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The Micelle Formation of Mixtures of Polyoxyethylene Type Nonionic Surfactants in Aqueous Solutions

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The critical micelle concentrations (CMC) of mixtures of nonionic surfactants with the same hydrocarbon, *i.e.* dodecyl group, and with various chain lengths of ethylene oxide, were determined. The observed values were compared with the values calculated by means of the equation derived from the pseudo-phase separation model on the assumption that the mixed micelle is a perfect solution. A good agreement between observed and calculated values was obtained in the mixtures of the surfactants with six or more ethylene-oxide units. However, the observed values of the two-component mixture, one component with five ethylene-oxide units, showed a small deviation from the calculated values. The difference between the above two cases was explained from the viewpoint of the most suitable packing of the first six or fewer ethylene-oxide units near the micelle core in the micelle state.

It is well known that mixtures of surfactants, either ionic-ionic, ionic-nonionic, or nonionic-nonionic, form mixed micelles in an aqueous solution. Especially, the mixed micelle formation of ionic surfactants has been widely investigated.[1,5] Also, in the work of mixed systems of ionic-nonionic surfactants, useful information has been obtained.[2,5] However, only a few studies have been made of the critical micelle concentrations (CMC) of mixture of nonionic surfactants.[3-5] Recently, using polyoxyethylene type nonionic surfactants with almost the same oxyethylene chain length, but with different hydrocarbon chain lengths, Shinoda-Nakagawa[4] and Lange[5] predicted the CMC of their mixtures by the use of a pseudo-phase separation approach, treating the mixed micelle as a perfect solution. For practical purposes, it is important to be able to predict the CMC of surfactant mixtures from the CMC of each component.

In the present work, by determining the CMC of two-, three-, and four-component mixtures of nonionic surfactants with various oxyethylene chain lengths and the same hydrocarbon chain length, we examined the CMC equation derived on the assumption that the mixed micelle behaves as a perfect solution in the pseudo-phase separation model.

Experimental

Materials. The nonionic surfactants, polyoxyethylene lauryl ethers ($C_{12}H_{25}O(CH_2CH_2O)_{\bar{n}}H$, $\bar{n}=5$, 6, 10, 15, 20, 29, 49, $\bar{n}$: the average number of ethylene oxide groups) were the same materials, supplied by the Kao Soap Co., Ltd., as those used in our previous paper.[6] The sharp distribution of the oxyethylene chain lengths could be assessed by means of the sharp breaks and the lack of, or small, minimum in the surface tension *vs.* logarithm of the surfactant concentration plots. Throughout this work, the difference in the number of oxyethylene groups between the components in mixtures was more than five units, so each component was regarded as a single species in making a good approximation for the purposes of the present work.

Method. The CMC was determined at 20 °C by the use of both the surface tension and the dye-color-change methods.[7] The details of the procedures of the former were described in a previous paper.[6] The dye used was pinacyanol chloride (Eastman Kodak Co.), and its concentration was 1×10^{-5} mol/l throughout this work. The shift of the absorption spectrum was measured with a DSB-70 spectrophotometer manufactured by the Beckman-Toshiba Co., Ltd. The procedure of direct calorimetry used to determine the standard entropy of micelle formation, $\Delta S_m{}^\circ$, was described in the previous paper.[6]

Results and Discussion

With an increase in the content of the component with a higher CMC, the extent of the minimum in the surface tension-logarithm of the concentration curve gets larger; however, we could detect distinct breaks in the curve even for four-component mixtures. These distinct breaks agreed with the CMC determined by the dye-color-change method. The CMC's of single surfactants with various lengths of ethylene-oxide chains in the aqueous solution at 20 °C are tabulated in Table 1. The CMC's of mixtures are shown in Figs. 1, 2, and Tables 2, 3, with the composition.

TABLE 1. CMC AND THE STANDARD FREE ENERGY OF MICELLE FORMATION $\Delta G_m{}^0$ OF THE SULFACTANTS WITH VARIOUS ETHYLENE OXIDE CHAIN LENGTHS IN THE AQUEOUS SOLUTION AT 20 °C

Ethylene oxide chain length, $\bar{n}$	CMC (10^{-5} mol/l)	$\Delta G_m{}^0$ (kcal/mol)
5	4.5	−8.15
6	6.0	−7.99
10	9.0	−7.75
15	12.0	−7.58
20	15.5	−7.43
29	26.0	−7.14
49	63.0	−6.62

Using the same pseudo-phase separation treatment as that of Lange *et al.* for two-component mixtures,[5] the equation of the CMC for multi-component mixtures of nonionic surfactants can be easily derived as follows.

