Solubilization of phenols in surfactant/polyelectrolyte systems

A.F. Olea and C. Gamboa [*]

Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile

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Abstract

The properties of the microheterogeneous systems formed by mixtures of cetyltrimethylammonium bromide (CTAB) and an alternating copolymer of maleic acid and styrene, MAS, and their anionic monoesters, MAS-n with $n = 2$, 4, 6, 8, were investigated. The fluorescence of pyrene was used to sense the polarity of the polymer/CTAB aggregates. Measurements of the ratio III/I in pyrene fluorescence spectra indicate that the polymer/CTAB aggregates are more hydrophobic than normal micelles. A series of p-alkyl substituted phenols were employed to probe the solubilization ability of these aggregates. The distribution constant K_S of phenol, p-methylphenol, p-ethylphenol, and p-propylphenol between water and MAS-n/CTAB aggregates and the corresponding free energy of transfer $\Delta\mu_t^0$ have been determined using the pseudo-phase model. The results show that the distribution is mainly determined by the phenol structure, and a linear free energy relationship has been found between $\Delta\mu_t^0$ and the structure of phenols. On the other hand, an increase in the number of methylene groups in the side alkyl chain has no effect on $\Delta\mu_t^0$. The results are discussed and compared with those obtained for ionic micelles.

Keywords: Poly(maleic acid-co-styrene); Polyelectrolytes; Cationic surfactant; CTAB; Polymer surfactant interaction; Solubilization

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1. Introduction

Interaction between polyelectrolytes and surfactants carrying opposite charges is a matter of current interest mainly because of the fundamental and technological importance of their mixtures [1–5]. In aqueous solution, surfactant molecules aggregate to form spherical micelles at a critical micelle concentration (cmc) [6]. In the presence of polymer and depending on the surfactant concentration, the systems can be treated as the binding of surfactant molecules to a polyelectrolyte skeleton or the interaction of micelles with the polymer [4,7,8].

It is known that the interaction starts as a cooperative association of monomer surfactant to the polymer chain [9,10], and it has been found that micelle-like clusters are formed at a surfactant concentration known as the critical aggregate concentration (cac) [11]. Often, the cac values are several orders of magnitude lower than the cmc, and further increase of surfactant concentration results in formation of insoluble compounds. Since this interaction is mainly electrostatic its magnitude depends on the ionic strength, the polymer linear charge density, and the micelle surface charge density. To avoid precipitation the last parameter has been adjusted using mixed micelles of nonionic and ionic surfactants [4].

It has been found that complexes formed by dodecyltrimethylammonium bromide (DTAB) and anionic hemiesters of an alternating copolymer of maleic acid and styrene, MAS-n, with $n = 0$–12, show synergism in their interface properties [12,13]. The pseudo-phase separation approach and regular solution approximation have been used to determine the interaction parameter, β, and the mole fraction of DTAB in the adsorbed layer X. The results were discussed in terms of the hydrophobic effect on the distribution of the aggregates between the interface and the bulk of the solution [12].

Since hydrophobic aggregates are formed at the cac, it is expected that they can solubilizate hydrophobic molecules. In the present study, the solubilization of phenols by mixed micelles formed by the interaction of cetyltrimethylammonium bromide, CTAB, with an alternating copolymer of maleic acid and styrene, MAS, and their anionic monoesters, MAS-n with $n = 2$, 4, 6, 8, was investigated. Fluorescence probing has been used to characterize the MAS-n/CTAB aggregates. The measurements of the solubilization of phenols in aqueous solution of MAS-n/CTAB were analyzed using the pseudo-phase model, where the incorporation of a substrate into micelles is treated as a distribution between

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[*] Corresponding author.
E-mail address: cgamboa@abello.dic.uchile.cl (C. Gamboa).

the aqueous phase and the micellar phase [6,14]. With this approach the thermodynamical parameters obtained are the partition coefficient and the standard free energy of transfer, $\Delta\mu_t^0$. Our results were compared to those obtained with CTAB micelles in order to assess the solubilization capacity of these mixed micelles.

