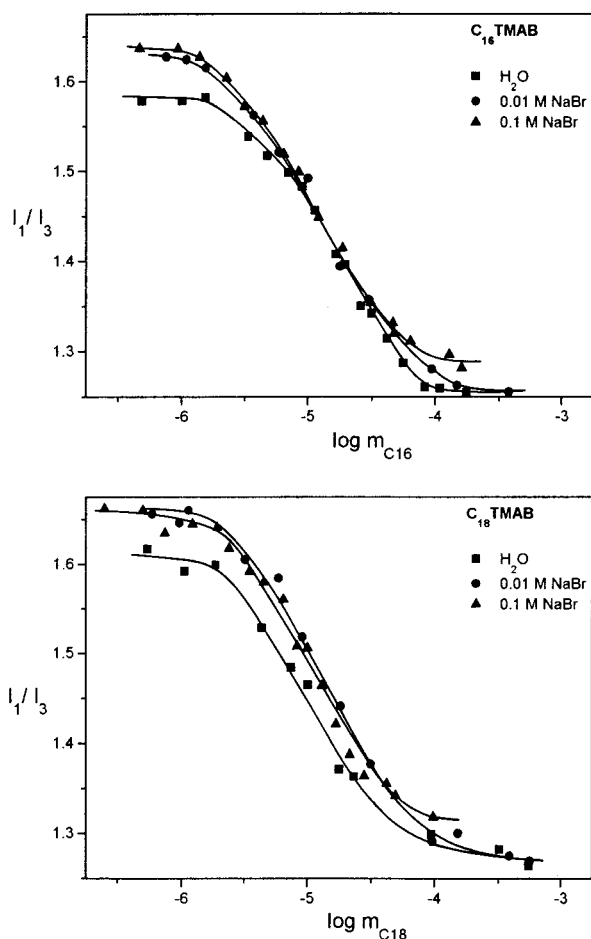
Figure 3. I_1/I_3 ratio of the fluorescence of pyrene in solutions of C_{16} and C_{18} surfactants in water, in 0.01 M NaBr, and in 0.1 M NaBr in the presence of 5×10^{-4} M NaPSS.

constant and has a value typical for aqueous solutions without hydrophobic aggregates[18,26] (between 1.55 and 1.65; NaPSS itself has no significant effect on the pyrene ratio). The presence of NaBr causes a slight increase of the ratio which is consistent with the increased polarity of the environment by the addition of simple electrolyte. At cac, I_1/I_3 starts to decrease because of probe solubilization in the micelle-like aggregates which gradually start to form along the polymer chain. cac values were determined as the first break in the curve.[15,16] Only a limited number of such aggregates can be bound to one chain. Eventually, above a certain detergent concentration a saturation point is reached. Afterward, the ratio remains approximately constant at a value between 1.25 and 1.35 indicating constant polarity of the local environment sensed by pyrene. This value is usually found for pyrene solubilized in surfactant micelles[18,26,27] and supports the idea of micelle-like aggregation of surfactant in presence of a polyelectrolyte.

The cmc values for each surfactant were determined from a plot of I_0/I (the ratio of intensities of biphenyl in the absence, I_0, and in the presence, I, of surfactant) vs surfactant concentration. Each plot shows a break at cmc.[23] All fluorimetrically determined cmc values are collected in Table 1 and graphically shown in Figure 4. A comment should be made regarding cmc values for C_{18} surfactant. The Krafft temperature of this surfactant is approximately

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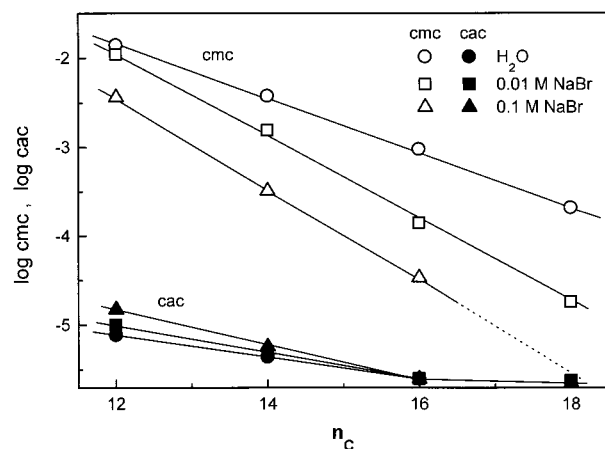
Figure 4. Dependence of cmc and cac values on the number of C atoms, n_C, in the hydrocarbon chain of surfactant.

