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Interactions between polyampholytes and ionic surfactants

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Abstract The interactions of two partially charged ampholytic terpolymers [consisting of acrylamide, sodium 2-acrylamido-2-methylpropanesulphonate, and 2-(methacryloyloxyethyl)trimethylammonium chloride segments with molar compositions 80/12/08 and 80/08/12] and two fully charged ampholytic copolymers (containing only the two latter comonomers with molar compositions of 80/20 and 50/50), with cationic surfactants [tetradecyltrimethylammonium bromide (TTAB) and cetyltrimethylammonium bromide (CTAB)] and the anionic surfactant sodium dodecylsulphate (SDS), are investigated. The studies include phase behaviour (swelling, solubilisation, precipitation), viscometry, electrical conductivity, and potentiometry (bromide ion and surfactant ion-specific electrodes). The 80/08/12 and 80/12/08 polyampholytes swell in water and are solubilised in the presence of cationic or anionic surfactants above a particular surfactant concentration that is proportional to the polymer concentration. The polyampolyte 80/20 is soluble in water but precipitates in the presence of TTAB, whereas 50/50 is insoluble in water and in the presence of TTAB, but is solubilised upon addition of SDS. The results indicate that TTAB binds to 80/12/08 with little or no cooperativity. Solubilisation appears to be the result of the increasing polyelectrolyte character of the polyampholyte upon neutralisation of its charged sites by bound surfactant ions of opposite charge. The binding of TTAB by the 50/50 polyampholyte is very weak and non-cooperative. In contrast, 80/20 binds TTAB cooperatively, much like a true polyelectrolyte-surfactant system of opposing charges. In particular, the binding is characterised by the existence of a critical aggregation concentration. A partial phase diagram for this system has been determined from the TTA^+-electrode potential data. The behaviour of true polyelectrolytes and polyampholytes, with respect to their interaction with surfactants, is discussed.

Key words Polyampholytes – Ionic surfactants – Polyampholyte-surfactant interactions – Polymer-surfactant interactions – Ion-specific electrodes

Introduction

There are extensive reviews of the interactions between polymers and surfactants in the literature, due to their applications in numerous industrial and biological processes that include enhanced oil recovery by polymer-micelle flooding [1], cosmetic formulations [2], and drug release processes [3, 4]. A systematic study of the differing combinations of macromolecules has shown the following trends.

Interactions between non-ionic polymers and surfactants are weak, with the strength of the interaction dependent on the polymer type. Hydrophilic polymers show no interaction with polyoxyethylene surfactants [5]; nevertheless, these surfactants may affect the cloud point of polymers with an increased hydrophobicity [5, 6]. The interaction between a non-ionic polymer and a charged surfactant begins at a 'specific' concentration that is below the critical micelle concentration (CMC), termed the critical aggregation concentration (CAC) [7–9]. Again, polymer hydrophobicity and surfactant type affect the strength of interaction [10–12].

The interaction between a polyelectrolyte and a surfactant of opposing charge is usually strong due to the Coulombic attraction, and the CAC may be two to three orders of magnitude lower than the CMC [13–15]. These systems often result in the precipitation of a polyelectrolyte-surfactant complex, though the phase separation process is highly dependent on polyelectrolyte concentration [13]. Interactions between a polyelectrolyte and a surfactant of similar charge are expected to be very weak due to repulsion effects [16, 17]. Surfactant binding may occur if the polyelectrolyte is made sufficiently hydrophobic, so that the attractive hydrophobic interactions overcome the repulsive electrostatic interactions [18, 19].

The presence of both cationic and anionic segments on the same polymer chain, i.e. a polyampholyte, further perturbs the interaction with ionic surfactants. In addition to charge-charge interactions between polymer and surfactant, the properties of a polyampholyte in solution are complex [20]. Studies of polyampholytes in the presence of anionic or cationic surfactants suggest that there is a decrease in the dimensions of the chain, and that the behaviour of the resulting polyampholyte-surfactant complex is dependent on the nature of the surfactant [21]. Many recent studies concern the interaction between anionic surfactants and the natural polyampholyte gelatin [22–26]. These systems exhibit an increase in solution viscosity with an increasing surfactant concentration [23]. Studies by pulsed-gradient spin-echo NMR (PGSE-NMR) [25] and small-angle neutron scattering [26] suggest that this increase is attributable to the formation of a network.

In the above systems [20–26], the interactions of charged surfactants with annealed polyampholytes, whose amphoteric nature is dependent on the solution pH, are studied. The aim of this study is a systematic investigation of the interactions between charged surfactants and quenched polyampholytes, whose net charge is determined by chemistry and is largely independent of solution pH, with particular emphasis on the solubilisation/precipitation behaviour of the polyampholyte in the presence of a surfactant.

Experimental

Materials

The polyampholytes were prepared by free radical microemulsion copolymerisation [27–30]. Two types of polyampholytes were prepared, those that were fully charged and those that contained neutral segments. The fully charged polyampholytes were copolymers of 2-(methacryloyloxyethyl)-trimethylammonium chloride (MADQUAT) and sodium 2-acrylamido-2-methylpropanesulphonate (NaAMPS), whilst the partially charged polyampholytes contained additional acrylamide segments. In order to eliminate impurities (monomers, residual salts, emulsifiers, etc.) the polymer powders were dissolved in 0.5 M NaCl (terpolymers) or 1 M NaCl (copolymers) aqueous solutions and dialysed against deionized water before recovery by freeze-drying. It should be noted that after dialysis, the samples tend to self-neutralise almost completely, i.e. the anionic and cationic monomers are completely paired when there is no residual sodium chloride left in the solution [27, 29, 30]. The average polyampholyte compositions, along with their nomenclature, are given in Table 1. The molecular weights of all the polymers investigated were high and around 1×10^7 [29, 30].

