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Counter Ion Release of Ionic Surfactant Micelles Induced by Solubilized Amphiphiles: Size Effect of a Polar Head Group

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The acceleration rate ($d\alpha/dX_{am}$) of the dissociation degree (α) of ionic SDS micelles to the mole fraction (X_{am}) of solubilized additives has been determined at infinite dilution by a differential conductivity method. The additives used were a homologous series of amphiphiles with different types of polar groups: alkylglucosides, MEGAs, diols, and cyclooctanol. The method allows us to determine the partition coefficient between the bulk water and the micelles (K_x) and the rate of depression (C_{sf}/C_{af}) of the monomer surfactant concentration (C_{sf}) to the monomer additive (C_{af}), in addition to $d\alpha/dX_{am}$. The results are as follows: (1) $d\alpha/dX_{am}$ in each homologous series is independent of the alkyl chain length, indicating a characteristic value of each polar group. (2) $d\alpha/dX_{am}$ increases with increasing molecular weight of the groups, representing the size effect on the counter ion dissociation. (3) For diols, $d\alpha/dX_{am}$ is higher than twice that of 1-alkanols, due to a large effective size. (4) K_x is dependent on the alkychain length, but independent of the polar group types, indicating that the net charge on the surface of the micelles remains unaltered by solubilization. (5) (C_{sf}/C_{af}) determined above cmc is identical with the cmc decreasing rate, $\Delta\mathrm{cmc}/\Delta C_a$, at cmc.

Controlling the electric charge on colloid particles is of great interest concerning the stability of colloid systems in industrial areas, such as condensational precipitation and basic science. The amount of charge induced by counter-ion dissociation on a colloid particle is considered to be a function of its surface charge density. So far, some studies on the relation have been carried out. As for linear rod-like polyelectrolytes, the function was studied by Manning.[1] In the case of a spherical hard electrolyte (dendrimers), the effective charge depends on the generation, i.e., the size.[2] For aggregation colloids of micelles, the following observations have been reported. In an oligomer surfactant, which consists of some ionic surfactants with their head groups linked by a spacer comprising a hydrocarbon chain, the ionization degree of micelles is higher with a longer chain spacer, and independent of the length of tail.[3] When a trace of alkanols is added to an ionic surfactant micellar solution, the concentration of free counter-ion increases through solubilization.[4] Another observation is that a polyelectrolyte forms complex with an ionic surfactant of, not a monomer, but of mixed micelles with non-ionic surfactant only when the mixed micelle attains to a critical composition.[5] These results indicate the possibility of controlling the net charge by changing the surface charge density. Thus, comprehensive studies on the surface charge density, not only theoretical, but also experimental studies [6] are desired. For such studies, the mixed micelles of ionic and non-ionic surfactants are useful in which the surface charge density can be varied with the composition.[6]

In a previous study on a system of SDS-isomeric alkanols[7] including 1-alkanols,[8] it was found that the OH group solubilized in ionic micelles of SDS accelerates the ionization degree (α) of micelles, and that the rate evaluated as $d\alpha/dX_{am}$ (X_{am}: additive mole fraction in micelles) had neither a dependence on the alkyl-chain length nor even the molecular structure (branching) of homologous isomeric alkanols at a limiting dilution. This fact suggests that individual polar head groups of an amphiphile has its own effective size for reducing the surface charge density. The correlation between the size and $d\alpha/dX_{am}$ for various types of polar moiety provides an advantageous series which is useful for the molecular designing of colloid systems. In the present study, it was attempted to construct a series of $d\alpha/dX_{am}$.

In order to determine X_{am} at infinite dilution of solubilizate, the partition coefficient between the bulk water and the micelles is essential. So far, many methods have been applied to determine the partition coefficient.[9] Manabe et al.[8] developed a unique method, a differential conductivity method, by which $d\alpha/dX_{am}$ can be evaluated in addition to the partition coefficient, as well as the other quantity, dC_{sf}/dC_{af}, the decreasing rate of the monomer concentration of the surfactant (C_{sf}) to the additive (C_{af}). The relation among these quantities has been discussed for elucidating the solubilization mechanism.