35 °C.[24] The stock solution of the surfactant (concentration about twice the cmc) was heated to this point so that the salt was completely dissolved. The solution was then slowly cooled to 25 °C and the titration was performed with the supersaturated solution. In this way, cmc for C_{18} was determined only in water and in 0.01 M NaBr. As we can see from Figure 4 the dependence of the logarithm of cmc on the number of C atoms (n_C) in the hydrocarbon chain of surfactant is linear. The C_{12} surfactant is slightly different from the others because it has one methyl group in the polar head exchanged for an ethyl group. Our cmc value for C_{12}EDMAB is from 14.0 to 14.5×10^{-3} M depending on the method used for the determination (see Table 1). In the literature we find the cmc value for C_{12}-EDMAB equal to[25-27] 14.5×10^{-3} M which is very close to the cmc for dodecyltrimethylammonium bromide, C_{12}-TMAB[10,14,25] ($14.4-15.2 \times 10^{-3}$ M). It was concluded[25] that the replacement of one methyl group for an ethyl group in the surfactant head has very little effect on cmc values. Obviously (cf. Table 1), cmc depends more on the hydrocarbon chain length than on this small difference in the size of the polar head group. The same conclusion can be drawn from the obtained linear relationship of log cmc vs n_C as clearly demonstrated in Figure 4. Therefore, in the following text no special attention will be paid to this difference.

The main purpose of following the fluorescence of pyrene was the determination of cac values. These are reported in Table 1 and presented in Figure 4 together with cmc values. Clearly, log cac exhibits the same hydrocarbon chain length dependence as does the log cmc: between C_{12} and C_{16} bromides it decreases approximately linearly with increasing hydrophobicity of the surfactant. The shorter the chain, the weaker the interaction between surfactant and polyelectrolyte which gives rise to a larger cac. However, the decrease in cac is not as steep as the decrease in cmc. The cac values for C_{16} and C_{18} even remain approximately the same. Something similar has been found for the rate of change of cmc in the homologous series of sodium alkyl sulfates in water.[28] Between about C_{16} and C_{18} members the cmc tends to decrease more slowly

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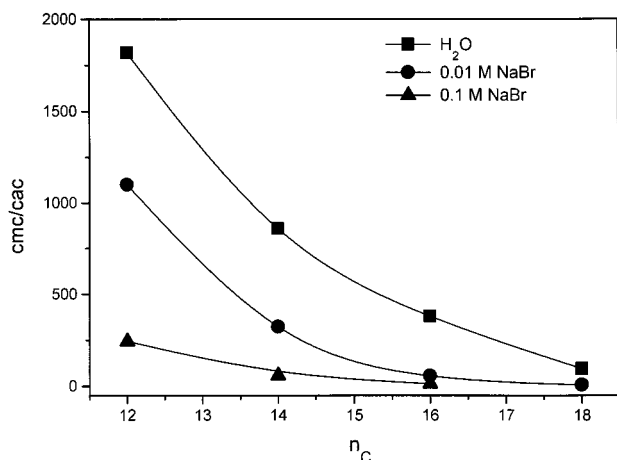(25) Peña, L.; Junquera, E.; Aicart, E. *J. Solution Chem.* **1995**, *24*, 1075.
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Figure 5. Dependence of the ratio cmc/cac on the number of C atoms, n_C, in the hydrocarbon chain of surfactant.

than for shorter chain lengths, and above C_{18} member it tends to remain approximately constant. This is probably due to the coiling of very long hydrocarbon chains and is presumably the reason for the leveling off of cac values in our case also. In any case, we can conclude that the hydrophobic character of the amphiphile plays an important part even when the aggregates are formed at the polyion.

