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SHORT COMMUNICATION

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The interaction of mixed surfactants with polyelectrolytes

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Abstract The interactions between a linear polymer, sodium poly(2-acrylamide-2-methylpropane sulfonate), and two cationic surfactants, dodecylpyridinium chloride and tetradecylpyridinium chloride and their mixtures with different ratios, were studied by a potentiometric titration method using a surfactant-selective electrode. The ideal mixing/ideal cooperative binding model we had proposed previously was applied to successfully predict the binding isotherms of the mixed surfactant systems and the critical aggregation concentrations of the binding. The binding of surfactant mixtures to polymers is similar to the ideal mixed micelle formation and a sort of synergetic effect was found during the binding process.

Key words Mixed surfactants – Polyelectrolyte – Binding isotherm – Ideal mixing – Cooperative binding

Introduction

In most practical applications surfactant mixtures are used rather than a pure species [1]. The reason for this is frequently based on more favorable characteristics of mixtures and the lower cost of production than preparing the individual surfactant components involved. The synergistic properties of mixed surfactants have motivated much of the research in this field [2].

Most of the studies on mixed surfactant systems have been concerned with mixed micelle formation and mixed monolayers [3–6]. Little work has been carried out on interactions of surfactant mixtures with polymers, one of the common additives in applications [7, 8]. In a previous paper, we developed an "ideal mixing/ideal cooperative binding" model of the interaction of binary surfactants, tetradecylpyridinium chloride (TeP) and decylammonium chloride (DeA), with the oppositely charged poly(L-glutamate) [P(Glu)] [9]. A surfactant-selective electrode was used to measure the equilibrium concentration of surfactant in solution and circular dichroism (CD) was used to investigate the conformational change of P(Glu) in the mixed surfactant solutions. Because the membrane electrode is much more responsive to TeP than to DeA (the electrode selectivity of DeA over TeP is about 0.003), at least the binding isotherms of TeP in the surfactant mixtures can be built up experimentally. Furthermore, with the help of theoretical considerations, individual binding isotherms were figured out separately. In order to see the applicability of the theoretical treatment, we have extended the investigation to a system composed of two homologous cationic surfactants, TeP and dodecylpyridinium chloride (DoP), and an anionic linear polymer, sodium poly(2-acrylamide-2-methylpropane sulfonate) (PAMPS). Since the linear polymer, PAMPS, does not assume any ordered structure in surfactant solution detectable by a CD method, spectroscopy is not suitable anymore. Moreover, the electrode membrane selectivity of DoP over TeP is about 0.12, i.e., the membrane is sensitive to both DoP and TeP. Neither the binding isotherms of TeP nor of DoP could be constructed from the experimental method. However, by using the same ideal mixing model, the binding isotherms of the mixed surfactants can be extracted from the limited experimental data, which helps us get an insight into the interaction of surfactant mixtures with polyelectrolytes.

Experimental

Materials

TeP and DoP were synthesised by treating 1-alkylbromides with corresponding chain lengths with dried pyridine followed by ion exchanging the bromides in concentrated sodium chloride solutions. The products were recrystallized 3 times from acetone. The critical micelle concentrations (cmc) determined by the electric conductivity method in aqueous solutions were 3.40 mM and 14.7 mM at 25 °C for TeP and DoP, respectively: these were in good agreement with figures reported in the literature [10].

The linear polymer PAMPS was synthesised from 2-acrylamide-2-methylpropane sulfonic acid (Wako Pure Chemical Industries) which had been neutralized with NaOH before use. Ammonium peroxodisulfate (Wako Pure Chemical Industries) was added to initiate the polymerization at 60 °C under deoxygenated conditions. The polymer was purified by dialysis against water for some days until the resistivity of the outside water was larger than $3 \times 10^5\ \Omega\ \mathrm{cm}^{-1}$.