In a sufficiently low concentration range, the CMC can be expressed by the mole fraction instead of by the activity in the chemical potential of the monomer. Recently, nuclear magnetic resonance studies have shown that the micelle contains some water molecules,[8] but their solubility can be neglected in a good approximation. In addition, assuming that the mixed micellar phase behaves as a perfect solution, the following equation holds for the *i*th-component:

$$x_i C_\mathrm{M} = x_i^\mathrm{m} C_i \tag{1}$$

where x_i, x_i^m: mole fraction of the *i*th-component in a mixture in the bulk solution and in the micellar phase respectively, C_M, C_i: the CMC (molar concentration) of a mixture and of a single system of the *i*th-component respectively.

The sum of the mole fractions of components in the micelle phase is unity; that is, $\sum x_i^\mathrm{m}=1$. Thus, Eq. (1) leads to:

$$C_\mathrm{M} = \frac{1}{\sum\limits_i (x_i/C_i)}. \tag{2}$$

The CMC values calculated from Eq. (2) are shown in Figs. 1 and 2 for two-component mixtures, and in Tables 2 and 3 for three- and four-component systems respectively, together with the observed values. Within the limits of experimental error, a good agreement between calculated and observed CMC's is usually obtained. However, in the case of one two-component system, $\bar{n}=5$—$\bar{n}=49$ (Fig. 2), a small disagreement is observed. The difference between the system containing $\bar{n}=5$ and the system containing $\bar{n}\geqq 6$ may be connected with the assumption made in the course of the derivation of Eq. (2). The assumption that the mixed micelle can be regarded as a perfect solution must be checked, since the other assumption, an ideal dilution in bulk solution, is sufficiently acceptable.

In order to clarify the situation, let us consider the following equation by Shinoda:[9]

TABLE 2. COMPARISON OF CALCULATED WITH OBSERVED CMC FOR THREE-COMPONENT MIXTURES AT 20 °C

Mole fraction of surfactants			CMC (10^{-5} mol/l)	
$\bar{n}=10$	29	49	Obsd	Calcd
0.333	0.333	0.333	18.7	18.2
0.125	0.25	0.625	29.0	29.9
0.125	0.625	0.25	23.0	23.9
0.625	0.125	0.25	12.3	12.8
0.222	0.222	0.555	24.5	23.8
$\bar{n}=10$	20	29	Obsd	Calcd
0.333	0.333	0.333	13.2	14.0

TABLE 3. COMPARISON OF CALCULATED WITH OBSERVED CMC FOR FOUR-COMPONENT MIXTURES AT 20 °C

Mole fraction of surfactants				CMC (10^{-5} mol/l)	
$\bar{n}=6$	15	29	49	Obsd	Calcd
0.25	0.25	0.25	0.25	13.5	13.1
0.125	0.5	0.25	0.125	12.5	13.5
0.25	0.125	0.5	0.125	13.0	13.6
0.125	0.125	0.125	0.625	21.5	21.7
$\bar{n}=10$	15	20	29	Obsd	Calcd
0.25	0.25	0.25	0.25	13.7	13.4

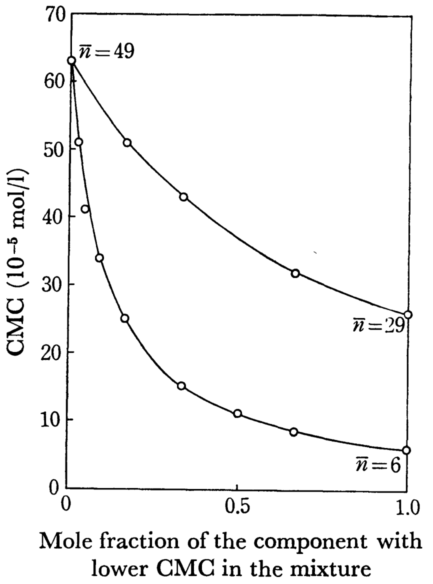

Fig. 1. Calculated and observed CMC for two-component mixtures at 20 °C ($\bar{n}=6$—$\bar{n}=49$, $\bar{n}=29$—$\bar{n}=49$)
○: observed, ——: calculated CMC from Eq. (2)