Another obvious feature (cf. Figure 4) is that cac is considerably lower than cmc. It is about three orders of magnitude lower for C_{12} in H_2O (~1800 times) but only 10 times lower for C_{18} in 0.01 M NaBr. These are the lowest cac values reported for alkyltrimethylammonium bromides. NaPSS is a strong polyelectrolyte with high linear charge density, so in comparison with some weak anionic polyelectrolytes (hyaluronate,[14,29] pectate,[4] alginate,[4] poly(methacrylate)[11]) this could be expected. Thalberg et al.,[14,29] for example, investigated interactions between sodium hyaluronate (NaHy), a weak polyelectrolyte with a stiff backbone, and alkyltrimethylammonium surfactants with 10, 12, 14, and 16 C atoms in the hydrocarbon chain. Binding in NaHy solutions is considerably weaker than in most other systems because of lower linear charge density of the polymer (about four times lower than that for NaPSS).[29] This is reflected in higher cac values: cac for C_{10} in NaHy is only slightly lower than the cmc of pure C_{10}, for C_{12} it is about one-half of the cmc, and for C_{16} it is nearly 30 times lower. In addition to the effect of charge density, the poly(styrene)-based chain of NaPSS is much more flexible than the polysaccharide chain of NaHy and can better wrap around a surfactant micelle thus making the aggregate more stable. For C_n-TMAB/NaPSS system, the difference between cac and cmc decreases with increasing chain length (see Figure 4). If we propose linear dependence of cmc values in 0.1 M NaBr up to $n_C = 18$, the cac and cmc for C_{18} would come very close to each other. In Figure 5, the ratio of cmc/cac is plotted as a function of the surfactant chain length. We can see that it decreases very quickly with increasing the number of C atoms in the chain. This observation is again in contrast with what is observed for cac values of C_n-TMAB surfactants in hyaluronate solutions[29] where the concentration gap between cac and cmc increases with increasing surfactant chain length (see Figure 10 in ref 29 or Figure 1 in ref 19). The same applies also to other polyelectrolytes independent of the charge density parameter: the slope of log cac vs n_C in ionic polymers is

higher than the slope of log cmc vs n_C. This indicates that the aggregate between C_nTMAB and NaPSS is less influenced by the length of the hydrocarbon chain of the surfactant and leads to a conclusion that other effects, characteristic for poly(styrenesulfonate), have to be considered. We will return to this point when we discuss the influence of salt on cac.

From the measured cmc and cac values we can calculate the standard free energy change when 1 mol of surfactant molecules is transferred from an aqueous phase to a micelle or to a polyelectrolyte/surfactant complex, $\overline{\Delta G_m^\circ}$ and $\overline{\Delta G_b^\circ}$, respectively. These values were obtained from expressions[28,32] 2 and 3

$$\overline{\Delta G_m^\circ} = RT \ln \text{cmc} \qquad (2)$$

$$\overline{\Delta G_b^\circ} = RT \ln \text{cac} \qquad (3)$$

and are reported in Table 1. The absolute values of the free energy of binding, $\overline{\Delta G_b^\circ}$, are in most cases much larger than the corresponding values of the free energy of micellization, $\overline{\Delta G_m^\circ}$, indicating a greater driving force for the polyelectrolyte-induced surfactant aggregation than for free micellization of the corresponding surfactant. The micelle formed in the polyion domain is more stable than the ordinary micelle, however, the enhancement in stability is much more evident for shorter chain lengths. For example, for surfactant with the longest hydrocarbon chain (C_{18}) we observed that the cac and cmc values came very close to each other (cf. Figure 4). In this case, the stability of the local micelle would be comparable to the stability of the free micelle.