It was previously found that microemulsion polymerisation yields copolymers with a more homogeneous composition than those prepared in solution [29, 31]. In particular, the fully charged polyampholytes have a microstructure not far from random, in contrast to copolymers obtained in solution which have a strong tendency to alternation [20, 29]. The reactivity of the monomers in the terpolymerisation is intermediate, between that determined for microemulsion binary copolymerisation, and for solution binary copolymerisation [32]. The polyampholytes investigated here were obtained at full conversion, and therefore, present a distribution of the net charge among the polymer chains that occurs even when the whole system of chains is, on average, neutral. This charge distribution considerably affects the solution properties of polyampholytes, as shown theoretically [33] and experimentally [20, 34].

Cetyltrimethylammonium bromide (CTAB) was obtained from Fluka in high purity grade, and used

Table 1 Polyampholyte nomenclature and average compositions

Polyampholyte nomenclature	Acrylamide mol%	NaAMPS mol%	MADQUAT mol%
80/12/08	80	12	8
80/08/12	80	8	12
80/20	0	80	20
50/50	0	50	50

without further purification. Tetradecyltrimethylammonium bromide (TTAB) was obtained from Sigma-Aldrich and recrystallised three times from ethanol. Sodium dodecylsulphate (SDS) was obtained from Sigma-Aldrich and used without further purification.

Methods

All measurements were performed at a temperature of 25 °C (except for CTAB, temperature 35 °C).

The sample preparation methods used for the various experiments were dependent upon the polyampholyte used. For the water-soluble polyampholyte (80/20) and for those that were 'partially soluble' (80/08/12 and 80/12/08), a stock sample was prepared at a given weight/weight percentage in water. Stock solution (1 ml) was placed in a container, and water/aqueous surfactant solution added to give 2 ml of sample with the desired polymer and surfactant concentrations. For the 50/50 samples, which are totally water-insoluble, a known mass of polymer was weighed into a container and then solvent/aqueous surfactant solution added. All samples were prepared in water from a Millipore RO/Milli RQ system with a resistance of ~18 MΩ.

Conductivity measurements were performed on all the systems investigated using a Wayne Kerr B905 automatic precision bridge, with a Tacussel conductivity cell, at 1 kHz. The bromide ion studies used a solid-state bromide ion-specific electrode (Orion Research, model 94-35 A) together with a double-junction reference electrode, supplied with 90-00-02 inner filling solution and 10% KNO_3 outer filling solution. A CTA^+ or TTA^+ ion-specific electrode membrane was prepared by plasticisation of poly(vinylchloride) (PVC) [19, 35], and the membrane was then adhered to an electrode body fabricated from a PVC tube, using PVC/tetrahydrofuran as an adhesive. The surfactant electrode half-cell contained a solution of the surfactant of interest as an internal reference (at about half the CMC value, in 10 mM KBr), and a calomel electrode was used as a constant reference. All electrodes were connected through an electrode switch (Orion Research, Model 607) to a digital ionalyzer (Orion Research, Model 701 A), enabling selection of the required combination of measuring and reference electrodes.

It was hard to construct a dodecylsulphate ion (DS^-) membrane electrode suitable for use over the wide SDS concentration range used. Although examples of such electrodes exist in the literature [36, 37], none were particularly suitable here since either the working range was too narrow (electrode becomes inoperable below 0.6 mM or above the CMC), and/or not reproducible for the same experiment, or they simply failed to respond suitably to changes in DS^- concentration.

Recall that the Nernst equation relates the measured potential, E, to the activity of the free ion, a, according to the equation $E = E^\circ - S \log a$, where E° is the constant reference potential, and S is the Nernstian slope [59 mV per decade of ion concentration (mV/dec) at 25 °C].

Results

All figures are plotted as a function of added surfactant concentration, denoted by c_x where x is either s, c, or t corresponding to SDS, CTAB, or TTAB, respectively.

Partially charged polyampholytes

Solubility

The polyampholyte 80/08/12 is insoluble in water, but it swells to form a hydrated globule. Solubilisation occurs in the presence of a sufficient quantity of SDS or CTAB. The required amount ($c_{x,sol}$) is proportional to the polymer concentration, as shown for the 80/08/12-surfactant system in Table 2. Note that $c_{x,sol}$ for CTAB

Table 2 Concentration of surfactant required to fully solubilise the polyampholytes ($c_{x,sol}$), and where changes of slope occur in conductivity ($c_{x,K}$), bromide ($c_{x,Br}$) and surfactant ($c_{x,surfactant}$) electrode potential for a given polymer content (c_p)