Experimental

Materials. Sodium dodecyl sulfate (SDS) was synthesized and purified by the usual method. No minimum was detected on the surface tension–concentration curve of the SDS solution.

As additives, the following substances were used as purchased: *N*-methyl-*N*-octanoylglucamide (MEGA-8: Dojindo Lab.), *N*-methyl-Nonanoylglucamide (MEGA-9: Dojindo Lab.), hexyl-β-D-glucopyranoside (> 98%: Sigma), heptyl-β-D-glucopyranoside (98%: Sigma), octyl-β-D-glucopyranoside (> 98%: Dojindo Lab.), octyl-α-D-glucopyranoside (> 98%: Sigma), Cyclooctanol (> 98%: Tokyo Kkasei), 1,8-Octanediol (> 99%: Tokyo Kasei), 1,9-nonanediol (> 98%: Tokyo Kasei), 1,10-decanediol (Kanto Chemical).

Conductivity Measurements. Conductivity measurements of SDS solution containing small amounts of additive were made on a LCR meter (HP, 4284A) at 25.0 ± 5/1000 °C, by using a titration-type conductivity cell with a cell constant of 0.10305 cm^{-1} in the same manner as in previous studies.[7,8] For determining the counter-ion releasing rate, $\mathrm{d}\alpha/\mathrm{d}X$, in addition to the partition coefficient (K_x) of the additive in an SDS micellar solution, the specific conductivity was measured as a function of the additive concentration (C_a) under a constant SDS concentration (C_s).

Contrary to this procedure, for determining the critical micelle concentration (cmc), of SDS in the presence of an additive, C_s was variable at a given C_a. Cmc was determined as C_s at the break point on the curve of $\mathrm{d}\kappa/\mathrm{d}C_s$ vs the square root of C_s.[8]

Results and Discussion

Determination of Characteristic Quantities. The specific conductivity (κ) of an SDS micellar solution with a certain concentration (C_s) was determined as a function of the concentration (C_a) of nonionic amphiphiles. The κ depends on C_a in the following aspect, as illustrated elsewhere in the systems of sodium alkyl sulufates-1-alkanols.[8,10] When C_s is sufficiently low, just above cmc_o (cmc of SDS itself), κ tends to decrease most steeply with C_a, whereas κ tends to increase with C_a when C_s is high. That is to say, the decreasing tendency becomes less remarkable with increasing C_s, and turns to an increasing one. As long as C_a is low enough, the κ–C_a curve can be regarded as being linear, and a differential conductivity denoted by $(\mathrm{d}\kappa/\mathrm{d}C_a)_o$ is determined as the limiting slope.

The obtained $(\mathrm{d}\kappa/\mathrm{d}C_a)_o$ for homologous β-alkyl glucosides is plotted against C_s in Fig. 1. It is apparent that each curve changes asymptotically from negative to positive, and that the change is more rapid for a longer chain derivative. The relation in Fig. 1 allows us to determine the partition coefficient of an nonionic additive between the bulk water and micelles of an ionic surfactant by applying a differential conductivity method developed by Manabe et al.[8] In Appendix, an outline of the method is described quantitatively by mathematical expressions together with some notations of significant quantities: the rate of increasing ionization degree of ionic micelles $(\mathrm{d}\alpha/\mathrm{d}X_{am})$ and the decreasing rate of monomeric surfactant concentration by the additive ($k = \mathrm{d}C_{sf}/\mathrm{d}C_{af}$).