Let us return to the influence of linear charge density on cac. The dramatic influence of this factor is furthermore seen when we proceed from weak to strong polyelectrolytes. For example, for sodium poly(acrylate), NaPA, Hayakawa et al.[4] observed significant interaction between NaPA and C_{12}TMAB at concentrations of surfactant that were about two orders of magnitude lower than in NaHy. Poly(acrylates) and poly(styrenesulfonates) have the same linear charge density due to the same distance between the charges on the backbone. However, comparing experimental values for C_{12}TMAB in poly(acrylate) solutions[4,16] with those determined by us for C_{12}EDMAB in poly(styrenesulfonate) solutions, we can see that cac values in NaPSS are from about 3 to 30 times lower than in NaPA solutions, depending on the ionic strength of solution. This is clearly demonstrated for the two polyelectrolytes in Figure 6 which shows the dependence of log cac on the logarithm of the total salt concentration, log m_S^{tot}, where m_S^{tot} (defined as $m_{NaPSS} + m_{NaBr}$) is the total concentration of sodium cations in solution. The results for C_{12}TMAB in NaPA were taken from ref 16 by Hansson and Almgren. The concentration of polyelectrolyte was the same in both cases. In contrast to the well-known salt dependence of cmc, cac increases with increasing ionic strength. This can be accounted for by the electrostatics: simple electrolyte screens the electrostatic interactions between the polyanion and surfactant cations. In the presence of simple electrolyte, the "local cmc", needed for self-aggregation of the amphiphile at the polymer, is thus

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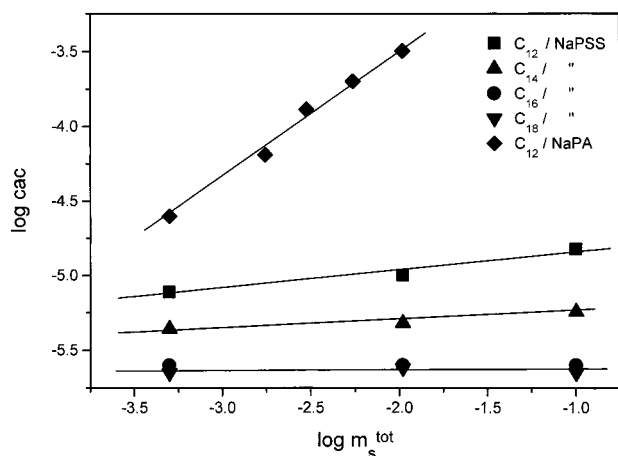
Figure 6. Dependence of cac on total salt concentration, log m_s^{tot} ($m_s^{tot} = m_{NaBr} + m_{NaPSS}$); ♦: data for C_{12}TMAB in 5×10^{-4} M NaPA, taken from ref 16.

reached at a somewhat higher total surfactant concentration, leading to an increased cac. The striking difference observed in cac behavior for NaPA and NaPSS solutions cannot be explained either by chain flexibility or by charge density, which are the factors that seem to be the most important for the polyelectrolyte-induced surfactant aggregation.

The explanation for the considerably different aggregation behavior of C_nTMAB in NaPSS solutions, as compared to other systems, should lie in the specific nature of the polymer chain. NaPSS contains hydrophobic aromatic side groups attached to the poly(styrene) chain, whereas other investigated polyelectrolytes are hydrophilic, including NaPA. NMR measurements[12] indicate that benzene-sulfonate groups of NaPSS take an active part in the micelle structure. The benzene rings are solubilized near the surface of the ionic micelle (near the β-CH$_2$ group). In this way, the binding with surfactant occurs not only via electrostatic interactions between the charged groups (as for NaPA) but also via hydrophobic interactions between the surfactant hydrocarbon chains and the aromatic rings of the polyelectrolyte. Such aggregate formation is very stable and compact, and therefore less sensitive to properties such as hydrophobicity of surfactant and ionic strength of surrounding solution.