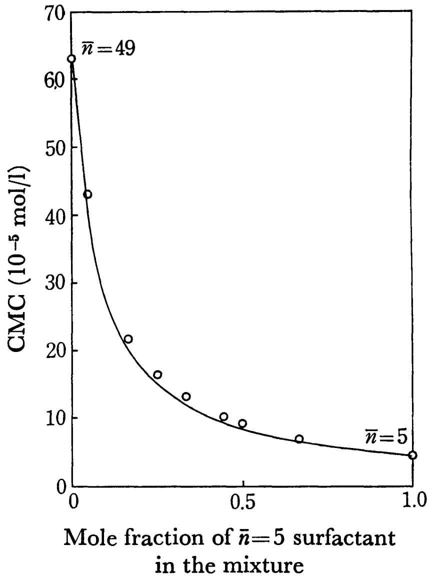

Fig. 2. Calculated and observed CMC for $\bar{n}=5$—$\bar{n}=49$ mixture at 20 °C
○: observed, ——: calculated CMC from Eq. (2)

$$\ln C = -\frac{\chi-\chi'}{kT} + \ln\frac{1000}{Nv} - 1, \tag{3}$$

where C: CMC in molarity, $\chi-\chi'$: the free energy difference of a surfactant between micellar and monomer states, N: the Avogadro number, v: the free volume of a surfactant molecule in a micelle.

In the case of nonionic surfactants,

$$\chi - \chi' = mw - \Delta,$$

where m: the number of methylene groups in a hydrocarbon chain, w: the free energy change per methylene group transferred from water into the micelle (constant value of *ca.* 1.1 kT), Δ: the free energy change of a polyoxyethylene chain between micelle and monomer states, containing the terms of dehydration energy, configuration entropy, and oxyethylene-oxyethylene interaction energy. It is possible to evaluate this term experimentally from the ln C *vs.* ethylene-oxide chain length plots. However, it is not necessary to evaluate it experimentally or mathematically in the discussion below, so we will treat it as a parameter.

We have obtained the following equation for nonionic surfactants with the same hydrocarbon chain in the most simple form:

$$\ln C_i = -\frac{mw}{kT} + \frac{\Delta_i}{kT} + \ln\frac{1000}{Nv_i} - 1. \qquad (4)$$

As each component has the same hydrocarbon chain, the assumption that the mixed micelle is a perfect solution needs an ideal mixing term, ln x_i^{m}, in Eq. (4):

$$\ln(x_i C_{\mathrm{M}}) = -\frac{mw}{kT} + \frac{\Delta_i}{kT} + \ln\frac{1000}{Nv_i} - 1 + \ln x_i^{\mathrm{m}} \qquad (5)$$

Of course, we obtain Eq. (2) from Eqs. (4) and (5). In other words, in the concept of a perfect solution, the free energy difference, $mw-\Delta_i$, is not altered by mixing in a micelle. That is, the free energy difference in a mixed system is the same as that in a single system.

If the mixing process brings a small variation in mw or Δ_i in Eq. (5),

$$\ln(x_i C_{\mathrm{M}}) = -\frac{mw}{kT} + \frac{\Delta_i}{kT} + \frac{\delta_i}{kT} + \ln\frac{1000}{Nv_i} - 1 + \ln x_i^{\mathrm{m}}, \qquad (6)$$

where δ_i is the quantity of deviation from mw or Δ_i in Eq. (5), neglecting the variation in v_i. In Eq. (6), δ_i corresponds to the heat of mixing term in the regular solution approximation, in analogy with a macroscopic solution. In Fig. 2, it may be seen that the deviation in the observed CMC's from the calculated values, *i.e.*, the ideal values, is small. Thus, Eq. (6) can be expected to be valid in this case. Alternatively and generally, by adding the excess term, ln γ_i^{m}, in Eq. (5), we obtain:

$$\ln(x_i C_{\mathrm{M}}) = -\frac{mw}{kT} + \frac{\Delta_i}{kT} + \ln\frac{1000}{Nv_i} - 1 + \ln x_i^{\mathrm{m}}\gamma_i^{\mathrm{m}} \qquad (7)$$

where γ_i^{m} is the activity coefficient of the ith-component in a mixed micelle. From Eqs. (4), (6), and (7), we obtain:

$$C_{\mathrm{M}} = \frac{1}{\sum_i (x_i/C_i\gamma_i^{\mathrm{m}})} = \frac{1}{\sum_i (x_i/C_i \exp(\delta_i/kT))} \qquad (8)$$

