Colloid Polym Sci 277:261–264 (1999)

SHORT COMMUNICATION

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Effect of the protonation equilibrium on the interaction of mixed micelles with their counterions

Received: 15 May 1998
Accepted in revised form: 30 September 1998

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Abstract Ionic/nonionic mixed micelle formation of dodecyldimethylamine oxide (DDAO) was studied by measuring the activities of $DDAO^+$ ions and Cl^- ions using surfactant-selective electrodes and Ag/AgCl electrodes at three pH values in the absence of added salt. DDAO monomer exists as either a nonionic or a cationic species depending on the pH of the aqueous solution and hence the two species are not independent of each other. A new relation between the activity of the surfactant ions and that of the counterions is presented which differs from the corresponding relation valid for ionic/nonionic mixed micelles consisting of independent components.

Key words Ionic surfactant – Mixed micelle – Surfactant-specific electrode – Dodecyldimethylamine oxide – Activity of surfactant ion

Introduction

Micelles composed of mixtures of different surfactants (mixed micelles) are of interest from both theoretical and industrial points of view [1, 2]. In practical applications, such as detergents and cosmetics, mixtures of surfactants are used widely. Properties of mixed micelles depend on various factors, such as combination, relative composition and charge of surfactants, etc. Theories have been developed to analyze mixed micelle formation [1–10]. For ionic/nonionic mixed micelles, the change in the electrostatic free energy with micelle composition has received much attention [7–10]. It is desirable to determine experimentally the activity of, at least, one of the components. Surfactant-selective electrodes have been used to determine the activity of surfactant ions [2, 9, 11, 12]. The electrode can measure the activity of surfactant ions not only below the critical micelle concentration (cmc) but also above it. The electrode has been used to study the interactions of ionic surfactants with polymers [13].

Ionic/nonionic mixed micelles have been studied mainly in the presence of salts. In the absence of added salts, Sepúlveda and Cabrera [14] investigated the mixed micelles formed by polyoxyethylene 23-lauryl ether (Brij 35) and hexadecyltrimethlyammonium bromide with surfactant-selective electrodes and the results were analyzed on the basis of the pseudophase separation model with the assumption that the chemical potential of the nonionic species is constant in the concentration range above the cmc.

In the present work, we study the mixed micelle formation of dodeyldimethylamine oxide (DDAO) in the absence of added salts. In the case of DDAO, the cationic and the nonionic species are not independent of each other because of the protonation equilibrium between them. We can estimate the activities of the nonionic species from those of the cationic species. We propose a different thermodynamic relation for the present system from that for the mixed micelles consisting of independent components.

Experimental

DDAO solution was purchased from Fluka. NaCl and standard HCl solutions were from Nacalai Tesque. In order to adjust the pH values of DDAO solutions within a narrow range (± 0.02), different but proper amounts of HCl solution were added to a series of DDAO solutions of different concentrations. The pH values examined in the present study were 2.00, 4.00, and 5.00.

The cationic surfactant-selective electrode was made according to the method of Takisawa et al. [12] The response of the electrode was good. Calibration of the electrode was performed using a series of DDAO solutions of the same pH in a concentration range below the cmc. The relationships between the electromotive forces obtained and the logarithm of DDAO concentrations were linear. At pH 2.00 the slope was 55.0 ± 0.5 mV and close to the Nernstian slope. In addition, it was confirmed that the electrode did not respond to the nonionic species. The cell used was

Ag/AgCl | KCl (3.3 M) | DDAO (3 mM, pH 2) ||
DDAO test solution | KCl (3.3 M) | Ag/AgCl .

The activities of Cl^- ions in DDAO solutions were measured by a Ag/AgCl electrode. The cell used was

Ag/AgCl | KCl (3.3 M) |KNO_3 (1 M) |
DDAO test solution | Ag/AgCl .

The electrodes were calibrated using NaCl solutions.

Results and discussion

Consider the following mixed micelle formation of DDAO with an aggregation number m,

$$m(1-\alpha_M)\,\mathrm{D} + m\alpha_M\,\mathrm{DH} + m\alpha_M\nu\mathrm{Cl}^- \leftrightarrow \text{micelle}(m,\,\alpha_M)\,, \tag{1}$$

where D and DH denote the nonionic and the cationic species, respectively. The degree of ionization of DDAO in the micelle is denoted as α_M. This is equivalent to the mole fraction of the cationic species in the mixed micelles. The apparent degree of counterion binding of the micelle is denoted as ν. In terms of the chemical potentials μ of the components, we have

$$(1-\alpha_M)\mu_D + \alpha_M\mu_{DH} + \alpha_M\nu\mu_{Cl} = \mu_{\text{micelle}}/m\ . \tag{2}$$

In terms of the activities a and the mole fraction of the micelle x_m, we have

$$(1-\alpha_M)\ln a_D + \alpha_M\ \ln a_{DH} + \alpha_M\nu\ln a_{Cl} = \Delta G^*/RT + (1/m)\ \ln x_m\ . \tag{3}$$

Here ΔG^* denotes the standard free-energy change per monomer for reaction (1).