In the deriving equations in Appendix, two opposing factors, increasing and decreasing the conductivity, are taken into account for explaining the concentration dependence of conductivity in Fig. 1, along with the following consideration. When a small amount of polar substance is added in the micellar solution of an ionic surfactant, the additive is partitioned between the bulk water phase and the ionic micellar one, based on the charged phase-separation model of micelle formation.[11,12] The portion of additive dissolved monomerically (concentration: C_{af}) in the bulk phase depresses the concentration of the monomerical surfactant (C_{sf}) at rate of $\mathrm{d}C_{sf}/\mathrm{d}C_{af}$ (= k defined in Eq. (A-6)) by a hydrophobic interaction. In the process, completely ionized free monomer surfactant ions are micellized to associate with a counter ion. As a result, κ decreases with C_a, i.e., $(\mathrm{d}\kappa/\mathrm{d}C_a)_o < 0$. The decrease is most remarkable just at cmc_o, where the entire amount of additive dissolves monomerically ($J \rightarrow 0$, Eq. (A-6)) and $(\mathrm{d}\kappa/\mathrm{d}C_a)_o \rightarrow (\bar{\kappa}_f - \bar{\kappa}_m)\,k$ in Eq. (A-8). Another factor also contributes to the increase in conductivity: $(\mathrm{d}\kappa/\mathrm{d}C_a)_o > 0$. The other portion of the additive is incorporated in micelles and the polar group of the additive is located in the surface of the micelles to enhance the ionization of micelles by reducing the surface charge density. Then, κ increases with C_a, i.e., $(\mathrm{d}\kappa/\mathrm{d}C_a)_o > 0$. The factor contributes most effectively at $C_s \rightarrow \infty$ ($J \rightarrow 1$) and $(\mathrm{d}\kappa/\mathrm{d}C_a)_o \rightarrow (\mathrm{d}\alpha/\mathrm{d}X_{am})\,\bar{\kappa}_m{}^*$ in Eq. (A-8).

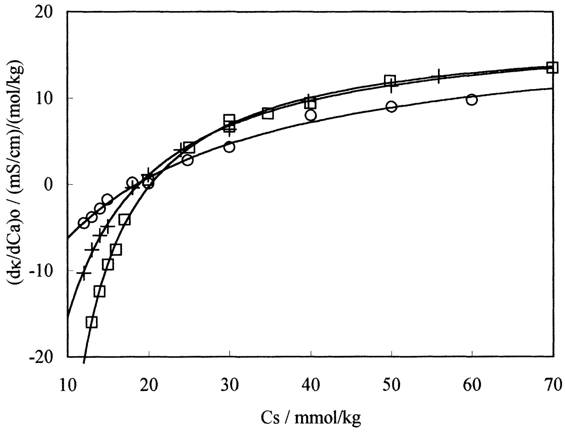

Fig. 1. Relation between differential conductivity on the addition of homologous β-glucosides and SDS concentration. Carbon number in alkyl-chain: ○: 6, +: 7, □: 8.

Respective factors are antagonistic in the conductivity at any C_s. The extent of each contribution is decided by K_x or J, which are correlated by Eq. (A-7). In order to evaluate the three significant quantities, $(\mathrm{d}\kappa/\mathrm{d}C_a)_o$ is expressed in the form of a linear function given in Eq. (A-8). According to Eq. (A-8), the asymptotic relation in Fig. 1 is converted into a linear one with J, as given in Fig. 2. The linear relation is obtained by a regressive analysis for K_x as an adjustable parameter. Respective intercepts, $J = 0$ and 1, lead to k and $(\mathrm{d}\alpha/\mathrm{d}X_{am})$ by using the values of the differential conductivity of SDS, itself: $\bar{\kappa}_f$, $\bar{\kappa}_m$, and $\bar{\kappa}_m{}^*$ in Appendix. The obtained values are listed in Table 1, together with those in the systems of SDS-1-alkanols,[7,8] for a comparison.

Dependence of $\mathbf{d}\boldsymbol{\alpha}/\mathbf{d}\boldsymbol{X}_{\mathbf{am}}$ on the Molecular Weight of Polar Group. It should be noted that the straight lines of a series of homologues cross each other at $J = 1$, whereas the slope becomes steeper with increasing alkyl-chain length. The crossing suggests that $(\mathrm{d}\alpha/\mathrm{d}X_{am})$ is the intrinsic value of an individual polar head group, independent of alkyl chain in accordance with the result of 1-alkanols.[7,8,10] As can be recognized in Fig. 3, $(\mathrm{d}\alpha/\mathrm{d}X_{am})$ can be regarded as being constant for each homologous series, within the determination uncertainties. The mean value for each series of homologues is given in Table 1, together with the data of 1-alkanols.