Polyampholyte	Surfactant	c_p (wt%)	$c_{x,sol}$ (mM)	$c_{x,K}$ (mM)	$c_{x,Br}$ (mM)	Slope (Br) (mV/dec)[(a)]	$c_{x,\text{surfactant}}$ (mM)	Slope (x) (mV/dec)[a]
80/08/12	SDS	1	20	2; 25	–	–	–	–
		2	40	50	–	–	–	–
	CTAB	0.5	20	0.5; 20	20	−58 (−35)	20	15 (−30)
		1	40	2; 40	40	−61 (−30)	–	–
		2	80	80	80	−59 (−32)	–	–
80/12/08	TTAB	0.005	0.7	3.5	4	−60 (−32)	3.5	52 (−26)
		0.05	3	5	5	−60 (−32)	6.5	48 (−26)
		0.5	10	0.5; 10	9	−60 (−33)	9	43 (−26)

[a] Values of the slope in a plot of bromide or surfactant electrode potential as a function of added surfactant, x. The values in parentheses correspond to the slope at high surfactant concentration

is almost twice that of SDS for a given polyampholyte content. This description of solubilisation is quantified in Figs. 1 and 2, which show plots of the volume fraction of non-solubilised material, ϕ_f (i.e. material that may be swollen/hydrated but remains insoluble), against the added surfactant concentration for the 80/08/12-SDS and 80/08/12-CTAB systems, respectively. The 80/08/12-SDS system (net charge-attractive polymer-surfactant interactions) shows a gradual decrease in ϕ_f, extending over a very large concentration range. For the 80/08/12-CTAB system (net charge-repulsive interactions) the change of ϕ_f with c_c is much steeper.

The system 80/12/08-TTAB (net-charge attractive interactions) has been investigated at lower polymer concentrations (c_p) than the other two systems (Table 2). At very low c_p, $c_{t,sol}$ is not proportional to c_p. This may be the result of the large errors that affect $c_{x,sol}$ owing to the difficulties in estimating the surfactant concentration at which the polymer is solubilised. Note that some separation occurs for the 80/08/12-CTAB and TTAB systems when samples remain undisturbed for several weeks, although the amount of precipitated material is too small to be measured accurately. The value for ϕ_f is therefore given as zero for these samples.

Conductivity

The plots usually show two or three linear regions of differing slopes, and a typical example is given in Fig. 3. Table 2 lists the surfactant concentration, $c_{x,K}$, at which a change occurs in the slope of a conductivity against c_x plot. For a given increase in c_p, there is an equivalent increase in $c_{x,K}$, at which the second change in slope occurs, similarly to $c_{x,sol}$. Furthermore, the values of $c_{x,sol}$ are rather close to those where the conductivity plots show the second change of slope (see Table 2).

Bromide ion concentration

Figure 4 shows the electrode potential, E, of a bromide ion-specific electrode for the 80/12/08-TTAB system. The plots in Fig. 4 are similar to those found for polymer-free surfactant solutions [19], showing two regions. Table 2 lists the concentration, $c_{x,Br}$, at which the slope changes between these two regions, and the values of the slopes. In the low surfactant concentration range, all plots have a Nernstian slope of −59 ± 1 mV/dec, indicating no binding of bromide ions. The decrease

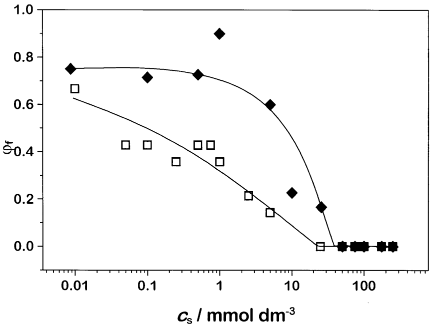

Fig. 1 The approximate volume of non-solubilised 80/08/12, ϕ_f, as a function of added Sodium dodecysulphate (SDS) concentration at differing c_p; c_p = □ 1 wt%, ◆ 2 wt%

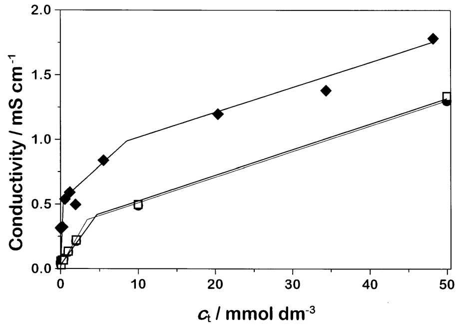

Fig. 3 Conductivity of 80/12/08-Tetradecyltrimethylammonium bromide (TTAB) systems at differing c_p as a function of added TTAB concentration, c_t; c_p = ● 0.005 wt%, □ 0.05 wt%, ◆ 0.5 wt%

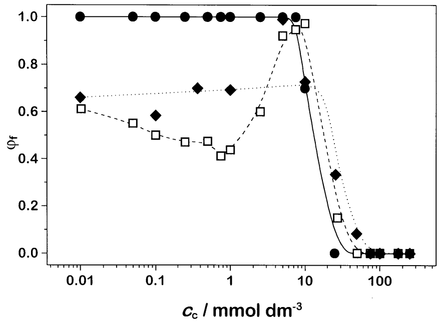

Fig. 2 The approximate volume of non-solubilised 80/08/12, ϕ_f, as a function of added Cetyltrimethylammonium bromide (CTAB) concentration at differing c_p; c_p = ● 0.5 wt%, □ 1 wt%, ◆ 2 wt%

