Photochemical determination of the interactions between surfactants and polyelectrolytes

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Abstract: The interaction of polyelectrolytes with oppositely charged ionic surfactants was studied at low surfactant concentrations using photochemical bound and free probes. Free probes migrate to initially formed pre-aggregates in systems with high charge-density polyelectrolytes, giving rise to excimer emission. For these systems the initial aggregation process seems to be due to electrostatic interactions. For larger surfactants or copolymers containing larger proportions of neutral monomer that interactions are of hydrophobic nature.

INTRODUCTION

Photochemical methods are used extensively in the study of microheterogeneous systems (ref. 1). Many compounds present different behaviour depending on the medium in which they are placed. Some probes, specially pyrene and other aromatic molecules, have absorption, emission and lifetimes that depend on the microenvironment around them (ref. 2). These properties can be correlated with the characteristics of the microenvironments and used to predict the existence and peculiarities of the hydrophobic and aqueous domains.

After extensive studies were done on the properties and characteristics of micelles, formed by the spontaneous aggregation of surfactants in aqueous solutions, the attention began to fall on the properties of polymers able to form hydrophobic domains with properties similar to those of classical micelles (ref. 3). Polymers of this type could be obtained by chemical modification of normal polymers, or by copolymerization of monomers with hydrophobic and hydrophilic groups. The hydrophobic domains formed in aqueous solutions of polyelectrolytes can be ascribed to interactions similar to those found in the formation of surfactant micelles, that is, the simultaneous existence of hydrophobic and hydrophilic groups on the chains. This was proved very nicely by the use of photophysical methods on poly(methacrylic acid) polymers, PAA, which presents hydrophobic domains at low pH, that are not present at higher pH when all the carboxylic groups are ionized (ref. 4).

A further development of these investigations was the study of systems involving polyelectrolytes and ionic surfactants. It was found, initially by Abuin and Scaiano (ref. 5) that these systems also formed hydrophobic domains, but the clusters so formed differed from the micelles formed in homogeneous aqueous solution in the sense that they began to form at concentrations much lower that the cmc of the surfactants, and the aggregation numbers were also smaller. These effects were correlated to the fact that the polyelectrolyte acts as a pattern for the aggregation of the surfactant, *i.e.*, the surfactant molecules are attracted electrostatically by the opposite charged groups of the polyelectrolytes. This results in a decrease of the repulsive interaction between the surfactant heads, facilitating their aggregation. Various investigations were performed on systems where the concentration of surfactant was similar to that of the charged groups on the polymer chain. In that region many of these systems start forming a second macroscopic phase and eventually precipitate. The properties of the systems in that concentration range were extensively studied concerning the influence of the charge density on the polymers, chain-length of the surfactant, effect of added salts and counterions, etc. (ref. 6). On the other hand, not much work was done on systems with concentrations of surfactants lower than that needed for charge equilibrium.
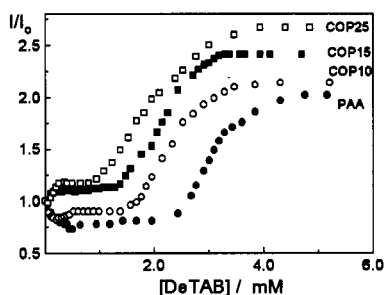
Figure 1. Fluorescence intensities of pyrene in PAA copolymers in the presence of DeTAB
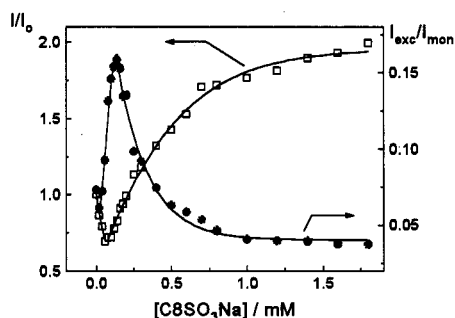
Figure 2. Fluorescence intensity and excimer to monomer ratio for pyrene in PALA in the presence of $C8SO_3Na$

DISCUSSION

Pre-aggregates. In a recent work (ref. 7) we monitored the behaviour of the emission intensity of pyrene in the presence of PAA, when a cationic surfactant was added to it (Figure 1). At very low surfactant concentration, even before the CAC was reached, an initial decrease of the intensity was found. This decrease was concomitant with an increase in the excimer emission. A similar behaviour was observed when a C8 anionic surfactant was added to poly(allylamine chloride), PALA (Figure 2). Therefore, it was assumed that at these low concentrations, a relatively small amount of pre-aggregates with hydrophobic characteristics was formed, as depicted in Scheme I.