From the fact that $(\mathrm{d}\alpha/\mathrm{d}X_{am})$ is positive for each polar group, it can be reasonably deduced that the incorporation of a polar group in the surface region of ionic micelles reduces the surface charge density, resulting in an acceleration of the

Table 1. Characteristic Values of Non-Ionic Amphiphiles Added in SDS Micellar Solution

Substance[a)]	Mwt[b)]	$10^{-2}\ K_x$[c)]	$-k$[d)]	$-\Delta\mathrm{cmc}/\Delta C_a$	$\mathrm{d}\alpha/\mathrm{d}X_{am}$	av[e)]
cAc8	17	36.0	0.472	0.56	0.246	0.246
Dio8	34	22.9	0.249	0.39	0.421	
Dio9	34	67.9	0.802	0.56	0.401	0.410
Dio10	34	255	2.60	1.97	0.409	
βGlu6	179	24.5	0.216	0.27	0.286	
βGlu7	179	66.2	0.608	0.60	0.290	0.285
βGlu8	179	184	1.84	1.56	0.280	
αGlu8	179	140	1.71	1.80	0.314	0.314
MEG7	222	74.3	0.751	0.95	0.441	0.429
MEG8	222	134	1.96	3.0	0.417	
*n*Ac4	17	3.61	0.0293	0.028	0.151	
*n*Ac5	17	9.44	0.0796	0.078	0.187	
*n*Ac6	17	24.4	0.240	0.21	0.172	0.160
*n*Ac7	17	64.4	0.669	0.53	0.159	
*n*Ac8	17	163	1.65	1.65	0.133	

a) cAc (cycloalkanol), Dio (alkandiol), α,βGlu (α- or β-glucoside), MEG (MEGA), *n*Ac (l-alkanol). The number in notation indicates carbon number in alkyl chain. The data for l-alkanols are taken from Ref. 7. b) Molecular weight of polar head group. c) Partition coefficient. d) $k = C_{sf}/C_{af}$. e) Average of $\mathrm{d}\alpha/\mathrm{d}X_{am}$ for each series of homologues.

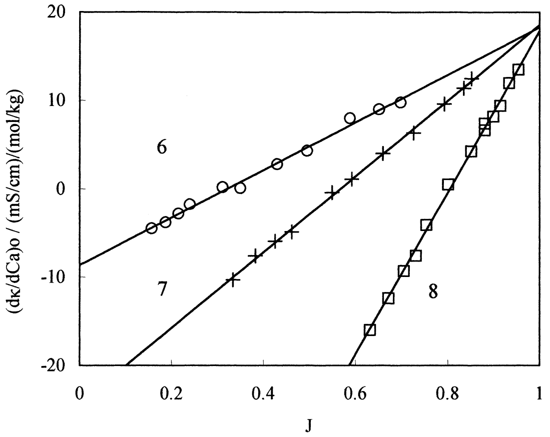

Fig. 2. Linear relation of differantial conductivity with solubilization fraction (*J*) in the system of SDS–β-glucosides. The number indicates the carbon number in alkyl-chain of glucosides.

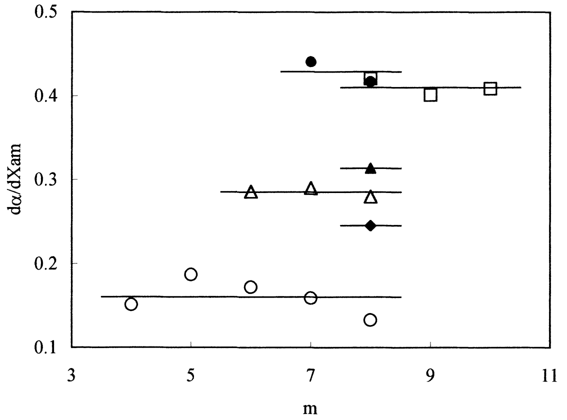

Fig. 3. Dependence of ionizing rate by homologous additives ($\mathrm{d}\alpha/\mathrm{d}X_{am}$) on alkyl-chain length (*m*). Refer to Table 1 for the 1 for the abbreviations of additives: ○ nAc, ◆ cAc, △ βGlu, ▲ αGlu, □ Dio, ● MEG.

counter-ion dissociation. Along with this explanation, the cross-sectional area of the polar group can be considered to be a determining factor. It is difficult, however, to consistently assign a reasonable size for each group. Therefore, the molecular weight of the head group is inevitably adopted as a parameter for size; and the relation between ($\mathrm{d}\alpha/\mathrm{d}X_{am}$) and the molecular weight is shown in Fig. 4.