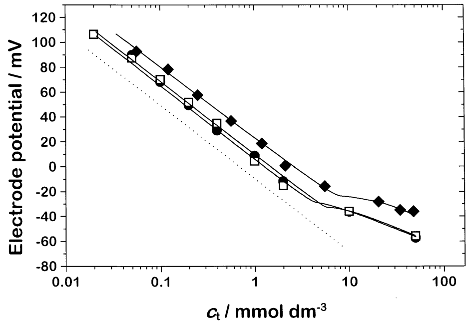

Fig. 4 Bromide electrode potential of 80/12/08-TTAB systems at differing c_p as a function of added TTAB concentration, c_t; c_p = ● 0.005 wt%, □ 0.05 wt%, ◆ 0.5 wt%, theoretical Nernstian slope (*dotted line*)

of slope at higher c_x indicates bromide ion binding. For both TTAB and CTAB, the values of $c_{x,Br}$ are higher than their CMC values in water (CMC values of 3.5 mM and 0.9 mM, respectively) and are close to those where the polymer is solubilised (a relatively large error in the determination of $c_{x,sol}$, $c_{x,K}$, and $c_{x,Br}$ may be anticipated due to the non-monophasic character of the systems studied). The only exception is the 80/12/08-TTAB system at the lowest polymer content. In this system, full solubilisation is achieved at a concentration lower than the CMC of TTAB, and $c_{t,Br}$ is found to be close to the CMC of TTAB in the absence of polymer. Furthermore, $c_{t,Br}$ increases with c_p.

Surfactant electrode studies

The results for the 80/12/08-TTAB system at differing polymer contents are presented in Fig. 5. The plots show two linear regions with a change from a positive to a negative slope, as seen in polymer-free surfactant systems [19]. The change of slope occurs at a concentration that can be considered as the effective CMC (CMC_{eff}) of TTAB in the presence of the oppositely charged polymer 80/12/08. For a polymer content of 0.005 wt%, the results indicate a CMC_{eff} value of 3.5 mM, i.e. equal to the CMC of TTAB in the absence of polymer. However, the slope of the plot at $c_t < CMC_{eff}$ is 52 mV/dec, a value that is less than expected for Nernstian behaviour. The value of the slope decreases further to 48 mV/dec at $c_p = 0.05$ wt%, and 43 mV/dec at $c_p = 0.5$ wt%. This reveals that a fraction of the added TTAB binds to the polymer at all c_t values below CMC_{eff}. Experiments on other systems also show that an appreciable binding may occur at concentrations below the CAC [22, 24, 25].

Unfortunately, there are no results of the surfactant ion activity for the 80/08/12-SDS system (or any of the other systems containing SDS) due to the unavailability of a reliable dodecylsulphate ion-specific electrode membrane (see Methods). Nevertheless, we may infer binding of SDS to the polyampholyte from the changes in ϕ_f and the corresponding changes in conductivity.

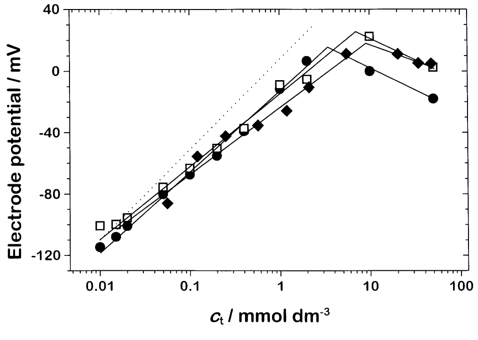

Fig. 5 TTA^+ surfactant ion-specific electrode potential of 80/12/08-TTAB systems at differing c_p as a function of added TTAB concentration, c_t; c_p = ● 0.005 wt%, □ 0.05 wt%, ◆ 0.5 wt%, theoretical Nernstian slope (*dotted line*)

Fully charged polyampholytes

Solubility

The differing solubility of the 80/20 and 50/50 polyampholytes in water highlights the effect of the polyampholyte/polyelectrolyte behaviour of these polymers. Polyampholyte 80/20 is fully soluble in water due to the excess of negative charge and, hence, polyelectrolyte characteristics. In contrast, the polyampholyte 50/50 is insoluble in water. This is due to dominant polyampholyte behaviour where attractions between segments of opposing charge induce a collapse of the polyampholyte chain.

The interactions of the 80/20 and 50/50 polyampholytes with surfactants show differing behaviour. At low TTAB concentration, the 80/20 polyampholyte remains solubilised. Above a given c_t, that is polymer content-dependent, precipitation of the polyampholyte occurs. For the 50/50-surfactant system, two phases exist at low c_x: a clear phase, presumably the aqueous surfactant solution, and a 'powder' phase which is the undissolved polyampholyte. For 0.5 wt% 50/50-TTAB, ϕ_f increases to a constant value of 1. For the 0.5 wt% 50/50-SDS system, two phases remain until the c_s=50 mM at which concentration the polyampholyte is solubilised. The differing solubility behaviour of 50/50 with TTAB and SDS is shown in Fig. 6. Note that for $c_x < 1$ mM in both systems, the value of ϕ_f is given as zero. However, in this low c_x range, the system contains non-solubilised polyampholyte. The value is given as zero since polyampholyte swelling does not occur ('powder' phase), and therefore, ϕ_f is very small. For SDS, swelling occurs in the c_s range between 1 and 10 mM before dispersion and solubilisation.