The stability of similar polyelectrolyte−surfactant aggregates formed between NaPSS and cetylpyridinium chloride (CPC) was indicated[9] by transport number measurements. In the moving boundary cell the NaPSS/CPC complex moved toward the positive electrode, revealing the net negative charge of the aggregate. The degree of complexation of NaPSS with CPC did not change during the electrolysis. Both facts indicate the exceptional stability of this formation.

Conductivity. Another approach that we applied to study the aggregation of C_nTMAB surfactants in NaPSS solutions was the measurement of the electrolytic conductivity. We measured the specific conductance, κ, of pure surfactant solution and of surfactant solutions in the presence of polyelectrolyte. The measurements were performed only in aqueous solutions without added NaBr. The results are shown in Figure 7. All curves show a change in slope at the concentration which is usually identified with the cmc value for pure surfactant solutions. The cmc values determined from κ vs c plots are reported in Table 1 and are in good agreement with fluorimetric determinations. A similar break in κ vs c curve is observed also in the presence of polyelectrolyte, but at a slightly
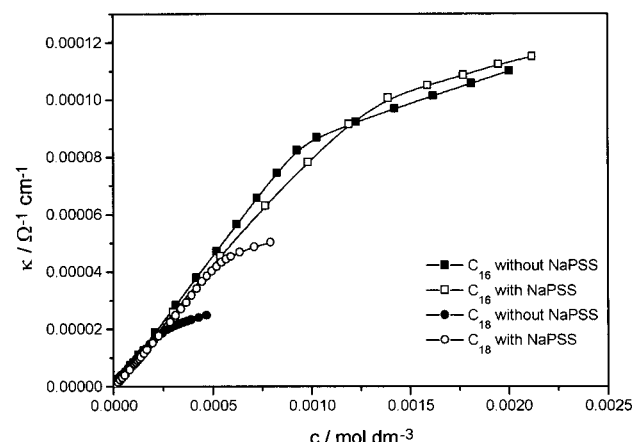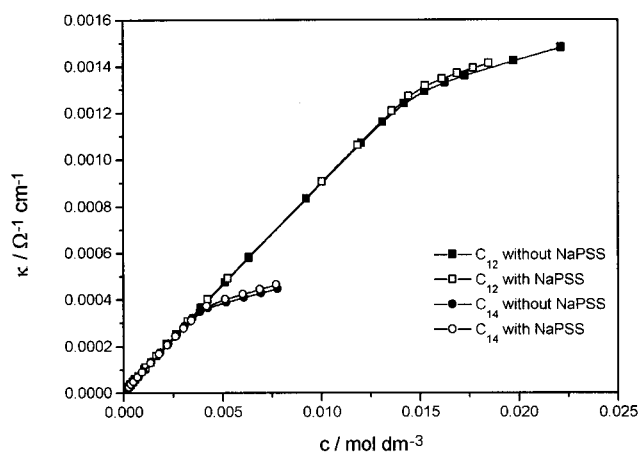
Figure 7. Specific conductance, κ, at 25 °C in aqueous solutions of C_nTMAB in the absence and in the presence of 5×10^{-4} M NaPSS.

higher concentration than in pure surfactant solutions. This concentration is referred to as the apparent critical micellization concentration (cmc*) and is also given in Table 1. It is higher than the corresponding cmc because surfactant preferentially forms a complex with the polyelectrolyte. After the complexation is completed, further addition of surfactant leads to the formation of ordinary micelles which are not bound to the polyion. From cmc* and cmc values we can also estimate the total degree of binding, β, from the expression

$$\beta = \frac{\text{cmc}^* - \text{cmc}}{m_P} \qquad (4)$$

which is given in Table 1 together with the results obtained by fluorimetry. We can see that the agreement between conductometric and fluorimetric determinations is good.