It is apparent that for straight-chain homologues with a single polar group (1-alkaols, glucosides, and MEGAs) $\mathrm{d}\alpha/\mathrm{d}X_{am}$ tends to increase with the molecular weight, consistent with the expected size effect. Some other significant observations are appreciated from a more careful survey of the plot in Fig. 4. The difference between the α- and β-alkyl glucosides is regarded to be slight. It is known that the molecular structure difference between them in the solid state is that glucose attaches to the alkyl-chain at a sharp angle for α-glucosides, although the chain becomes straight for β-glucosides, as diagramed in a paper.[13] The structure implies that the effective size of the polar group of α-glucosides must be larger than the β-glucosides. Accordingly, the slight difference of ($\mathrm{d}\alpha/\mathrm{d}X_{am}$) can be attributed to a free rotation of the link in the solubilized liquid state.

For the OH group of cyclooctanol, ($\mathrm{d}\alpha/\mathrm{d}X_{am}$) is higher than that in 1-alkanols. As mentioned below in Fig. 6, the K_x of cy-

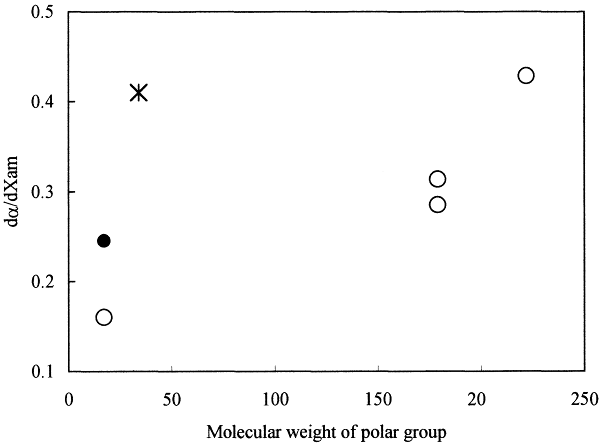

Fig. 4. Relation between ionization rate by homologous additives ($d\alpha/dX_{am}$) and molecular weight of head group of additive. Refer to Table 1 for the abbreviations of addotives. ○ mono-group additives (nAc, Glu, MEG), ● cAc, ✳ Dio.

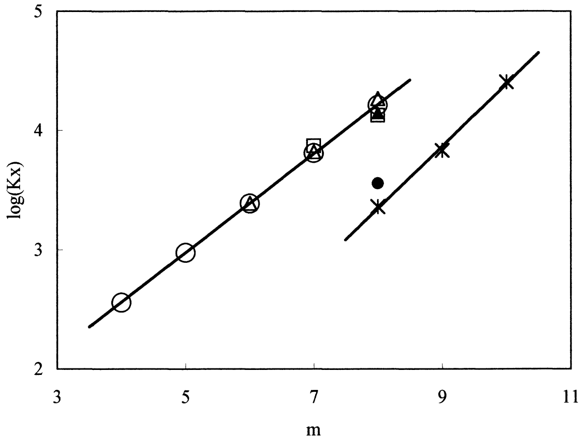

Fig. 5. Dependence of partition coefficient of homologous additives on their carbon number in alky-chain (*m*). Refer to Table 1 for the abbreviations of additives:○ nAc, △ *β*Glu, □ MEG, ▲ *α*Glu, ● cAc, ✳ Dio.