Conductivity

For the 80/20-TTAB system, two changes in the slope of the plot of conductivity against c_t are observed for 80/20 contents of 0.05 and 0.5 wt%, but only one change for the 0.005 wt% system, as shown in Table 3. The value of $c_{t,K}$ at the second change of slope is shifted to higher concentrations as the polyampholyte content is increased. The first change of slope occurs at a surfactant concentration very close to $c_{t,ppt}$, where the polymer/surfactant complex precipitates (see Table 3), and is thus probably reflecting this effect. Note that precipitation occurs at a lower concentration as the polymer content is increased, as for the c_t value corresponding to the first change of slope. The first change of slope was not observed for the 80/20 content of 0.005 wt%, probably because the effect associated with such a low polymer concentration was too small to be measured.

Bromide ion electrode

Figures 7 and 8 show plots of the bromide electrode potential for differing 80/20 and 50/50 contents as a function of the TTAB concentration, c_t. The results for the two systems are very similar. All plots show a change of slope at a TTAB concentration, $c_{t,Br}$, that increases with c_p. For both systems, at the lowest polymer content, the $c_{t,Br}$ value of 3.5 mM is equal to the CMC of TTAB in the absence of polymer; the slope of all plots below $c_{t,Br}$ is close to the Nernstian one. As the 80/20 content is increased from 0.005 wt% to 0.05 wt% and then 0.5 wt%, $c_{t,Br}$ shifts from 3.5 to 6 and then 10 mM. These values are very close to those of $c_{t,K}$ at which the second change of slope occurs in the conductivity plots (see Table 3). The increase of $c_{t,Br}$ is less significant for 50/50, increasing from 3 to 7 mM as the polymer content is increased from 0.1 wt% to 0.5 wt%

Surfactant electrode

The results for the 80/20-TTAB and 50/50-TTAB systems show some similarities and also some important differences, shown in Figs. 9 and 10. All the plots change from a positive to a negative slope, that is ascribed to micelle formation in solution, and enables determination of $\mathrm{CMC_{eff}}$. For the 50/50-TTAB system, the slope of the plot below $\mathrm{CMC_{eff}}$ is Nernstian at 0.1 wt% and slightly less than Nernstian at 0.5 wt%, indicating weak non-cooperative binding of TTAB to this statistically neutral polymer. The $\mathrm{CMC_{eff}}$ appears to increase from 4.5 to 8.5 mM as the 50/50 content is increased from 0.1 to 0.5 wt%.

The behaviour of the 80/20-TTAB system is more complex. For the lowest content of 0.005 wt%, a slope of 6 mV/dec at low c_t is indicative of strong cooperative binding. Indeed, the constancy of the electrode potential with increasing c_t implies the binding of all the $\mathrm{TTA^+}$ added. This low slope is followed by a concentration range with a slope that is much larger than the Nernstian value (super-Nernstian) prior to reaching the $\mathrm{CMC_{eff}}$. In this cooperative binding range, the surfactant binds to the polymer as aggregates. The results for the higher 80/20 contents of 0.05 wt% and 0.5 wt% are even more complex. At very low c_t, the behaviour described for the 0.005 wt% content is preceded by a range with a small slope, indicating quantitatively important binding that is qualitatively either weakly coperative or non-cooperative. This range is probably too narrow to be observed in the 0.005 wt% system. Note, the slope for the 0.005 wt% system is close to Nernstian at higher c_t (between 0.6 and 4 mM, i.e. below the $\mathrm{CMC_{eff}}$). This range is not observed with higher 80/20 contents, and

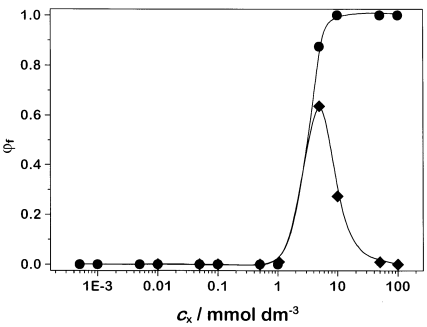

Fig. 6 Approximate volume fraction of non-solubilised material for 0.5 wt% 50/50 in the presence of either ● TTAB or ◆ SDS

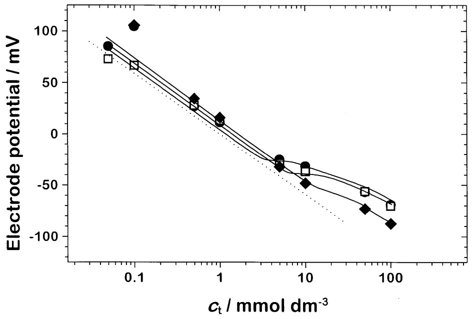

Fig. 7 Bromide electrode potential for the 80/20-TTAB system with differing polyampholyte contents; c_p = ● 0.005 wt%, □ 0.05 wt%, ◆ 0.5 wt%, theoretical Nernstian slope (*dotted line*)

Table 3 Concentration of TTAB required to precipitate the 80/20 polyampholyte ($c_{t,ppt}$), where changes of slope occur in conductivity ($c_{x,K}$) and bromide electrode potential ($c_{x,Br}$) plots (with the slopes for the bromide electrode potential), and the effective CMC ($\mathrm{CMC_{eff}}$) in the presence of 80/20 for a given polymer content (c_p)

System	c_p (wt%)	$c_{t,ppt}$ (mM)	$c_{t,K}$ (mM)	$c_{x,Br}$ (mM)	Slope (mV/dec)[a]	$\mathrm{CMC_{eff}}$ (mM)
80/20-TTAB	0.005	–	3	3.5	−59 (−37)	4
	0.05	0.5	0.8; 5	6	−59 (−37)	10
	0.5	0.2	0.2; 10	10	−59 (−38)	30