It may be seen in Fig. 2 that the observed CMC deviates positively from the ideal CMC. Then, at least, judging from Eq. (8), the activity coefficient of one component in a mixed micelle must be greater than unity. In a non-ideal macroscopic solution composed of two components, the deviation from ideality occurs in the same direction for both components. Therefore, we may conclude that the activity coefficients of both components in the mixed micelle are greater than unity. The free energy difference, $mw-\Delta_i-\delta_i$, in a mixed system is smaller than the $mw-\Delta_i$ in a single system. Thus, the micelle environments of both components are less stable than those in a single system. This conclusion is only the sufficient condition for the validity of positive deviation from the ideal CMC shown in Fig. 2. This point will be explained further in the subsequent discussions.

In the present work, the plots of the standard free energy of micelle formation, $\Delta G_{\mathrm{m}}^{\circ}$ ($\Delta G_{\mathrm{m}}^{\circ}=RT \ln X_{\mathrm{c}}$, where X_{c} represents the CMC in mole fraction) against $\bar{n}$, the number of ethylene-oxide (EO) units, yield two lines and cross around $\bar{n}=6$, *i.e.*, around the sixth unit (Table 1). In addition, the standard entropy of micelle formation, $\Delta S_{\mathrm{m}}^{\circ}$, for the surfactant with 5 EO units is 41 ± 6 e.u./mol, while the values of $\Delta S_{\mathrm{m}}^{\circ}$ for the surfactants with 6 to 31 units are almost constant, *ca.* 52 e.u./mol in aqueous solutions at 20 °C.[6] Crook *et al.* found the similar trend for *p,t*-octylphenoxyethoxyethanol in the aqueous solution below 50 °C.[10] From the break at the sixth EO unit in the plots of the thermodymanic quantities of micelle formation against EO units, Ray and Nemethy assumed as follows:[11] in the micelle state, the first six or less EO units, near the nonpolar core of the micelle, pack together and lose some of their hydration water because of the need for close packing of the nonpolar tails, while in longer chains, the EO units beyond the sixth are located sufficiently far from each other so that their local environment is changed very little compared to that for the monomer. This picture can be applied to the present CMC data in order to explain why the deviation from the ideal mixing in the mixed micelle occurs only in the $\bar{n}=5$—$\bar{n}=49$ system.

As the steric interaction among the EO units beyond the sixth in the micelle state is not very strong, the mixing of the surfactants with six or more EO units brings little difference in the micelle environment of EO units between mixed and single micelles. In addition, as each component has the same hydrocarbon chain, the free energy difference in the hydrocarbon chain and EO units between the micelle and monomer states, $mw-\Delta_i$ in Eq. (5), is independent of the number of components in a micelle, as has already been described. Thus, the above situation leads to the concept that the mixed micelle is a perfect solution.

On the other hand, in Fig. 2, the surfactant of $\bar{n}=49$ only needs the packing of the first six EO units, while the other component has five EO units. Therefore, the positive deviation from the ideal mixing may be expected to occur only for the surfactant of $\bar{n}=49$. In this case, the activity coefficient of $\bar{n}=5$ in the mixed micelle must be unity, and that of $\bar{n}=49$ must be *ca.* 10 at 0.5 of the mole fraction in a bulk solution, in order to satisfy the experimental results in Fig. 2. However, the value of the activity coefficient, $\gamma^{\mathrm{m}}=10$, corresponds to the heat of mixing term, $\delta=2.3\,kT$, which is too large to explain the small deviation from the ideal CMC. Thus, the micelle state of the surfactant of $\bar{n}=5$ in a mixed system may be also be obliged to deviate from the most suitable packing in a single system by the surfactant of $\bar{n}=49$. This deviation brings about the decrease in the free energy difference of each surfactant in a mixed system between micelle and monomer states compared to each single-component system; that is, $\delta_i>0$ in Eq. (6). Then, the surfactant with five EO units brings about the positive deviation from the ideal CMC shown in Fig. 2.

From the viewpoint of predicting the CMC, it may be concluded that the CMC's of multi-component mixtures, in which each component has six or more EO units, can be determined by means of Eq. (2).

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