2. Experimental

2.1. Materials

Poly(maleic anhydride-co-styrene) (Aldrich) with average molecular weight equal to 350,000 was used as received. The sodium salt of this copolymer, MAS, was obtained by first dissolving the copolymer in a bicarbonate solution, and then dialyzing and lyophilizing these solutions. Anionic monoesters, MAS-n, with $n = 2, 4, 6, 8$ were prepared by hydrolysis of poly(maleic anhydride-co-styrene) with n-alkyl alcohols. Thus, n indicates the number of carbon atoms in the alkyl side chain. The esterification reactions were carried out in tetrahydrofuran solution at 65 °C in the presence of 4-dimethylaminopyridine as catalyst. Alcohols from ethanol to 1-octanol (Aldrich) were used as received. A detailed characterization of these copolymers has been given elsewhere [15]. Pyrene and CTAB (Aldrich) were used as received. Phenol was distilled, while p-methylphenol, p-ethylphenol, and p-propylphenol were sublimated prior to be used. All samples were prepared with distilled and deionized water obtained from an EASYpure RF (Barnstead) deionization system.

2.2. Measurement of distribution coefficients

In the pseudo-phase model the solubilization process is represented by the equilibrium

$$S_W + \text{MAS-}n/\text{CTAB} \Leftrightarrow S_{(\text{MAS-}n/\text{CTAB})}. \qquad (1)$$

For which the equilibrium constant K_s is given by

$$K_S = \frac{[S_M]}{[S_W][\text{MAS-}n]}\frac{f_M}{f_W}, \qquad (2)$$

where $[S_W]$ and $[S_M]$ denote molar concentrations of substrate in aqueous and in mixed micellar phase, respectively, $[\text{MAS-}n]$ is the concentration of polymer units forming the mixed micelles, and f_W and f_M are the activity coefficient of the substrate in the respective phase. In Eq. (2) it is assumed that all repeat units of the polymer are involved in the formation of the mixed micelle. In addition, in these experiments, the concentration of surfactant is almost two orders of magnitude lower than the molar concentration of repeat units. Consequently, the concentration of this pseudo-phase is taken as the molar concentration of the monomer units, $[\text{MAS-}n]$. Alternatively, this equilibrium constant can be defined on a mole fraction basis, K_X, by

$$K_X = \frac{X_M}{X_W}\frac{f_M}{f_W}, \qquad (3)$$

where X_M and X_W are the mole fractions of substrate in the micellar and aqueous phases, respectively. These quantities are related to $[S_M]$ and to $[S_W]$ through the following equations:

$$X_M = \frac{[S_M]}{[S_M] + [\text{MAS-}n]}, \qquad (4)$$

$$X_W = \frac{[S_W]}{[S_W] + 55.5}. \qquad (5)$$

Thus, the two equilibrium constants are related by

$$K_X = \frac{55.5K_S}{1 + K_S[S_W]}. \qquad (6)$$

At low substrate occupation numbers $K_S\ [S_W] = [S_M]/[\text{MAS-}n] \ll 1$, and Eq. (6) can be approximated by

$$K_X = 55.5K_S. \qquad (7)$$

The free energy of transfer from water to the pseudo micellar phase is expressed as

$$\Delta\mu_t^0 = \mu_M^0 - \mu_W^0 = -RT\ln K_X. \qquad (8)$$

The distribution coefficients (K_S) were obtained by ultrafiltration in an Amicon 202 cell with a PM10 membrane. Aqueous solutions of phenols (0.1 mM) in the presence of CTAB (0.1 mM) and different concentrations of copolymer (6–10 mM on a monomolar unit basis) were filtered, and the absorbances of the filtrate were measured at 269 nm. The molar concentration of phenols in the filtrate, $[S_W]$, were obtained from a calibration curve. With this result and from $[S_{\text{Total}}] = [S_W] + [S_M]$, the ratio $f = [S_W]/[S_M]$ was calculated and plotted according to Eq. (2). The equilibrium constants, K_S, were calculated from the initial slope, where the activity coefficients can be assumed to be unity.

2.3. Fluorescence probing

Pyrene (1 µM) was added to aqueous solutions of mixtures of CTAB and MAS-n at surfactant concentrations well above the cac, and the fluorescence spectra of pyrene were recorded. Fluorescence spectra were obtained on a ISS PC1 Photon Counting spectrophotofluorometer. The ratio III/I corresponds to the ratio of intensities of peak three ($\lambda = 384$ nm) to peak one ($\lambda = 373$ nm). This ratio indicates the polarity of the pyrene microenvironment [16,17].