These pre-aggregates, due to their hydrophobicity, attract pyrene molecules which when present in pairs (or higher occupancies) will reduce the monomer emission in favour of the excimer (dimer) emission. There is a clear correlation between the decrease in the monomer fluorescence and the increase in the excimer emission, as shown in Figure 2. Upon addition of further amounts of detergent, the fluorescence increased again to a plateau for a certain concentration interval, and then increased sharply again at the concentrations considered to be the CAC. Although in some earlier work the decrease of the emission intensity was attributed to fluorescence quenching by the Br^- counter-ions (ref. 5), the same effect was found when using the chlorine salt of the detergent. Quenching by a possible higher concentration of solubilized oxygen can also be ruled out because no difference was found between air-equilibrated and degassed solutions. This hypothesis of probe migration is confirmed analyzing the emission of bound and free anthracene used as probe for the behaviour poly(methacrylic acid), PMA, in the presence of decyltrimethylammonium bromide, DeTAB, as can be seen in Figure 3.

⊖ = charged monomer
● = probe
⊕⌇⌇⌇ = surfactant
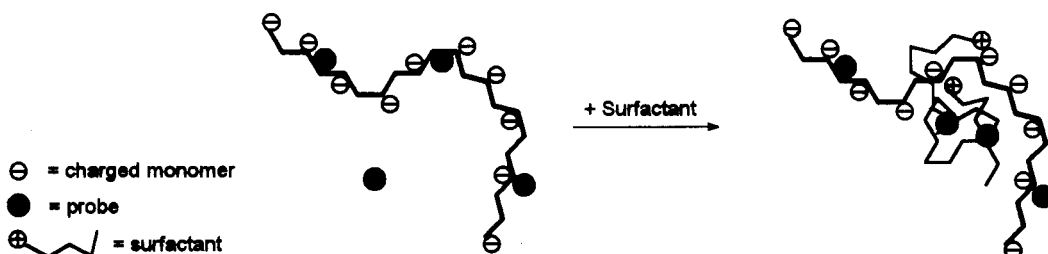
+ Surfactant

Scheme I

decrease disappeared completely for the copolymers with higher proportions hydrophobic monomers or when surfactants with larger chains were used. That picture suggests that there are two different ways of forming the initial surfactant pre-aggregates on the polymers. For pure PAA and polymers with little amount of hydrophobicity, there would be an initial electrostatic interaction between the surfactant heads and the charges on the polyelectrolyte (See Scheme I). In this way the hydrophobic tails of the surfactants will entangle offering a better hydrophobic medium for the pyrene than the quasi-aqueous environment of the pure polyelectrolyte, inducing their migration to these domains, giving raise to local concentrations sufficiently high to produce excimer emission.

On the other hand, when the polyelectrolyte includes hydrophobic units, the added surfactant molecules will add to the already existing hydrophobic domains, with no alteration of the distribution of the probe (Scheme II). In these cases a small initial increase in the emission intensity is observed, which may be assigned to the increase of the hydrophobicity of the domains due to the presence of the larger surfactant tails.

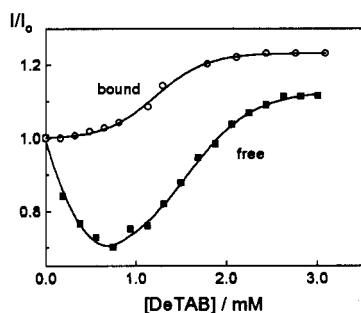● = hydrophobic monomers
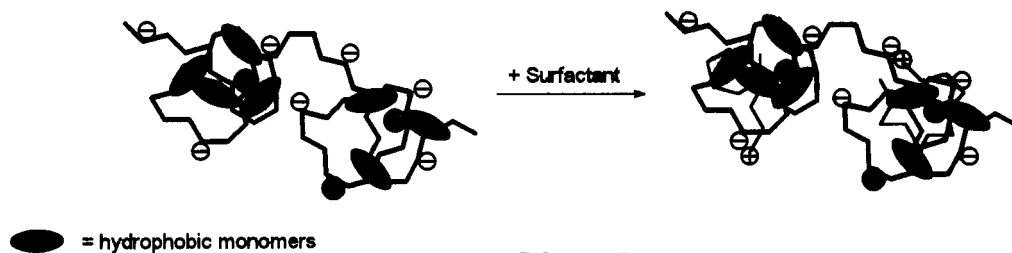
Scheme II