[a] The values in parentheses correspond to the slope at high surfactant concentration

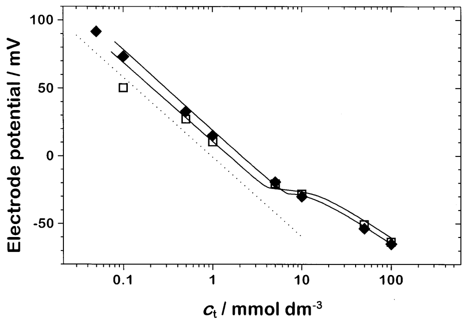

Fig. 8 Bromide electrode potential for the 50/50-TTAB system with differing polyampholyte contents; c_p = ☐ 0.1 wt%, ◆ 0.5 wt%, theoretical Nernstian slope (*dotted line*)

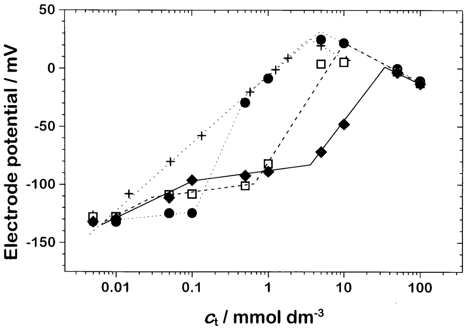

Fig. 10 TTA$^+$ surfactant ion-specific electrode potential for the 80/20-TTAB system with differing polyampholyte contents; + no polyampholyte (reference), c_p = ● 0.005 wt%, ☐ 0.05 wt%, ◆ 0.5 wt%

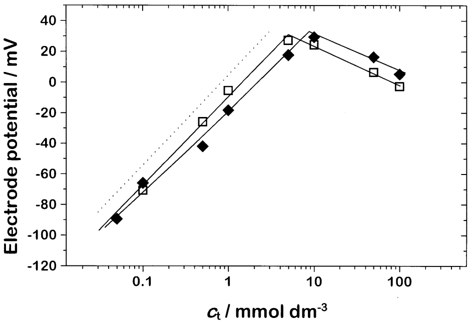

Fig. 9 TTA$^+$ surfactant ion-specific electrode potential for the 50/50-TTAB system with differing polyampholyte contents; c_p = ☐ 0.1 wt%, ◆ 0.5 wt%, theoretical Nernstian slope (*dotted line*)

the CMC$_{\mathrm{eff}}$ is slightly above the limit of the super-Nernstian range.

The results for the 80/20-TTAB systems are very similar to those found for the binding of charged surfactants to polyelectrolytes of opposing charge [13, 14, 19]. It can be seen that the linear part of the three plots at the lowest surfactant concentration invariably intercepts the reference plot (E vs c_t in the absence of polymer) at a c_t of 7 μM. This value represents the CAC of the 80/20-TTAB system and is 500 times lower than the CMC of TTAB in water. This CAC is relatively independent of polymer concentration, as for other polyelectrolyte-surfactant systems of opposite charge [19, 38]. For the 0.5 wt% system, the concentration of negative charges not compensated by positive ones can be calculated to be around 15 mM. Assuming a CMC$_{\mathrm{eff}}$ value of 30 mM, there are approximately two bound TTA$^+$ per non-compensated negative charge. This result, together with the existence of 80/20-bound surfactant aggregates at $c_{t,\mathrm{Br}}$ < CMC$_{\mathrm{eff}}$, explains that some bromide ions bind to the aggregates before free micelles appear in the system. As a consequence, a change of slope is observed in the bromide electrode plot at a c_t < CMC$_{\mathrm{eff}}$, Fig. 7. The effect, if it exists, is much smaller for the 50/50-TTAB system. However, it must again be emphasised that the values of CMC$_{\mathrm{eff}}$ and of $c_{t,\mathrm{Br}}$ may be influenced by large errors due to the complexity (non-homogeneity) of the system. The differences between the values of CMC$_{\mathrm{eff}}$ and of $c_{t,\mathrm{Br}}$ for the 50/50-TTAB system are within the experimental error.

Discussion

This section considers solubilisation, precipitation and swelling aspects, and compares the behaviour of polyampholytes and polyelectrolytes.

Partially charged polyampholytes

The main results obtained for the 80/08/12-SDS, 80/08/12-CTAB, and 80/12/08-TTAB systems are briefly recalled here:

1. The anionic and cationic surfactants used are able to solubilise the polyampholytes investigated, even when polymer and surfactant are of similar effective charge.
2. The surfactant concentration for polymer solubilisation, $c_{x,\mathrm{sol}}$, is proportional to the polymer concentration at $c_p \geq 0.5$ wt%. $c_{x,\mathrm{sol}}$ is generally larger than the CMC of the surfactant for polymer-free solutions. Also, $c_{x,\mathrm{sol}}$ is larger when the polymer and the surfactant are of like charge than when they are of opposite charge, presumably since electrostatic repulsions decrease the amount of bound surfactant.
3. For the systems investigated, a change of slope in the conductivity plots occurs at a concentration $c_{x,K}$, which is close to $c_{x,\mathrm{sol}}$.
4. The surfactant (TTA$^+$, CTA$^+$) and bromide ion-specific electrode potential data show a change of slope at a similar concentration, $c_{x,\mathrm{Br}}$, which is close to $c_{x,\mathrm{sol}}$ and $c_{x,K}$, and can be considered as the CMC$_{\mathrm{eff}}$ of the

surfactant in the presence of polymer. This concentration increases with c_p, and at low c_p is close to the surfactant CMC for polymer-free solutions.