Electrode

The binding of TeP, DoP, and their mixtures to PAMPS with composition ratios 3:1, 1:1 and 1:3 was studied by potentiometric titration at 25 °C using an electrode of the following concentration cell:

Ag/AgCl || reference solution | PVC membrane | sample solution || Ag/AgCl.

In the case of the mixed-surfactant system, the composition ratio of the binary surfactants in the reference solution was the same as that of sample solution. The PVC membrane eletrode is responsive to the cationic surfactants. The preparation of the electrode was described elsewhere [11, 12]: the membrane was composed of partially sulfonated PVC, polymerized plasticizer (Elvaloy 742 Du Pont) and tricresyl phosphate (Wako Pure Chemical Industries) to improve the sensitivity (3:4:2 in weight). The electrode selectivity for DoP over TeP (K_{ij}), was determined to be 0.12 by the method described by Cutler et al. [13]. The electromotive force (emf) was measured with a digital voltmeter (Advantest TR6845). All the experiments were carried out in the presence of 10 mM NaCl at 25 °C.

Review of the binding model

Cooperative binding of ionic surfactant to the oppositely charged polyelectrolyte usually occurs in a concentration range much lower than the cmc. The surfactant concentration at the sudden onset of binding is defined as the critical aggregation concentration (cac), in analogy with the cmc. Below the cac, the concentrations of surfactant components 1 and 2 in the polymer solutions are

$$C_1 = \omega_1 C_t \tag{1}$$

$$C_2 = (1 - \omega_1)\, C_t \ , \tag{2}$$

where C_t is the total surfactant concentration of the mixture, ω_1 is the mole fraction of component 1 in a weigh-in concentration of the mixed surfactants.

Above the cac but below the cmc, i.e., where there are no micelles, the mole fraction of component 1 in the polymer-surfactant complex (cluster), X_1, can be written as

$$X_1 = \frac{C_1 - C_1^{\mathrm{f}}}{C_t - C_1^{\mathrm{f}} - C_2^{\mathrm{f}}} \ , \tag{3}$$

where C_s^{f} ($s = 1, 2$) is the concentration of the singly dispersed surfactant in the bulk solution.

Assuming that the activity coefficient of the surfactant is unity and the micelle-like clusters behave as in an ideal mixture, the chemical potentials for surfactant 1 in the bulk solution, μ_1, and in the micelle-like cluster phase, $\mu_{1,\mathrm{c}}$, can be expressed as

$$\mu_1 = \mu_1^0 + RT \ln C_1^{\mathrm{f}} \tag{4}$$

$$\mu_{1,\mathrm{c}} = \mu_{1,\mathrm{c}}^0 + RT \ln X_1 + z_1 F \Phi_\beta \ , \tag{5}$$

where μ_1^0 and $\mu_{1,\mathrm{c}}^0$ are the standard chemical potentials of the singly dispersed and the aggregated surfactants, respectively. Φ_β is the electrostatic potential of the micelle-like cluster, where the potential in bulk solution is zero. This parameter is assumed as a function only of the degree of surfactant binding, i.e., the electrostatic potentials of the polymer-surfactant cluster in single and in mixed surfactant systems are supposed to be the same at the same degree of binding.

In the polymer system with a single surfactant ($X_1 = 1$), at a certain degree of binding, we have,

$$\mu_1^* = \mu_1^0 + RT \ln C_1^{\mathrm{f}*} \tag{6}$$

$$\mu_{1,\mathrm{c}}^* = \mu_{1,\mathrm{c}}^0 + z_1 F \Phi_\beta^* \ . \tag{7}$$

The asterisk here represents the state of a single surfactant. At equilibrium, in the single and mixed surfactant system at the same degree of binding, $\mu_1 = \mu_{1,\mathrm{c}}$, $\mu_1^* = \mu_{1,c}^*$ and $\Phi_\beta = \Phi_\beta^*$. From Eqs. (4)–(7), we obtain