The proton dissociation constant K is written as follows:

$$a_D\,a_H/a_{DH} = K\ . \tag{4}$$

By eliminating a_D from Eqs. (3) and (4), we have Eq. (5) under the pseudophase approximation for the charged micelles,

$$\ln a_{DH} + \alpha_M\nu\ln a_{Cl} = \Delta G^*/RT - (1-\alpha_M)\ln(K/a_H)\ . \tag{5}$$

Variations of a_{DH} and a_{Cl} accompanying a change in the total surfactant concentration C_t can be described with Eq. (5). In the no-added-salt system, the change in the ionic strength of the solution with C_t cannot be negligible. Strictly speaking, ΔG^* is expected to decrease with increasing C_t but at the same time α_M is expected to increase with C_t at a constant pH (a_H). If we assume that both α_M and ΔG^* are kept constant at a given pH irrespective of the total concentration C_t, Eq. (5) can be written as Eq. (6).

$$\ln a_{DH} + \alpha_M\nu\ \ln a_{Cl} = \text{constant}\ . \tag{6}$$

Plots of $\log a_{DH}$ versus $\log a_{Cl}$ at three pH values for a change in C_t are shown in Figs. 1 and 2. As we expect from Eq. (6), $\log a_{DH}$ decreases linearly with $\log a_{Cl}$ at all pH values examined. The result suggests the validity of the above analysis.

It is pertinent to discuss briefly the implications of Eq. (6) here. For the solutions with no added salt as

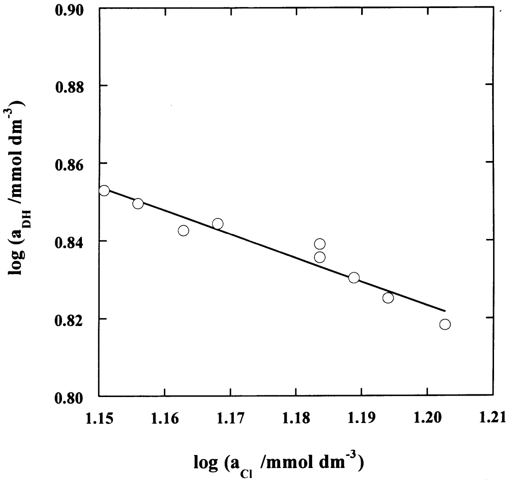

Fig. 1 The relation between the activities of the cationic species a_{DH} and those of the counterion a_{Cl} at pH 2.00

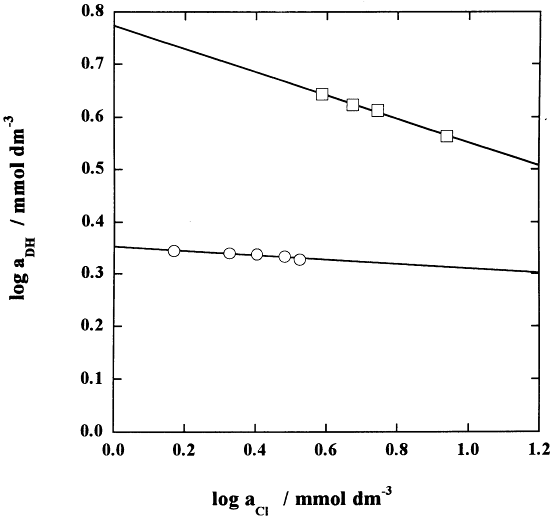

Fig. 2 The relations between the activities of the cationic species a_{DH} and those of the counterion a_{Cl} at pH 4.00 (□) and 5.00 (○)

encountered in the present study, Eq. (6) describes the effect of the total concentration C_{t}. Any change in a_{Cl} is induced by the corresponding change in C_{t}. In the presence of an added salt, for example NaCl, on the other hand, the constancy of the right-hand side of Eq. (6) is satisfied to a better extent. At the same time, however, both a_{DH} and α_{M} scarcely change with C_{t}. Instead, we can change the counterion activity a_{Cl} by changing the salt concentration C_{s}. In this case, both a_{DH} and $v\alpha_{\mathrm{M}}$ change with C_{s} at a constant pH and Eq. (6) predicts the nonlinear relation between $\log a_{\mathrm{DH}}$ and $\log a_{\mathrm{Cl}}$.

In the solution of pH 2.00 where the DDAO monomer is completely protonated, the slope of the plot is −0.64 ± 0.01. On the other hand, the slope of the Corrin–Harkins plot for DDAO at $\alpha_{\mathrm{M}} = 1$ is 0.64 in the low salt concentration range ($C_{\mathrm{s}} < 0.5$ M) [15]. The Corrin–Harkins relation at $\alpha_{\mathrm{M}} = 1$ describes the change in the cmc (hence a_{DH}) with the counterion concentration which is close to a_{Cl}. So, this coincidence clearly indicates the validity of Eq. (6) in the case of $\alpha_{\mathrm{M}} = 1$.