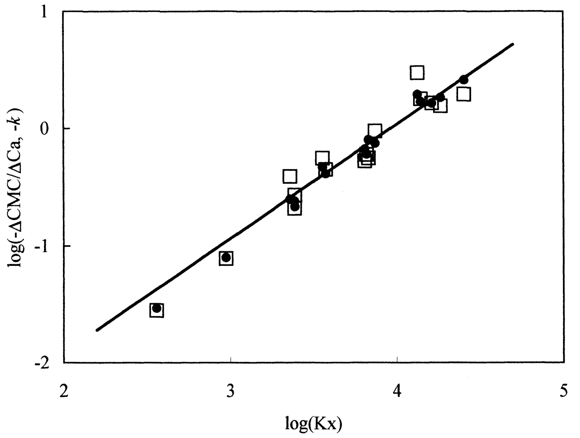

Fig. 6. Dependence of both $\Delta cmc/\Delta C_a$ and *k* on K_x. Closed mark ($\Delta cmc/\Delta C_a$), open mark (*k*),

clooctanol is lower than octane derivatives bearing a single polar group, in line with the fact that the isomerization of alkanols weakens their hydrophobicity.[7,14] Both facts imply a solubilization model in which a part of the ring wedges in the surface region to reduce the surface charge density more effectively than the OH group alone.

It is worth mentioning that ($d\alpha/dX_{am}$) of glycols is higher than twice that of 1-alkanols, close to MEGAs. Such a high value suggests a solubilization model of glycols: some central part of the hydrocarbon-chain in a glycol molecule is wedged in the polar region of a micelle, and the two OH groups left in the polar surface region occupy, not independently, but cooperatively an effectively wide area with the exclusion of any ionic head groups.

Dependence of K_x on m. The relation between K_x and m is given in Fig. 5 in semilogarithmic form. It is obvious that in each homologous series the relation is linear and parallel to each other, in determination uncertainties, not only the monohead group derivatives, but also the di-head group ones (diols). The free energy of transfer per methylene group from water to micelles is evaluated as $\Delta G°(CH_2) = -RT\Delta \ln K_x/\Delta m$, from each pair of the nearest neighbor *m* of the homologues. The averaged value of $\Delta G°(CH_2)$, including the values for dilos, is around -2.4 kJ/mol, which is consistent with the values in corresponding processes.[15,16] This finding is compatible with the reported result that $\Delta G°(CH_2)$ ($=-2.46$ kJ/mol) of diols longer than $m = 6$ agrees with that of 1-alkanols longer than $m = 4$, determined from the quantity of $\Delta cmc/\Delta C_a$.[17] It is concluded that in the present homologous additives, some CH_2 groups in such a long the hydrocarbon-chain are solubilized in the same mechanism.

It is astonishing that the values of K_x for different series of homologues bearing a mono-head group (alkanols, glucosides, and MEGAs) agree with each other, at $m = 7$ and 8 in Fig. 5, where the hydrophobic part is assigned based on the molecular structure in such a simple way as the alkyl-chain length. This fact indicates that K_x does not depend on the type of polar head groups, whereas $d\alpha/dX_{am}$ depends on it (Fig. 4). An appropriate explanation for the independence of K_x is that the electrostatic contribution to the free energy of transfer is not influenced by the polar group, but remains constant in the solubilizing process. In other words, the constancy of the electrostatic term, such as the surface charge density and the surface potential, might be held in the manner that the polar group located in the surface region of ionic micelles decreases the surface charge density, but the decrease is compensated by a further dissociation of counter ions to maintain the same surface charge density. This mechanism may be valid, at least at very low C_a.

Relation of *k* and $\Delta cmc/\Delta C_a$ with K_x. It can be recognized from Table 1 and Fig. 6 that for each additive, *k* is in good agreement with $\Delta cmc/\Delta C_a$, which stands for the cmc decreasing rate on the addition of an additive, estimated as the limiting slope of the cmc–C_a curve. On the other hand, *k*, defined as Eq. (A-6), is the corresponding rate in the bulk water in a micellar solution. The identity reveals that the interaction between different monomerically dissolving species (surfactant and additive) at cmc remains the same way even to far above than cmc, as long as $C_a \to 0$.

