The Effect of Added Inorganic Salts on the Micelle Formation of Nonionic Surfactants in Aqueous Solutions

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In order to divide the inorganic salt effect on the micelle formation of nonionic surfactants into the effects on the hydrocarbon and on the hydrophilic moieties of the surfactant, the critical micelle concentrations(CMC) of nonionic surfactant homologs (8,10,12 methylene and 6 oxyethylene groups) were determined in aqueous salt solutions. The salt-effect parameters of methylene and hexa(oxyethylene) groups were calculated from the CMC data. The orders of both the parameters with respect to the anion obeyed the Hofmeister series. The variation in the extent of the parameters with respect to the cation was much less than that with respect to the anion. These phenomena were discussed in terms of the direct and indirect effects of ions on the water structure around the hydrocarbon and hydrophilic moieties of the surfactants. In addition, the salt effect on the cloud point (CP) and the amount of solubilization toward the Yellow OB dyestuff in aqueous solutions were discussed in connection with the salt effect on the hydrophilic moiety.

The critical micelle concentrations (CMC) of nonionic surfactants in aqueous solutions are lowered by the addition of most inorganic salts.^{1–5)} In explaining this phenomenon, it has been suggested that salts bring about the dehydration of the hydrophilic moiety of the surfactant "monomer," causing the enhancement of the tendency toward micelle formation, *i.e.*, CMC lowering.2,3) This mechanism has thus far been the standard view, although others have been suggested.6,7) However, the micelle formation, *i.e.*, the CMC, is determined by the balance of surfactant stability between that in the monomer and that in the micelle state. Salts have influence not only on the dissolved state of monomers, but also on that of micelles in the solution, and so the dehydration mechanism is questionable. Recently, Mukerjee proposed a salting-out mechanism of the hydrocarbon moiety of surfactant, in which the salt effects on the hydrophilic moieties of the monomer and micelle were assumed to be almost equal in magnitude and to cancel each other out in determining the CMC.7,8) More recently, Ray and Nemethy9) and Kresheck10) examined Mukerjee's suggestion. However, their discussion is insufficient because Mukerjee's assumption of the cancellation of the salt effect on the hydrophilic moiety was not fully taken into consideration. In order to get rid of this ambiguity, it is necessary to estimate separately the salt effects on hydrocarbon and hydrophilic moieties.

In this study, the salt-effect parameter of each moiety during micellization was estimated. Also, we discussed qualitatively the salt effect on the dissolved state of nonionic surfactants in an aqueous solution, since there have been no theories concerning the quantitative clarification of the salt effect on aqueous polar or nonpolar substances.11–17) In this connection, the cloud points (CP) and the amount of solubilization toward Yellow OB in aqueous salt-nonionic surfactant mixed solutions were determined and discussed.

Experimental

Materials. The nonionic surfactants, poly(oxyethylene) alkyl ethers (abbreviated as C_mE_n; m: the number of methylene groups; n: the number of ethylene oxide groups), were the same materials as those used in a previous paper.18) All the inorganic salts were of a reagent grade (min 99.0 or 99.5% pure), supplied by the Wako Pure Chemical Co., and were used without further purification. The purification of the Yellow OB dyestuff (1-(o-tolylazo)-2-naphthylamine) as a solubilizate was described in the previous paper.18)

Method. The CMC values of C_8E_6, $C_{10}E_6$ and $C_{12}E_6$ in aqueous salt solutions at 20 °C were determined by plotting the surface tension against the logarithm of the concentration. The surface tensions were measured with the Du Noüy tensiometer. In Table 1 are tabulated the CMC values of C_8E_6, $C_{10}E_6$ and $C_{12}E_6$ in a pure aqueous solution. The cloud points were determined as the temperatures at which a sudden turbidity appeared or disappeared in the 1 wt% $C_{12}E_6$ aqueous solutions containing salts, when the solutions were heated or cooled at a constant rate of 0.5 °C/min under stirring. The change in the transparency of the solutions was observed with the naked eye. The procedure for determining the amount of solubilized Yellow OB in the aqueous $C_{12}E_{10}$-salt solutions at 30 °C has been described elsewhere.18)