5. The bromide electrode potential data indicate no bromide ion binding up to $c_{x,Br}$, whereas the surfactant electrode potential data reveal that the TTA^+ surfactant ions start binding non-cooperatively to the polymer at very low surfactant concentrations (80/12/08-TTAB system).

Points 4 and 5 indicate that the TTA^+ ions bind individually, or as very small aggregates, to the oppositely charged 80/12/08; binding is non-cooperative, or weakly cooperative, and not accompanied by bromide ion binding. This binding eventually results in the solubilisation of the polyampholyte at a surfactant concentration higher than the CMC of TTAB in polymer-free systems (points 1–3) and close to the CMC_{eff}.

The difference between the CMC_{eff} and the CMC in polymer-free systems can be considered as the amount of surfactant bound. At this stage, it is interesting to compare the concentration of bound surfactant ions (TTA^+) to the concentration of negatively charged groups in 80/12/08. For $c_p = 0.5$ wt%, using an average molecular weight for each repeat unit of 120, the latter concentration (NaAMPS) is found to be 5 mM. This value is close to CMC_{eff}-$CMC = 9 - 3.5 = 5.5$ mM. For $c_p = 0.05$ wt% and 0.005 wt%, the concentrations of negatively charged groups are 0.5 and 0.05 mM, respectively. These values can be compared to CMC_{eff}-CMC values of 2.5 mM and 0 mM. The errors in all these numbers are large, but the agreement can be considered as satisfactory. This approach provides an immediate explanation to the proportionality between c_p and $c_{x,sol}$.

Note that once the polymer is saturated with TTA^+ ions, all of its negative charge is neutralised, but it remains charged since its positive charges are not compensated. This explains its solubilisation. The same mechanism is probably operative in the symmetric 80/08/12-SDS system. In the 80/08/12-CTAB system where polymer and surfactant are of like effective charge, this mechanism is still operative. However, polymer solubilisation is expected to occur at higher surfactant concentration, because CTAB has to overcome the electrostatic repulsion exerted by the polymer 80/08/12 before becoming bound, as observed experimentally (point 2).

The solubilisation of 80/08/12 by CTAB as well as the conductivity and bromide electrode data show that interaction (binding) is taking place. The interaction of a charged polyampholyte with another similarly charged species has been discussed experimentally [39, 40] and theoretically [41, 42]. A recent theoretical study [42] predicts that a polyampholyte chain may adsorb onto a sphere with a similar net charge in the absence of salt, leading to so-called 'super-stable complexes' (particles that have an increased effective charge following adsorption). This effect may account for the swelling of the precipitated phase, and eventual solubilisation, of a polyampholyte-surfactant system with similar net electrical charges.

ϕ_f shows a similar trend for both SDS and CTAB in the presence of 80/08/12, however the rate at which the decrease in ϕ_f occurs is much higher for CTAB than for SDS. This may be an indication of the net electrical repulsion/attraction between the polyampholyte chain and the surfactant. For SDS this is a net attractive force, whilst for CTAB it is repulsive. An increase in ϕ_f for both CTAB and SDS may be a consequence of swelling, caused by the repulsion of small adsorbed surfactant aggregates. It is also interesting that for the 80/08/12-CTAB system, the bromide ion-specific electrode does not appear to detect the aggregation of surfactant onto the polyampholyte chain. This behaviour is similar to that noted for the interaction between polymers and surfactants of opposite charge, where the polyelectrolyte segments essentially compensate the surfactant aggregate [38].

At this stage it is interesting to compare the effect of surfactants on the behaviour of true polyelectrolytes (one type of charge) to that of the partially charged polyampholytes used here. Addition of an ionic surfactant to a solution of an oppositely charged true polyelectrolyte results in the precipitation of a stoichiometric polyelectrolyte/surfactant complex, even at relatively low surfactant concentration. Such studies are always carried out at low polyelectrolyte concentration [19] since polyelectrolyte solubility is lost through charge neutralisation. On the contrary, no binding is observed when surfactant and polyelectrolyte are of like charge. With partially charged polyampholytes, interactions occur with both anionic and cationic surfactants and result in solubilisation, via neutralisation of one type of charge by the added surfactant. The remaining non-neutralised charges confer a polyelectrolyte character to the polyampholyte, ensuring its solubilisation. These observations suggest that the insolubility of the partially charged polyampholyte in the absence of surfactant is the result of strong interactions between its positively and negatively charged groups [43]. Note that insoluble polyampholytes such as 80/12/08 or 80/08/12 become soluble in the presence of a large excess of salt, e.g. 0.25 M NaCl [39, 44], due to the screening of these attractions by the added salt. Solubilisation is achieved at much lower concentrations with surfactant suggesting that hydrophobic interactions are probably involved.

Fully charged polyampholytes

The differing solubility of 80/20 and 50/50 in water, in the absence of any additives, is due to the competing polyelectrolyte/polyampholyte effects of these polymers

[20]. Briefly, with the polyelectrolyte effect there is strong repulsion between similarly charged monomers leading to highly swollen, stretched chains and solubilisation. In contrast, the polyampholyte effect is the attraction between oppositely charged monomers leading to chain collapse, with the effect that polyampholyte globules show reduced solubility and usually form a precipitated phase.