3. Results and discussion

3.1. MAS-n/CTAB aggregates

Addition of CTAB to aqueous solution of MAS-n copolymers results in the formation of aggregates at a surfactant concentration lower than the cmc of pure CTAB. The presence of these aggregates was detected using pyrene as a hydrophobic fluorescent probe. Measurements of the ratio III/I

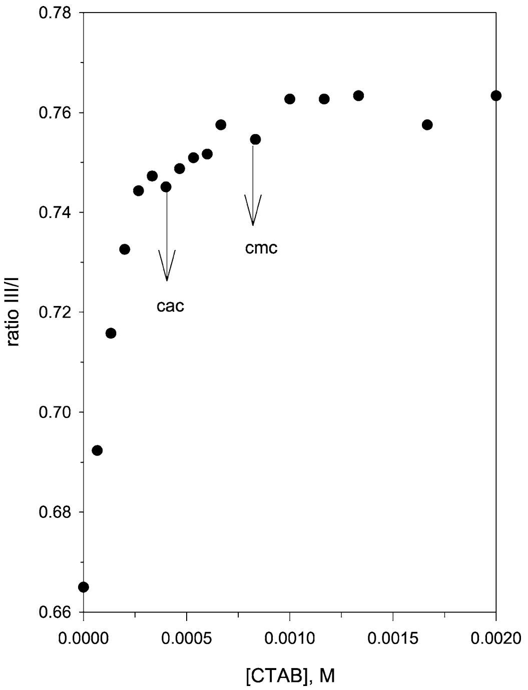

Fig. 1. Plot of the ratio III/I of pyrene in aqueous solutions of MAS-1 as a function of CTAB concentration.

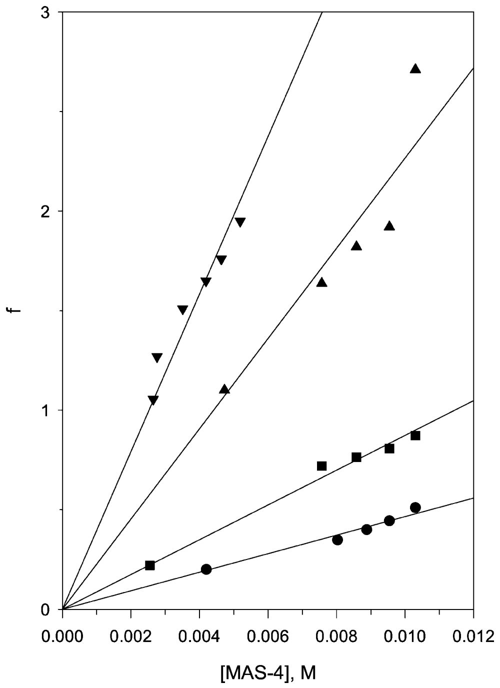

Fig. 2. Plot of f as a function of [MAS-4] expressed on a molar repeat unit basis for (●) phenol, (■) p-methylphenol, (▲) p-ethylphenol, and (▼) p-propylphenol.

in an aqueous solution of MAS-1 as a function of CTAB concentration are shown in Fig. 1. The ratio III/I exhibits a sharp increase with increasing CTAB concentration until it level off at a value ca. 0.76, which indicates the presence of a hydrophobic environment. This kind of behavior has been explained in terms of an early micellization process induced by the polyelectrolyte. At CTAB concentrations below the cac the MAS-*n* chains adopt an extended form due to the electrostatic repulsion between the carboxylate groups present in each repeat unit, and the ratio III/I reflects a polar environment. The association of opposite charged surfactant molecules to the ionic groups decreases the electrostatic repulsion and the polymer chains tends to a more compact form. During this process, which is a very cooperative process, pyrene senses a more and more hydrophobic microdomain reaching a maximum when micelles are formed. The hydrophobicity of these aggregates, as measured by the ratio III/I, depends on the length of the alkyl side chain. Thus, the final value of the ratio III/I ranges from 0.76 (for MAS/CTAB) to 0.94 (for MAS-8/CTAB). It is worth noting that the value of the ratio III/I is 0.77 in micelles of CTAB [16], and it ranges from 0.66 to 0.90 in aqueous solutions of MAS to MAS-8, in the absence of CTAB. Hence, the hydrophobicitiy of the aggregates formed by CTAB and MAS-*n* is similar to that measured for normal CTAB micelles.