Figure 3. Fluorescence intensities of free 9-Me-anthracene in PMA/DeTAB (■); and anthracene bound to the polymer (O)
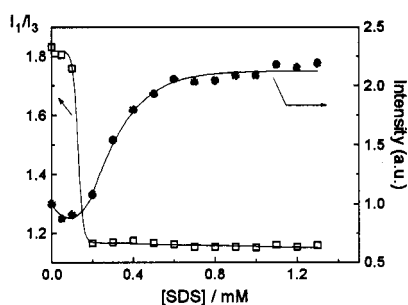
Figure 4. Pyrene fluorescence and I_1/I_3 ratio in the PALA/SDS system.

The use of cationic polyelectrolytes with anionic surfactants presented some interesting effects regarding the behaviour of the probe emission intensity in the low surfactant region, like in the PALA/SDS system (Figure 4), or poly(vinylbenzyltrymethylammonium chloride)/C8SO₃Na (Figure 5). Contrary to what is found in the cases discussed above, there is no plateau between the initial decrease and the subsequent increase due to the formation of the induced micelles. The effect can be traced to the lower critical aggregation concentration and faster growth of the SDS micelles. A hint of this can be obtained from Figure 4, where the I_1/I_3 ratio is plotted together with the emission intensity, evidencing that highly hydrophobic domains are already present at surfactant concentrations where the emission intensity is still lower than in the absence of the surfactant. This result is very important when trying to determine the CAC for these systems. As can be seen, it does not seem to be reasonable to draw those values from the intensity curves when using a free probe. The true CAC values should be determined from the inflection point of the I_1/I_3 curve.

As seen in Figure 6, when adding extra salt to the polyelectrolyte / surfactant systems, the minimum displaces to higher surfactant concentrations and its depth increases. Two effects are concurrent to this behaviour. On one side, the increase in the ionic strength will decrease the electrostatic interactions between the opposite charges of the polyelectrolyte and the surfactant, shifting the formation of pre-aggregates to higher surfactant concentrations. On the other hand, increasing the ionic strength also displace the CAC to higher concentrations (ref. 8). This will allow a larger concentration interval between the initial pre-aggregates and the CAC, so that the depth of the minimum may reach a lower value. Considering that for these systems the initial interactions between the polyelectrolyte and the surfactant are of electrostatic nature, the energy associated to this process could be written as

$$\Delta G(SS) + \Delta G(SP),$$

where the first term is positive and represents the interaction between the surfactant heads and the second is the attractive interaction between the surfactant heads and the charges on the polymer. Both these terms
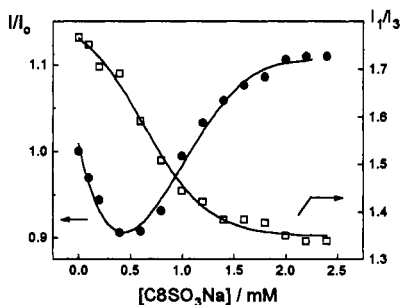
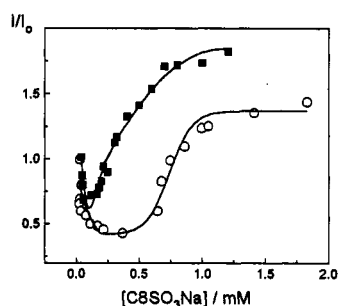**Figure 5.** Pyrene fluorescence and I_1/I_3 ratio in the PVBTA/C8SO3Na system.

Figure 6. Pyrene fluorescence in the PALA/C8SO3Na system in the absence (O) and presence (■) of added NaCl.

will be affected by the addition of salt, but the effect on the second term, which regulates the initial formation of ionic pairs should be more important. On the other hand, if the driving force to form the initial aggregates would be hydrophobic, that term would not be affected by the addition of the salt and the minimum would be displaced to lower surfactant concentrations.