TABLE 1. THE VALUES OF THE CMC OF NONIONIC SURFACTANTS USED IN THIS STUDY IN AN AQUEOUS SOLUTION AT 20 °C

Surfactant	CMC (10^{-3} mol/dm^3)
C_8E_6	8.3
$C_{10}E_6$	0.86
$C_{12}E_6$	0.074

Results and Discussion

Salt-effect Estimation from CMC Measurements. By considering the equilibrium between N' surfactant monomers and a micelle in an aqueous salt solution, it is shown that the molar standard free energy for micelle formation, $\Delta G_m^{(c)0}$, is expressed by the following equation:

$$\Delta G_m^{(c)0} = \frac{1}{N'}(\mu_m^{(c)0} - N'\mu_2^{(c)0})$$
$$= kT \ln c_2'f_2' - \frac{kT}{N'} \ln c_m'f_m', \quad (1)$$

where $\mu^{(c)0}$ denotes a molar standard chemical potential; the subscripts m and 2 refer to the micelle and the monomer respectively, and where c' and f' denote a molar-concentration and a molar-activity coefficients respectively. The molar activity coefficients of the monomer and the micelle are expressed by the well-known Setschnow equation:

$$\log f_2' = k_2 C_s, \qquad \log f_m' = k_m C_s, \tag{2}$$

where k is a salt-effect parameter and C_s is the molar concentration of salts. Here, it may be assumed that the concentrations of the monomer and the micelle are low enough and, therefore, that ideality holds near the CMC in the aqueous solution free of salts.15) By introducing Eq. 2 into Eq. 1, and by using Phillips' definition for CMC in the mass-action model,19) the following equation is derived:

$$\Delta G_m^{(c)0} \simeq kT \ln C' + 2.303\, kTk_2 C_s - \frac{2.303kT}{N'} k_m C_s, \tag{3}$$

where C' is the CMC in the aqueous salt solution. In the aqueous solution free of salts, the molar standard free energy, $\Delta G_m^{(c)0}$, is expressed as follows:

$$\Delta G_m^{(c)0} \simeq kT \ln C, \tag{4}$$

where C is the CMC in the aqueous solution. From the standpoint of the pseudo-phase separation model,20) the following CMC equation holds:21)

$$kT \ln C = -m\omega + \Delta + K(T, P), \tag{5}$$

where ω and Δ denote the free energy difference of methylene and poly(oxyethylene) groups between in the monomer state and in the micelle state respectively; K is a constant at constant temperature and pressure, and m is the number of methylene groups in the hydrocarbon chain of the surfactant. We assume the additivity for the salt-effect parameters to be as follows:

$$k_2 = mk_{CH_2} + k_{p,2}, \qquad k_m = N'k_{p,m}, \tag{6}$$

where k_{CH_2} and $k_{p,2}$ are the salt-effect parameters of the methylene and poly(oxyethylene) groups in the monomer respectively and where $k_{p,m}$ is that of the poly(oxyethylene) group in the micelle, because the hydrocarbon moieties form the micelle core and are shielded from the aqueous environment containing salts if we neglect the exposure of some of the hydrocarbon tails to the solvent near the micelle surface.22) Then, the following equation is derived formally from Eqs. 3—6:

$$kT \ln C' = -m\omega' + \Delta' + K, \tag{7}$$

where

$$\omega' = \omega + 2.303kTk_{CH_2}C_s, \tag{7a}$$

and

$$\Delta' = \Delta + 2.303kT(k_{p,m} - k_{p,2})C_s. \tag{7b}$$

The values of the salt-effect parameters, k_{CH_2} and $k_{p,m} - k_{p,2}$, can be determined by the use of Eqs. 7, 7a, and 7b as follows. The value of ω' can be determined from the slope in the log C' *vs.* m plots at a constant salt concentration C_s; a representative example is shown in Fig. 1 for the case of the sodium chloride additive. These plots form a straight line and then give a well-defined ω' value. The value of ω' thus determined is plotted in Fig. 2 against C_s. These plots also form a straight line, and the value of k_{CH_2} can be determined from the slope of the line. The value of Δ' at a constant C_s can be calculated by introducing the value of ω' and the experimental C' into Eq. 7. Figure 3 shows the plots of Δ' *vs.* C_s, whose slope gives the value of $k_{p,m} - k_{p,2}$. The calculated respective salt-effect param-