3.2. *Distribution of phenols*

The equilibrium constants, K_S, were obtained from the initial slope of a plot of f against [MAS-*n*], expressed on a molar repeat unit basis, according to Eq. (2). Results obtained for phenol, p-methylphenol, p-ethylphenol, and p-propylphenol in the presence of MAS-4/CTAB are shown in Fig. 2. It can be seen that the magnitude of association increases with increasing number of carbon atoms in the p-alkyl group of phenol.

The values of K_S and K_X obtained for phenol and the p-alkyl derivatives in aqueous solutions of all MAS-*n*/CTAB systems are given in Table 1. The data show that the equilibrium constant increases with increasing size of the alkyl group of the phenol and that the value of K_S is almost

Table 1
Distribution constants K_S and K_X of phenol and p-alkylphenols between the aqueous phase and mixed micelles formed by CTAB and MAS-*n* copolymers

	Phenol		p-Methylphenol		p-Ethylphenol		p-Propylphenol	
MAS-*n*	K_S	K_X	K_S	K_X	K_S	K_X	K_S	K_X
0	19	1055	82	4573	215	11932	499	277678
2	42	2353	68	3774	140	7770	424	23532
4	47	2625	86	4761	227	12582	396	21978
6	45	2520	84	4684	231	12820	467	25919
8	59	3280						

Table 2
Standard free energies of transfer ($\Delta\mu_t^0$, (kJ mol^{-1})) of p-alkylphenols from the aqueous phase to the MAS-n/CTAB aggregates (data corresponding to normal micelles have also been included)

	Phenol	p-Methylphenol	p-Ethylphenol	p-Propylphenol
MAS	−17.2	−20.8	−23.2	−25.3
MAS-2	−19.2	−20.4	−22.2	−24.9
MAS-4	−19.5	−20.9	−23.3	−24.7
MAS-6	−19.4	−20.9	−23.4	−25.1
CTAB[a]	−23.8	−25.1	−26.3	−28.0
SDS[a]	−19.6	−20.9	−22.6	−23.8

[a] From Ref. [19].

not affected by changes in the length of the alkyl side chain of the polymer. These results indicate that the distribution of phenols between the aqueous phase and the MAS-n/CTAB micelles is mainly determined by the structure of the hydrophobic substrate. A similar result has been found for the transfer of phenols from the aqueous phase to the polymer micelles formed by the sodium salts of alternating copolymers of maleic acid and olefins, PA-nK$_2$ [18].

The effect of the substrate structure on the distribution process can be analyzed in terms of the standard free energy of transfer, $\Delta\mu_t^0$ (given in Table 2). The standard free energy of transfer of phenols from the aqueous phase to the micellar phase, $\Delta\mu_t^0 = \mu_M^0 - \mu_W^0$, calculated from Eq. (8), is assumed to be composed of additive contributions from different groups [6,19],

$$\Delta\mu_t^0 = \Delta\mu_{\mathrm{Ar}}^0 + n_C\Delta\mu_C^0, \qquad (9)$$

where $\Delta\mu_{\mathrm{Ar}}^0$ denotes the contribution of the parent aromatic group, $\Delta\mu_C^0$ is the incremental free energy per methylene group, and n_C is the number of these groups attached to the parent group. In Fig. 3 the values of $\Delta\mu_t^0$ obtained for the transfer from water to MAS-4/CTAB aggregates are plotted against the number of carbon atoms in the p-alkylphenol. For comparison, the results reported for transfer to sodium dodecylsulfate (SDS) [19], CTAB [19], and PA-18K$_2$ micelles [18] have been included. The values of $\Delta\mu_{\mathrm{Ar}}^0$ and $\Delta\mu_C^0$ obtained from the intercepts and slopes of these plots, respectively, are given in Table 3. The data show that the contribution from the aromatic group is greater in CTAB and PA-18K$_2$ than in MAS-4/CTAB and SDS. The enhanced solubilization of the benzene group of phenols in CTAB compared to that in SDS has been attributed to a specific interaction between the head groups of CTAB and the aromatic ring [19]. This effect is lost in the MAS-n/CTAB aggregates due to the electrostatic interaction between CTAB and the polymer chain. Consequently, the value of $\Delta\mu_{\mathrm{Ar}}^0$ obtained in MAS-4/CTAB is almost the same than that found in SDS micelles.