The behaviour of the 80/20 and 50/50 polyampholytes in the presence of differing surfactants show important dissimilarities. Clearly these arise from the essentially polyelectrolyte behaviour of 80/20 (high charge density), whereas 50/50 is a pure polyampholyte with a statistical compensation of the positive and negative charges. In the same way as for polyelectrolytes, the CAC of the opposingly charged 80/20-TTAB surfactant system is very low and binding occurs cooperatively. After the precipitation of 80/20-TTAB complexes, possible resolubilisation of these complexes at increased c_t, as observed for other polyelectrolyte-surfactant systems [45], did not occur.

In Fig. 10, which shows the TTA^+ electrode potential for the 80/20-TTAB system, each plot shows a number of changes of slope which, in the order of increasing c_t, correspond to the CAC, the limit of non-cooperative binding, the end of cooperative binding, and the formation of free micelles in the system. Using the corresponding concentrations, a schematic phase diagram that shows the state of the system, both as a function of surfactant and polyampholyte concentration, is given in Fig. 11. The solid lines passing through the experimental data delineate various domains. Domain A corresponds to systems where the surfactant binds non-cooperatively, or with low cooperativity, to charged sites on the polymer, as either individual ions or small aggregates. In domain B, surfactant binding is strongly cooperative, the surfactant is in the form of aggregates, and the concentration of free surfactant varies little. Binding continues in domain C, though the amount of free surfactant now increases (super-Nernstian range). In domain D, the polymer is saturated by aggregates of bound surfactant, which coexist with free surfactant micelles and free surfactant ions. Lastly, domain E represents a range existing only at very low polymer concentrations, and corresponds to polymer saturated by bound surfactant aggregates, in equilibrium with free surfactant ions only, with no micelles in solution.

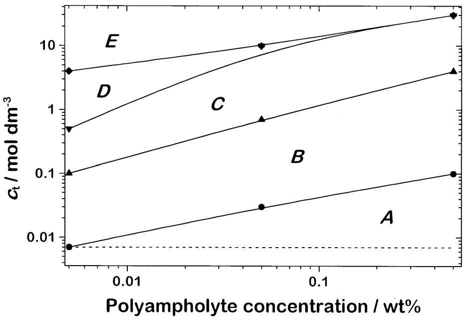

Fig. 11 The proposed binding regions for the 80/20-TTAB system (see text for explanation of boundaries and regions). The dashed line represents the critical aggregation concentration of this system

The interaction of the 50/50 sample with TTAB is very weak, resulting in some swelling of the polymer in the presence of water and a small amount of bound surfactant. On the contrary, SDS brings about a full solubilisation of 50/50. These results are similar to those for neutral water-soluble polymer/charged surfactant systems, where an interaction (binding) is usually observed with anionic surfactants and no, or only very weak, interaction occurs with cationic surfactants. However, binding of anionic surfactant to such polymers is cooperative, contrary to that for 50/50. Note that 1 M NaCl is required for the solubilisation of 50/50 [27].

Possible explanations for the differing solubilities of the 50/50-surfactant systems are (1) a difference in the binding mechanism, (2) the differing solubility of the chain components that remain exposed to the solvent (the solubility of the NaAMPS and MADQUAT constituents differ in water), or (3) solvent quality for the polyampholyte-surfactant complex [46]. The net charge and microstructure of the polyampholyte [34] are paramount in determining which of these possibilities occur. For polyampholytes with a net charge, the chain conformation results from the competition between the polyelectrolyte effect, that expands the coil dimensions, and the polyampholyte effect that induces collapse [27, 43]. Since these samples are dialysed, the polyampholytes also tend to self-neutralise [27] and the surfactant requires the thermal fluctuations of the chain to expose suitable binding sites. Furthermore, the net charge distribution can vary from chain to chain [34] with the cooperativity of surfactant binding increasing with an increased charge density [47].

Conclusions

The partially charged polyampholytes 80/12/08 and 80/08/12, which swell in water, are solubilised in the presence of cationic and anionic surfactants at concentrations above a surfactant concentration that is proportional to the polymer concentration. Solubilisation results from the non-cooperative binding of surfactant ions to the oppositely charged groups of the polyampholyte. This binding turns the polyampholyte into a water-soluble, low-charge density polyelectrolyte.

The polyampholyte 80/20 is soluble in water but precipitates out in the presence of TTAB. Surfactant ion-specific electrode data show that, after an initial binding range that is of low cooperativity, the binding of TTAB to 80/20 is strongly cooperative. The bound surfactant is therefore in the form of aggregates. The electrode potential data also show the existence of a CAC that is very low (about 7 μM). Thus in the context of surfactant-induced precipitation and surfactant binding, 80/20 behaves like a strongly charged polyelectrolyte. A phase diagram for the 80/20-TTAB system was constructed from the surfactant electrode data, showing the various types of systems present at various polyelectrolyte and surfactant concentrations.

The polyampholyte 50/50 is insoluble in water and remains so in the presence of TTAB, but it is solubilised upon addition of SDS, suggesting binding of this surfactant. The TTA^+ electrode potential data reveal a weak and non-cooperative binding of TTAB. Overall the 50/50 polymer which has an average global charge of zero, appears to behave like a neutral water-soluble polymer, such as polyoxyethylene or polyvinylpyrrolidone, in the presence of surfactants.

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