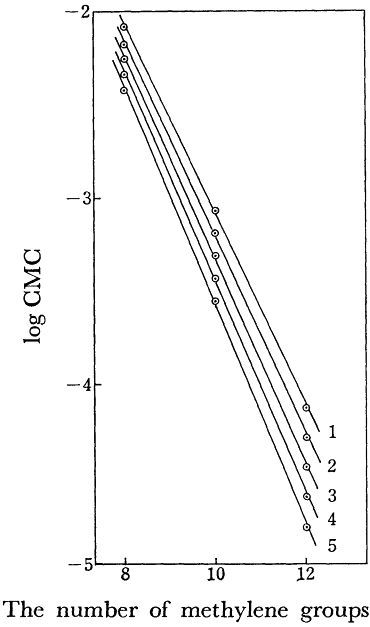

Fig. 1. log CMC *vs.* the number of methylene groups in C_mE_6 in aqueous sodium chloride solutions at 20 °C. Sodium chloride conc.: (1) 0, (2) 0.38 M*), (3) 0.75 M, (4) 1.28 M, (5) 1.50 M.

*) Throughout this paper, 1 M = 1 mol dm^{-3}.

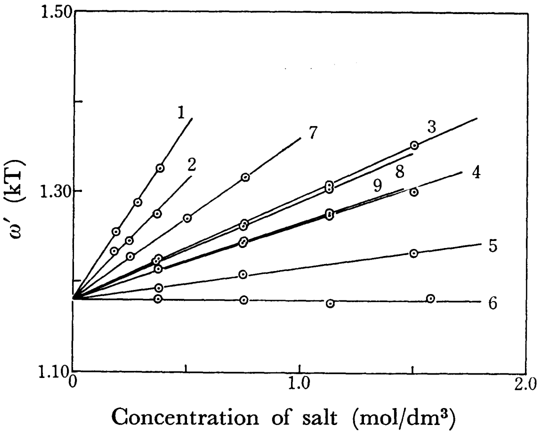

Fig. 2. The plots of ω' against the concentration of salts at 20 °C.
(1) Na_2SO_4, (2) $NaIO_3$, (3) NaCl, (4) NaBr, (5) NaI, (6) NaSCN, (7) $MgCl_2$, (8) KCl, (9) LiCl.

Table 2. Calculated salt-effect parameters of methylene and hexaoxyethylene groups for nonionic surfactants' micellization at 20 °C

Salt	k_{CH_2} (dm³/mol)	$k_{p,m} - k_{p,2}$ (dm³/mol)
Na_2SO_4	0.17_0	0.76_2
$NaIO_3$	0.11_6	0.51_2
NaCl	0.05_0	0.17_4
NaBr	0.03_6	0.07_4
NaI	0.01_5	-0.01_3
NaSCN	0.00_0	-0.18_4
KCl	0.04_8	0.18_2
LiCl	0.03_7	0.16_9
$MgCl_2$	0.07_9	0.36_0

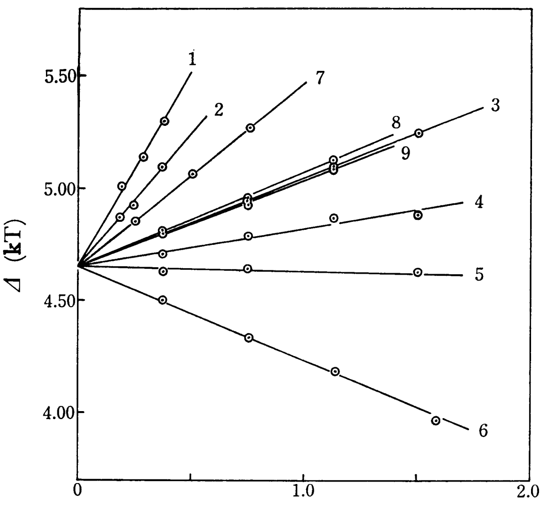

Fig. 3. The plots of Δ' against the concentration of salts at 20 °C.
(1) Na_2SO_4, (2) $NaIO_3$, (3) NaCl, (4) NaBr, (5) NaI, (6) NaSCN, (7) $MgCl_2$, (8) KCl, (9) LiCl.