On the other hand, the incremental free energy of transfer per methylene group is slightly higher in MAS-4/CTAB than in the other micelles, but still lower than that determined for transfer to heptane [6] (3.27 kJ mol^{-1}). The low values of $\Delta\mu_C^0$, measured in ionic micelles, have been explained in terms of penetration of water molecules into the aggregate, which reduces the micelle hydrophobicity. However, a comparison of the ratio III/I values obtained in these systems (see Table 3) reveals that the hydrophobicity of the aggregates formed by MAS-4/CTAB and PA-18K$_2$ is higher than in ionic micelles. Thus, the low values of $\Delta\mu_C^0$ found for the polymeric systems has been attributed to a configurational reorganization of the polymer chains required to accommodate the alkyl chain of the phenols.

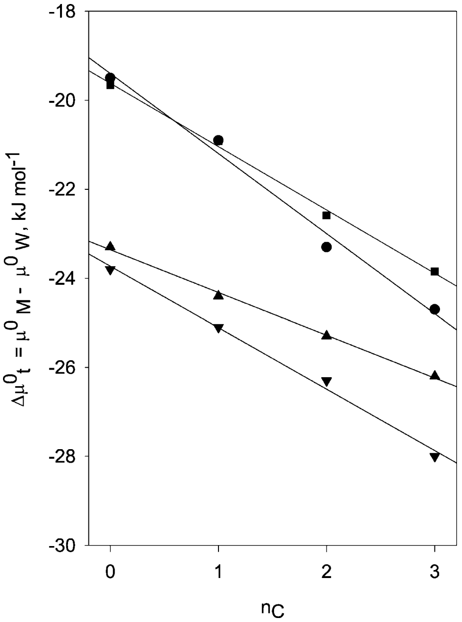

Fig. 3. Standard free energies of transfer of phenols from water to polymer and ionic micelles as a function of the number of carbon atoms in the p-alkyl group of phenols: (●) MAS-4/CTAB, (▲) PA-18K$_2$, (■) SDS, (▼) CTAB.

Table 3
Aromatic and methylene group contributions to the standard free energy of transfer, and ratio III/I in ionic and polymer micelles

Micelle	$-\Delta\mu_{\mathrm{Ar}}^0$ (kJ mol^{-1})	$-\Delta\mu_C^0$ (kJ mol^{-1})	Ratio III/I
MAS-4/CTAB	19.4	1.8	1.09
PA-18K$_2$	23.4	0.97	1.07
CTAB	23.4[a]	1.34	0.77[b]
SDS	19.4[a]	1.5	0.88[b]

[a] From Ref. [19].
[b] From Ref. [17].

4. Conclusions

The interaction between CTAB and the oppositely charged copolymers MAS-n generates aggregates where hydrophobic molecules can be dissolved. The distribution constants of phenols between aqueous phase and the MAS-n/CTAB aggregates and the corresponding standard free energies of transfer were determined using the pseudophase model. The distribution constants are not affected by changes in the length of the side alkyl chain, and they depend exclusively on the substrate structure. The effect of the phenol structure on the free energy of transfer has been analyzed in terms of two contributions: the free energy due to the aromatic moiety and the incremental free energy per methylene group. The value of $\Delta\mu^0_{\mathrm{Ar}}$ in MAS-*n*/CTAB was found to be lower than that in CTAB and equal to that measured in SDS. This result has been explained as a consequence of the interaction of the head groups of CTAB with MAS-*n* chains, preventing any specific interaction of CTAB molecules with the benzene group of phenols. On the other hand, the value of $\Delta\mu^0_C$ was found to be slightly higher in MAS-*n*/CTAB aggregates than in normal micelles, but lower than the transfer to *n*-heptane. This behavior is ascribed to the higher hydrophobicity of the MAS-*n*/CTAB aggregates and a configurational reorganization of the polymer chains.

Acknowledgments

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