$$C_1^{\mathrm{f}} = C_1^{\mathrm{f}*} X_1 \ . \tag{8}$$

Similarly for surfactant component 2 we obtain

$$C_2^{\mathrm{f}} = C_2^{\mathrm{f}*}(1 - X_1) \ . \tag{9}$$

Substituting C_1^{f} and $C_2^{\mathrm{f}*}$ in Eqs. (8) and (9) into Eq. (3), we get

$$(C_2^{\mathrm{f}*} - C_1^{\mathrm{f}*})X_1^2 + [C_t - (C_2^{\mathrm{f}*} - C_1^{\mathrm{f}*})]X_1 - C_1 = 0 \ . \tag{10}$$

At the cac, the free surfactant concentration is equal to the total surfactant concentration. Therefore, in a single-surfactant system, $C_s^{f*} = \mathrm{cac}_s\ (s = 1, 2)$; and in the mixed system, $C_s^{f} = C_s\ (s = 1, 2), C_t = \mathrm{cac}$. From Eqs. (1), (2), (8) and (9), the following equation can be derived easily by eliminating X_1:

$$\frac{1}{\mathrm{cac}} = \frac{\omega_1}{\mathrm{cac}_1} + \frac{1 - \omega_1}{\mathrm{cac}_2} \quad . \tag{11}$$

To solve Eq. (10) numerically, we need to know C_s^{f*} at a certain degree of binding in the case of the single-surfactant system. Since the binding isotherm of the single-component surfactant can be obtained using the surfactant-selective electrode, the value of C_s^{f*} at any degree of binding can be derived readily by simulating the binding isotherm with the Satake–Yang equation [14] which describes cooperative binding. Then, the mole fraction of surfactant 1 in mixed clusters at the same degree of binding, X_1, can be solved. Therefore, we can extract the binding isotherms of the mixed surfactant systems from the present ‘ideal mixing/ideal cooperative binding'' model.

Results and discussion

Figure 1 shows the emf response from the surfactant-selective electrode in aqueous surfactant solutions, in the absence and in the presence of polyelectrolyte, where the emf is plotted against the logarithm of the total surfactant concentration. The calibration curves obtained from polymer-free solution are linear for all five systems (DoP, TeP, and their mixtures in the ratios 3:1,1:1 and 1:3) with a slope in the range 57–59 mV/decade. In the presence of PAMPS, a certain number of surfactants are bound to the polymer, which causes the deviations from the calibration line.

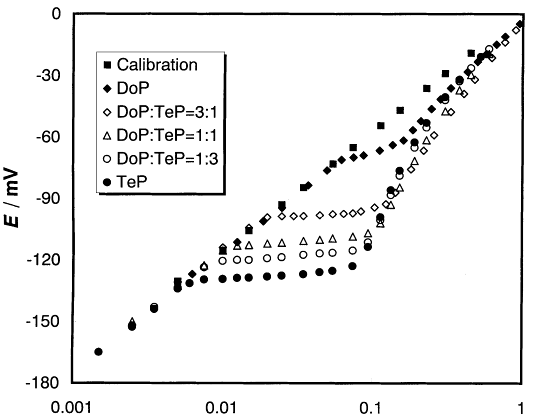

Fig. 1 Electromotive force versus surfactant concentration of tetradecylpyridinium chloride (TeP), dodecylpyridinium chloride (DoP), and their mixtures in the absence and presence of sodium poly(2-acrylamide-2-methylpropane sulfonate). C_p = 0.2 mM residue