Conductivity measurements reveal also the formation of surfactant aggregates above cac which is much below the cmc. The complex formation cannot, however, be seen from κ vs c curves. It can be detected from plots of the molar conductivity Λ (defined as κ/c). In Figure 8, Λ is plotted as a function of the square root of surfactant concentration. The dependence of Λ on $\sqrt{c}$ for pure surfactant solutions shows only one break, again indicating micelle formation. Conversely, the curve in the presence of polyelectrolyte exhibits a very different behavior. At first, a steep decrease in molar conductivity is observed. In this range the mobility of surfactant cation is strongly reduced because of the electrostatic field of the polyanion. This concentration region corresponds to the gradual formation of minimicelles. In this region it was
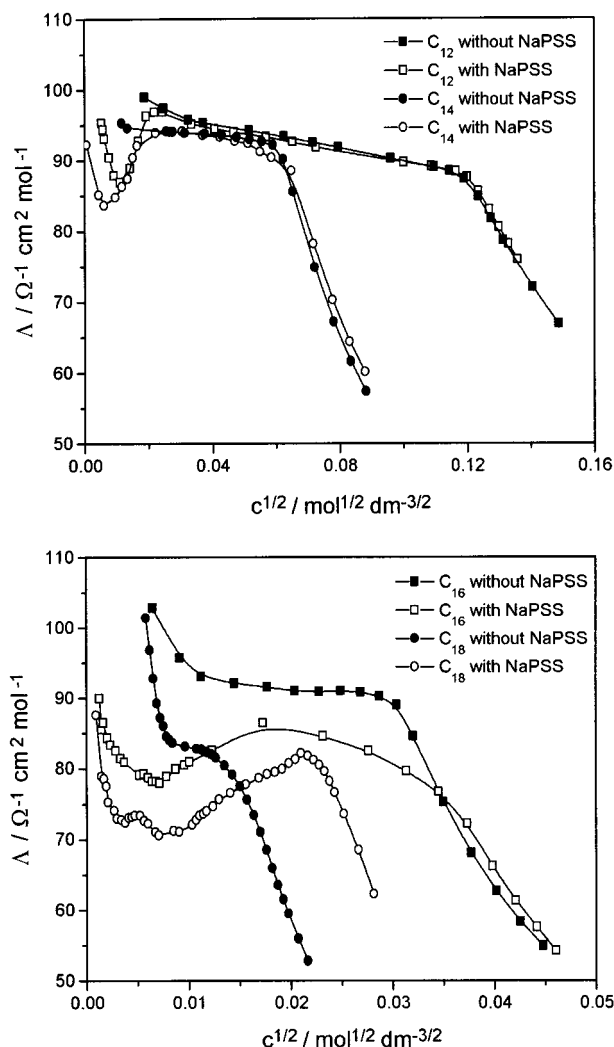
Figure 8. Molar conductivity, Λ, at 25 °C in aqueous solutions of C_nTMAB in the absence and in the presence of 5×10^{-4} M NaPSS.

observed above that the I_1/I_3 ratio of pyrene decreases from the value typical for polar aqueous environment without hydrophobic aggregates to the value for micelle-solubilized probe at the saturation point. The minimum in the Λ vs $\sqrt{c}$ curve occurs at approximately the saturation point obtained by pyrene. The position of the minimum for C_{14}, C_{16}, and C_{18} is at approximately 5×10^{-5} M, but for C_{12} it is at about two times higher concentration. This is again an indication that the complexation between NaPSS and C_nTMAB is not appreciably influenced by the hydrocarbon chain length of surfactant, especially the parameters such as the degree of coverage of the polyion with surfactant in micelle and monomer form.

Some authors identify the concentration at the minimum in Λ with the cac.[30] In the literature, we find different ways to determine this concentration. Chu and Thomas,[11] for example, identify the cac for $C_{10}TMAB$ in poly-(metacrylate) as the midpoint of the transition in a plot of I_1/I_3 vs c. Zhen and Thung[31] on the other hand regard the cac to be at the saturation point. In this article, we followed the method proposed by Hansson and Almgren[15,16] and determined cac at the first break of the intensity ratio obtained by pyrene. After the minimum the conductivity starts to increase with increasing surfactant concentration. The flexible poly(styrenesulfonate) chain wraps around surfactant micelles, acting as a counterion cloud.