At pH 4.00 ($\alpha_{1} = 0.86$; $\alpha_{\mathrm{M}} = 0.47$), the slope was −0.24 ± 0.01 and v was 0.51 ± 0.02. At pH 5.00 ($\alpha_{1} = 0.38$; $\alpha_{\mathrm{M}} = 0.27$), the slope was −0.04 ± 0.01 and v was 0.15 ± 0.05. The decrease in v with decreasing α_{M} can be understood from the standpoint of the surface charge density of the micelle.

In many ionic/nonionic mixed micelles where the two components are independent, the equation corresponding to Eq. (6) is

$$r \log a_{\mathrm{N}} + p \log a_{\mathrm{I}} + q \log a_{\mathrm{X}} = \text{constant} \ , \qquad (7)$$

where N and I denote the nonionic and the ionic surfactants, respectively and X denotes the counterions. If it is assumed that the activity of the nonionic surfactant is constant in the concentration range higher than the cmc [14], we have Eq. (8) in terms of $v = q/p$.

$$\log a_{\mathrm{I}} + v \log a_{\mathrm{X}} = \text{constant} \ , \qquad (8)$$

As expected from Eq. (8), it was shown that $\log a_{\mathrm{I}}$ decreases linearly with $\log a_{\mathrm{X}}$ [14] with slope v instead of $v\alpha_{\mathrm{M}}$. The activity of the nonionic species does not appear in Eqs. (6) and (8). However, the underlying mechanisms are different. In the case of DDAO, Eq. (6), the activity of the nonionic species is not an independent variable because of the protonation equilibrium and hence it can be eliminated. In Eq. (8) the activity of the nonionic species does not appear simply because it is assumed to be constant.

The degree of counterion binding θ obtained from the measurement of the counterion activity in the media of no added salt is evaluated according to Eq. (9).

$$\theta = (C_{\mathrm{Cl}} - a_{\mathrm{Cl}})/[(C_{\mathrm{t}} - C_{1})\alpha_{\mathrm{M}}] \ , \qquad (9)$$

where C_{1} denotes the monomer concentration of both the nonionic and the cationic species. When C_{1} is approximated by the cmc, the values of θ are 0.42 ± 0.02 and 0.22 ± 0.01 for $\alpha_{\mathrm{M}} = 0.47$ and 0.27, respectively [16]. The coincidence between v and θ is good for $\alpha_{\mathrm{M}} = 0.27$ but not good for $\alpha_{\mathrm{M}} = 0.47$. This may be partly caused by the approximation of C_{1} by the cmc. If correct C_{1} values are employed in Eq. (8), θ values will increase. It is found in another system [14] that the v values obtained from Eq. (8) are larger than the θ values evaluated with Eq. (9).

Acknowledgement The authors thank Mitsui Du Pont Polychemical Co. for kindly supplying Elvaloy 742.

References

1. Rubingh DN (1979) Solution chemistry of surfactants. Plenum, New York, pp 337–354
2. Holland PM, Rubingh DN, (eds.) (1992) Mixed surfactant systems. ACS, Washington DC
3. Funasaki N, Hada S (1979) J Phys Chem 83:2471–2475
4. Hoffmann H, Pössnecker G (1994) Langmuir 10:381–389
5. (a) Puvvada S, Blankschtein D (1992) J Phys Chem 96:5567–5579; (b) Puvvada S, Blankschtein D (1997) J Phys Chem 5579–5592
6. Sarmoria C, Puvvada S, Blankschtein D (1992) Langmuir 8:2690–2697
7. Rathman JF, Scamehorn JF (1986) Langmuir 2:354–361

8. Rathman JF, Scamehorn JF (1987) Langmuir 3:372–377
9. Hall DG, Mears P, Davidson C, Wyn-Jones E, Taylor J (1992) In: Holland PM, Rubingh DN (eds) Mixed surfactant systems. ACS, Washington DC. Symp. Ser. 501:128–141
10. Maeda H (1995) J Colloid Interface Sci 172:98–105
11. Sasaki T, Hattori M, Sasaki J, Nukina K (1975) Bull Chem Soc Jpn 48:1397–1403
12. Takisawa N, Hall DG, Wyn-Jones E, Brown P (1988) J Chem Soc Faraday Trans 1 84:3059–3070
13. Hayakawa K, Kwak JTC (1991) In: Rubingh DN, Holland PH (eds) Cationic surfactants. Dekker, New York, pp 189–248
14. Sepúlveda L, Cabrera WJ (1989) J Colloid Interface Sci 131:8–17
15. Maeda H, Muroi S, Kakehashi R (1997) J Phys Chem B 101:7378–7382
16. Imaishi Y, Kakehashi R, Nezu T, Maeda H (1998) J Colloid Interface Sci 197:309–316