For a single-surfactant system, the binding isotherm can be constructed by plotting the degree of binding (β) against the equilibrium concentration C_f, as given in Fig. 2, where

$$\beta = C_b/C_p = (C_s - C_f)/C_p \tag{12}$$

and C_p is the residual concentration of PAMPS. The resulting binding isotherms of TeP and DoP were analyzed using the Satake–Yang equation,

$$\beta = \frac{1}{2}\left[1 - (1 - s)/\sqrt{(1 - s)^2 + 4s/u}\right] \quad , \tag{13}$$

where $s = C_f/C_{f\ (\beta=0.5)}$, a reduced concentration, and $u = 1/KC_{f(\beta=0.5)}$, a cooperativity parameter. K is an intrinsic binding constant [14]. These parameters were obtained by fitting the lower part of binding isotherms, typically $\beta < 0.3$, where the electrostatic potential around the polyelectrolyte is kept relatively constant because of counterion condensation [15], which is in accordance with the assumption in Eq. (13). The total binding affinity uK and the respective parameters are summarized in Table 1.

For the mixed surfactant systems, however, it is not straightforward to construct binding isotherms by using the emf data without the independent knowledge of the equilibrium concentration of TeP or DoP in the bulk

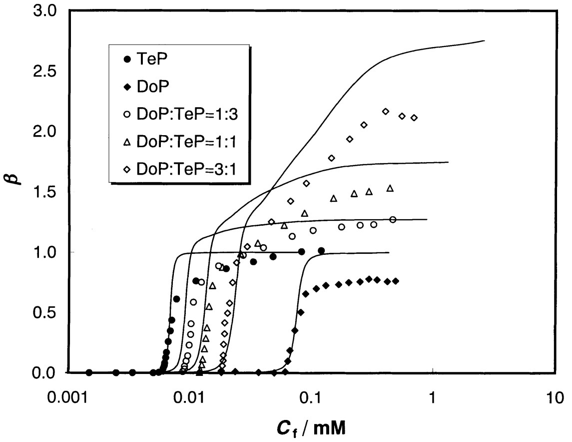

Fig. 2 Binding isotherms of TeP and DoP and apparent binding isotherms for the binary surfactants. *Solid line*: simulated by ideal mixing/ideal cooperative binding model

Table 1 Binding parameters of single-surfactant systems

	uK	u	K/mM^{-1}
DoP	13.2	259	0.051
TeP	146.2	1057	0.138

solution. So only "apparent" binding isotherms of the mixed surfactant systems $[\beta_{\mathrm{app}} = (C_t - C'_{\mathrm{f}})/C_{\mathrm{p}}]$ on the basis of the "apparent" total free concentration $(C'_{\mathrm{f}} = 10^{E/\mathrm{slope}})$ derived from Fig. 1 are given in Fig. 2.

We employ the "ideal mixing/ideal cooperative binding" model described above to reproduce the apparent binding isotherms of mixed surfactant systems by calculation. The apparent binding isotherms can be well predicted by the present model (the solid line in Fig. 2). In addition, the cac of binding is also in good agreement with the one calculated from Eq. (11), as shown in Fig. 3.

The model is used to derive the respective binding isotherms of DoP or TeP in the mixed surfactant systems, which cannot be obtained from the experimental emf data alone. The results are given in Fig. 4. Compared with the single surfactant systems, the binding isotherms of TeP or DoP shift to the lower concentration range with increasing composition of cosurfactant, suggesting that binding is enhanced in the presence of the cosurfactant. The greater the concentration of one surfactant component in the mixture, the more favorable the binding of its partner. Note that the binding isotherm of TeP even bends backwards a little in the mixing ratio [DoP]:[TeP] = 3:1. It is expected that in the absence of the cosurfactant, the individual surfactant has to bind to the polymer by itself, while the binding may be more enhanced in the mixed surfactant system since the cosurfactant should provide a hydrophobic environment around its partner. This is a sort of synergetic effect. Similar results are also found in the binding of TeP and DeA to P(Glu) [9].