eters are tabulated in Table 2. As may be seen from Table 2, the salt effect on the hydrophilic moiety during micellization is found not to cancel out; *i.e.*, $k_{p,m}-k_{p,2}\neq 0$. The positive value of $k_{p,m}-k_{p,2}$ means that $k_{p,m}>k_{p,2}>0$. That is, a salting-out effect occurs on the hydrophilic moieties in the monomer and micelle states, and the extent of the effect on the micelle is greater than that on the monomer state. This salting-out effect, $k_{p,m}-k_{p,2}>0$, contributes to raising the CMC, as can be seen from Eqs. 7 and 7b. Therefore, in this case, the CMC lowering is caused by the salting-out effect on the hydrocarbon moiety, $k_{CH_2}>0$, which overcomes the $k_{p,m}-k_{p,2}>0$ effect from Eqs. 7 and 7a. On the contrary, the negative $k_{p,m}-k_{p,2}$ means that $k_{p,m}<k_{p,2}<0$; *i. e.* it is a salting-in effect, which contributes to lowering the CMC. Especially in the solution containing sodium thiocyanate, the CMC lowering is attributable to the salting-in effect on hydrophilic moieties, because the value of k_{CH_2} is nearly zero. As has been mentioned above, the various modes for the salt effect on the micelle formation are shown according to the kind of salts.

In addition, two features are found in Table 2; (1) the salt effects on the hydrocarbon and hydrophilic moieties give the same order with respect to the relative efficiency, and (2) the variation in the extent of the salt effect with respect to the anion is larger than that with respect to the cation. By considering the above two features, the salt effect can be explained qualitatively as follows. In the case of sodium salts, the order of the salt effect follows the Hofmeister series or the order of the water-structure-making or -breaking capacity of salts.[23–26] That is, the more strongly water-structure-making salt gives the greater, positive *k*-value, whereas the more strongly water-structure-breaking salt gives the smaller, negative *k*-value. Water molecules are oriented around the water-structure-making ions, which leads to the reduction of the hydrophobic or hydrophilic hydration of the surfactants as a salting-out effect. On the contrary, the water-structure-breaking ions increase the ratio of monomeric water molecules in the bulk and promote the hydration of the surfactants as a salting-in effect. However, the second feature suggests another source for the salt effect. The following fact is suggestive in considering the second tendency; an air– or hydrocarbon–water interfacial tension is increased by the kind of anion to a greater extent than in the case of cations.[12,27–30] This fact shows that cations are almost completely excluded from an air– or hydrocarbon–water interface because of their requirement for hydration, whereas the less hydrated anions exhibit a large variation in the degree of their exclusion, and may even be concentrated at the interface. This situation may be applied to the exclusion of ions from the water region around the hydrocarbon moiety of a surfactant. That is, the more weakly hydrated anions are excluded to a less extent and then directly disturb the hydrophobic hydration around hydrocarbon moieties to a greater extent, which leads to salting-out. On the contrary, the more strongly hydrated anions are excluded to a greater extent and so exhibit a less direct effect on hydration. Cations also exhibit a less direct effect. As a result of the two factors inferred from the above two features, (1) and (2), the more strongly water-structure-making (more strongly hydrated) anions and cations have, for the most part, an indirect salting-out effect. The more strongly water-structure-breaking (more weakly hydrated) anions have an indirect salting-in and a direct salting-out effect, which cancel each other out for the most part in the overall salt effect, *e.g.*, $k_{CH_2}\simeq 0$ for sodium thiocyanate. As for the water region near the polar poly(oxyethylene) moiety of a surfactant, ions will be less excluded from this region than in the case of the water region near the hydrocarbon moiety. The weakly hydrated anions, *e.g.*, thiocyanate and iodide anions, may even be concentrated in this region; especially, the magnesium cation forms an oxonium compound with the lone-pair electrons of ether oxygen atoms in the poly(oxyethylene) moiety[31] to cause salting-in. It may be because of these factors that we find the experimental $k_{p,m}-k_{p,2}<0$ for sodium thiocyanate and iodide, and the large difference between the value of $k_{p,m}-k_{p,2}$ for magnesium chloride and that for sodium sulfate, in which the two salts have nearly equal water-structure-making capacities. As we have mentioned, the salt effect includes two types of effects on the hydrophobic and hydrophilic hydration of surfactants: the direct effect by the accessibility of ions to the water region near the monomers and the micelles, and the indirect effect.