This can be accompanied by a release of counterions originating from both the polyion and the surfactant micelle. As a consequence, the conductivity starts to increase. The minimum, observed in the NaPSS/C_nTMAB solutions, is very pronounced in comparison, for example, with β-cyclodextrin/$C_{12}TMAB$ system where it is rather shallow.[30] Both NaPSS and C_nTMAB micelles bind a considerable amount of their counterions. The degree of counterion binding for the free micelle is from ~50% to 80%.[32a] Poly(styrenesulfonate) anion binds about 70% of sodium counterions at this polyelectrolyte concentration.[33] The effect of releasing the counterions may therefore be very strong for the particular system and can have an important influence on the reduction of the cmc because of the favorable positive contribution to the entropy.

All conductivity curves reach a maximum at the concentration of surfactant approximately equal to the monomolar concentration of the polyion. For C_{18} this coincides with the change in slope at cmc* (at approximately 5.1×10^{-4}). At the "equivalent point" a white colloidal precipitate is formed between polyion and bound surfactant ions which readily redissolves with further addition of surfactant. As we can see from Figure 8 the maximum in Λ is more pronounced for longer chain lengths of surfactant. The part of the Λ vs $\sqrt{c}$ curve beyond the maximum again resembles behavior similar to that of pure surfactant solutions. The cmc and cmc* determined from Λ are reported in Table 1, as well as the β values calculated from eq 4.

Conductivity measurements thus complete the picture which emerges from fluorescence investigations of solutions of NaPSS with added alkyltrimethylammonium bromides. They confirm the formation of polyelectrolyte-bound minimicelles at very low concentrations, and indicate that the complex is very stable. It exists in solution even when free surfactant micelles are formed. It would be interesting to investigate other types of cationic surfactants in combination with NaPSS. It was revealed by potentiometric and enthalpy of binding measurements of alkylpyridinium cations to poly(styrenesulfonate) anion[6] that these surfactants also interact with the polyion in the form of many small surfactant aggregates. Unfortunately, these amphiphiles are often used as quenchers of fluorescence, and therefore the application of this method to this particular system seems to be difficult.

Conclusions

We investigated the aggregation phenomena of alkyltrimethylammonium bromides with four different chain lengths in the presence of sodium poly(styrenesulfonate) by fluorescence and conductivity measurements. As revealed by fluorimetry, NaPSS induces micelle formation of these surfactants at a cac which is much lower than the cmc. Compared to other anionic polyelectrolytes, this is the largest reduction. The effect is most pronounced in pure water where cac is about 1800 and 100 times lower than cmc for $C_{12}EDMAB$ and C_{18}, respectively. The addition of simple electrolyte (NaBr) has a shielding effect on the interactions between polyion and surfactant ion with opposite charge. Nevertheless, the micelle-like aggregation of surfactant still takes place at somewhat higher cac values.

The cmc/cac ratio is a measure of the strength of interaction between the surfactant and the polyelectrolyte. The polyelectrolyte-induced micelle is much more stable than the free micelle of the corresponding surfactant. The

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enhancement in stability of the local micelle compared to that of the free micelle decreases exponentially with increasing hydrocarbon chain length of the surfactant.

The influence of salt on cac in NaPSS/C_nTMAB is not very pronounced. Together with extremely low cac values this is an important finding, especially if one compares effects of NaPSS and NaPA. The finding indicates that in addition to strong electrostatic forces between the polyion and surfactant micelles, specific interactions also have to be taken into account. The binding of surfactant to NaPSS takes place also via solubilization of the aromatic rings of the polyelectrolyte in the minimicelles. For hydrophilic NaPA no such interaction is possible. The strong complexation between NaPSS and surfactants with opposite charge is furthermore confirmed by conductivity measurements. It is shown that the mobility of surfactant ions is strongly reduced in the presence of the polyion. The flexible poly(styrenesulfonate) chain wraps around the surfactant micelle. This can be accompanied by a simultaneous release of counterions originating from polyions and from micelles and has a positive entropic effect on the aggregation.