Moreover, the critical deaggregation concentration (cdac), defined as the concentration at which the less hydrophobic surfacant (here, the short-chain surfactant DoP) starts to leave the polymer-surfactant clusters [9], is also found in the present systems. The degree of binding of DoP begins to decrease above the cdac, and even diminishes to zero on increasing the total surfactant concentration, suggesting that DoP is finally kicked out from the binding sites. This phenomenon is reminiscent of the existence of the critical demicellization concentration in the micellization of mixed surfactants, which was introduced by Mysels [16]. The existence of the cdac in the binding of mixed surfactants to polymers is probably due to the competition and saturation of the binding sites.

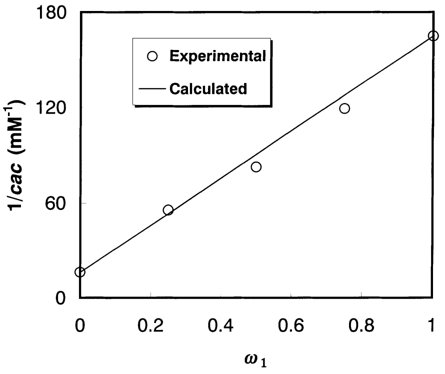

Fig. 3 The relationship between the reciprocal of the critical aggregation concentration (cac) and the mole fraction of TeP, ω_1

Finally, the "real" binding isotherms of total surfactant in the mixed surfactant systems calculated from the model are given in Fig. 5. The binding isotherms of surfactant mixtures are located between the binding isotherms of the individual single-surfactant systems.

It is seen that the "ideal mixing/ideal cooperative binding" model can be successfully applied to the binding of DoP and TeP mixtures to PAMPS.

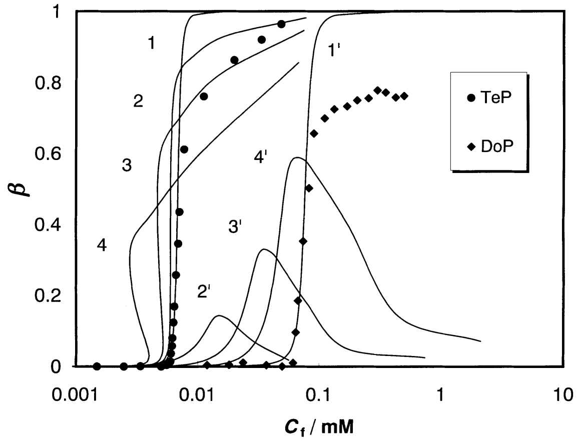

Fig. 4 Binding isotherms of TeP and DoP in pure and mixed surfactant systems. *Solid line*: predicted by ideal mixing/ideal cooperative binding model: *1* TeP in pure system; *2* TeP in DoP:TeP = 1:3 mixed system; *3* TeP in DoP:TeP = 1:1 mixed system; *4* TeP in DoP:TeP = 3:1 mixed system; *1′* DoP in pure system; *2′* DoP in DoP:TeP = 1:3 mixed system; *3′* DoP in DoP:TeP = 1:1 mixed system; *4′* DoP in DoP:TeP = 3:1 mixed system

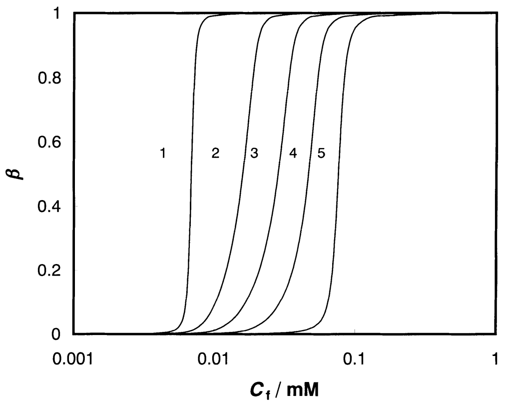

Fig. 5 Calculated binding isotherms of single and binary surfactants by ideal mixing/ideal cooperative binding model: *1* TeP; *2* DoP:TeP = 1:3; *3* DoP:TeP = 1:1; *4* DoP:TeP = 3:1; *5* DoP

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