Salt Effect on Cloud Points and Solubilization. The cloud points of 1 wt% $C_{12}E_6$ in aqueous salt solutions were measured; results similar to those reported in the literature were obtained.[2,31–34] Cloud points can be regarded as a measure of the affinity of the oxyethylene groups in a nonionic surfactant for the water environment.[35] Then, the limiting slope in the plots of the cloud point *vs.* the salt concentration, $\lim_{C_s\to 0}(\mathrm{d}\,CP/\mathrm{d}C_s)$, may be regarded as the variation of this affinity by salt. These slopes are plotted in Fig. 4 against the values of $k_{p,m}-k_{p,2}$ for various salts. The plots give

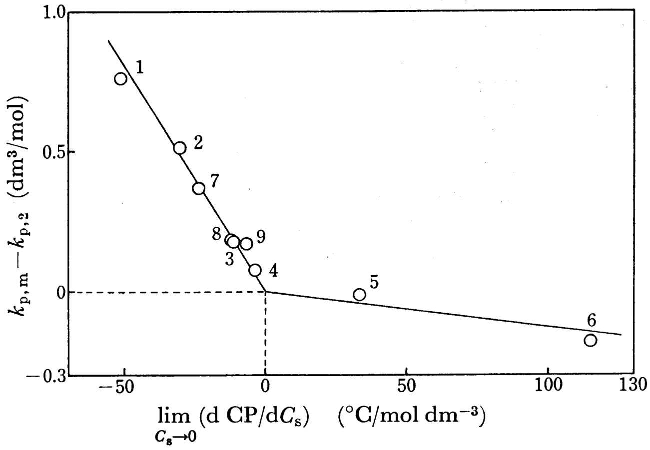

Fig. 4. $k_{p,m}-k_{p,2}$ *vs.* $\lim_{C_s\to0}$(d CP/dC_s) plots for various salts.
(1) Na_2SO_4, (2) $NaIO_3$, (3) NaCl, (4) NaBr, (5) NaI, (6) NaSCN, (7) $MgCl_2$, (8) KCl, (9) LiCl.

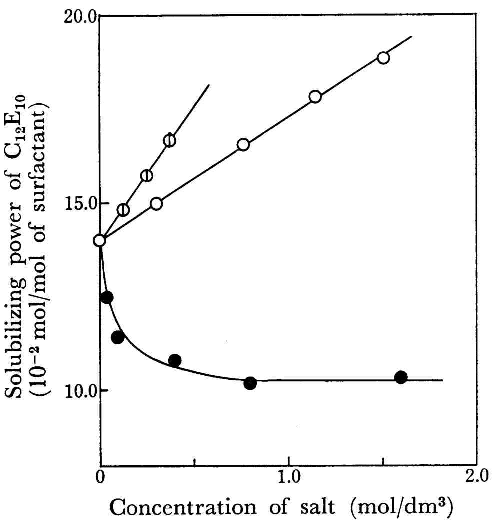

Fig. 5. Solubilizing power of $C_{12}E_{10}$ in aqueous salt solutions at 30 °C.
(⦶) Na_2SO_4, (○) NaCl, (●) NaSCN.

two straight lines, which cross at the point that $\lim_{C_s\to0}$(d CP/d C_s)$=k_{p,m}-k_{p,2}=0$ and which divide the salts into the two groups, salting-out and -in. From the discussion in the previous section, this correlation shows that the strengthening or weakening of the affinity of oxyethylene groups for the water environment by salts is brought about through the promotion or reduction of the hydration of oxyethylene groups respectively. The strengthening of the affinity is also caused by the ion concentration in the water region near oxyethylene groups.

Next, the amount of solubilization toward Yellow OB was determined at 30 °C in the aqueous $C_{12}E_{10}$ solutions containing sodium chloride, sulfate, and thiocyanate; it was found to increase linearly with the concentration of $C_{12}E_{10}$. The slopes of the lines, referred to as the solubilizing power,[36] are plotted in Fig. 5 against the concentrations of three representative salts. It may be found from Fig. 5 that the salts exhibiting a salting-out or -in effect on oxyethylene groups give an increased or decreased solubilizing power respectively with the salt concentration as compared with that in the salt-free solution. The solubilizing power depends sensitively on the compactness of the poly(oxyethylene) shell of the micelle,[18,36] and so the following explanation is possible. The oxyethylene groups on the micelle cohere as a result of the weakening of the hydration of these groups, and then this increased compactness brings about the increased solubilizing power. On the contrary, the enhancement of the hydration of the oxyethylene groups on the micelle leads to a decreased compactness, which causes a decrease in the solubilizing power.

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