These experiments provide evidence as to the nature of the pre-aggregates formed when adding surfactants to polyelectrolytes. Further work is in progress to determine some of the thermodynamic properties of those pre-aggregates, like the discrimination between the hydrophobic and electrostatic contributions to their formation (obtained from measurements of the CAC using cationic and anionic detergents), and the size of the pre-aggregates (obtained from dynamic quenching of the probes placed in them).

CAC Determination and Effect of Charge Density. As pointed out before, care has to be taken when the CAC of induced micelles is determined from the behaviour of the emission intensity of photochemical probes. Nevertheless, for some systems, like that depicted in Figure 1, the interval between the pre-aggregate formation and the rise due to the formation of large micelles is large enough as to allow the use of those probes. The presence of non charged monomers on the chain displaces the CAC to higher surfactant concentrations as seen in Figure 1. In Table 1 are shown the CAC and aggregation numbers of induced C10TAB micelles in the presence of PAA-EMA copolymers.

The smaller CAC are a result of the facility of forming micelles in the presence of the charges and the neutralization of the electrostatic repulsion between the surfactant heads. Higher EMA content does add to this effect a larger hydrophobic interaction. It is easier to determine the CAC from the fluorescence intensity curves when there are less charges on a copolymer, as in this case the cooperative effects decrease and a steeper increase for the dependence is found, as shown in Figure 7.

CONCLUSIONS

When ionic surfactants are added to polyelectrolytes of opposite charge, small pre-aggregates (30-40 for C10TAB molecules on PAA) are formed at low surfactant concentrations. Free probes will migrate to this probes if the microenvironment they form is hydrophobic enough.

Depending on the size of the detergent chains and the composition of the polyelectrolytes, the first interactions may be of hydrophobic or electrostatic nature.

Critical aggregation concentrations should not be determined from the behaviour of the fluorescence intensity, but by other methods like the I_1/I_3 ratio.

EXPERIMENTAL

Polyelectrolytes were from commercial origin or synthesized by free radical polymerization. The copolymers were obtained by joint polymerization of both monomers using feeding relationships which would assure random distribution of the units in the chain. The contents of charged monomer were determined by acid/base titration. Surfactants and probes were commercial samples and purified by standard methods when required. The polyelectrolyte with bound anthracene was prepared by copolymerizing 9-vinylanthracene with methacrylic acid. The final content of anthracene in the polymer was about 0.5%.

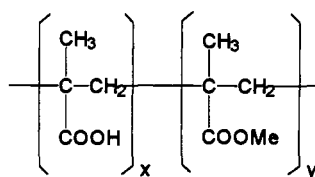**Table 1.** CAC and aggregation numbers of C10TAB
in PAA-EMA copolymers.

Polymer	CAC (mM)	N_{agg}
(C10TAB)	65.0	48
PAA	3.6	120
PAA+10%EMA	2.3	73
PAA+15%EMA	2.1	48
PAA+25%EMA	1.9	42
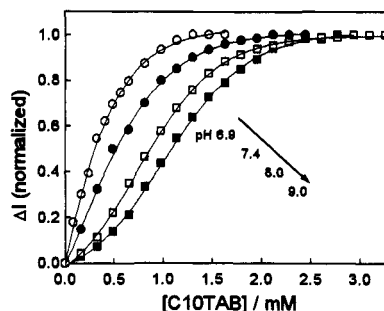
Figure 7. pH dependence of the emission of anthracene bound to PMA-33%MMA
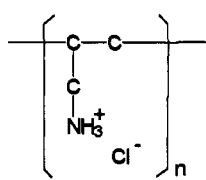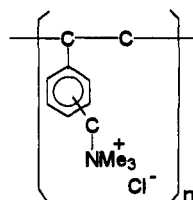
The structures of the copolymers were
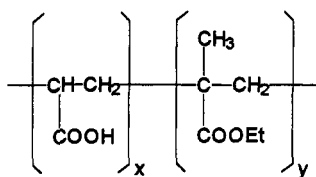
PAA-EMA

PMA-MMA

PALA

PVBTA

All samples were prepared in Millipore-Q water. Concentrations of polymers and copolymers were kept always between 0.5 and 1.0 g/L, and the probes below 5×10^{-6} M. Fluorescence measurements were made on Hitachi F4500 and Aminco-Bowman J8 spectrofluorometers and using the steady state facility of an Edinburgh Instruments CD900 system. The latter was also used for determining the aggregation numbers using single photon counting techniques.

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