The interaction may be due to a hydrophobic one, which also contributes to K_x. Manabe et al.[18] discussed the relation between $\Delta\mathrm{cmc}/\Delta C_a$ and K_x, related as

$$-\Delta\mathrm{cmc}/\Delta C_a = \theta\,(\mathrm{cmc_o}/n_w)\,K_x, \tag{1}$$

based on the data from a system of SDS-1-alkanols. Here, θ[19,20] is a constant concerning the activity coefficients of all coexisting species, and n_w refers to the mole number of water in 1 kg of aqueous solution. In the present study, the values for different types of homologues from 1-alkanols[8] were determined. Then, the validity of Eq. 1 was confirmed by using the data of $-\Delta\mathrm{cmc}/\Delta C_a$, k and K_x shown in Table 1, for all additives studied here. $-\Delta\mathrm{cmc}/\Delta C_a$ together with $-k$ was plotted against K_x in log-log form (Fig. 6). The linear relation determined by the least-squares method applied to the data, except for short chain 1-alkanols ($m = 4, 5$), was obtained as

$$\log\,(-\Delta\mathrm{cmc}/\Delta C_a, -k) = 0.99551\log\,(K_x) - 3.866, \tag{2}$$

where the intercept gives $\theta = 0.97$, although $\theta = 0.46$ if short derivatives are involved. This is very close to the expression in the ideal form of $\theta = 1$, at which the slope is unity and the intercept is -3.85 ($= \log\,(0.0078/55.5)$). The present result suggests a possibility that such solubilization systems behave ideally in thermodynamics as long as there is at infinite dilution of the additives, since the electrostatic contribution remains unaltered by the addition of nonionic substances.

Appendix

A differential conductivity method exists for determining partition coefficient of nonionic substances in an ionic surfactant micellar solution.[8]

The concentrations (C) of a surfactant ($_s$) and an additive ($_a$) in free monomer ($_f$) and micellar ($_m$) states are related as

$$C_s = C_{sf} + C_{sm}\ ;\ C_a = C_{af} + C_{am}. \tag{A-1}$$

The differential conductivity ($\bar{\kappa}$) of free monomer and micellar surfactant species of an ionic surfactant are defined by differentiating the specific conductivity (κ) with the concentration of the respective species of the surfactant:

$$\bar{\kappa}_f = \mathrm{d}\kappa/\mathrm{d}C_{sf},\ \bar{\kappa}_m = \mathrm{d}\kappa/\mathrm{d}C_{sm}. \tag{A-2}$$

Here $\bar{\kappa}_f$ and $\bar{\kappa}_m$ are the differential conductivities below and above cmc, respectively. Then, the κ of a micellar solution can be expressed as a linear combination of the differential conductivity and the concentration of the respective species,

$$\kappa = \bar{\kappa}_f C_{sf} + \bar{\kappa}_m C_{sm}. \tag{A-3}$$

When a small amount of a non-ionic substance is added in a micellar solution with a given C_s, the rate of conductivity change represented in the form of ($\mathrm{d}\kappa/\mathrm{d}C_a$) can be derived by differentiating Eq. (A-3) with C_a under the condition of a constant C_s,

$$\begin{aligned}\mathrm{d}\kappa/\mathrm{d}C_a = {} & \bar{\kappa}_f(\mathrm{d}C_{sf}/\mathrm{d}C_a) + \bar{\kappa}_m(\mathrm{d}C_{sm}/\mathrm{d}C_a)\\ & + (\mathrm{d}\bar{\kappa}_m/\mathrm{d}C_a)C_{sm}.\end{aligned} \tag{A-4}$$

In the derivation, the term of ($\mathrm{d}\bar{\kappa}_f/\mathrm{d}C_a$) can be neglected from the experimental result. Further, $\bar{\kappa}_m$ is taken to be correlated with the degree of the counter-ion dissociation of the micelles (α),

$$\bar{\kappa}_m = \alpha\,\bar{\kappa}_m{}^*, \tag{A-5}$$

where $\bar{\kappa}_m{}^*$ is a hypothetical differential conductivity of completely ionized micelles with $\alpha = 1$.

Now, the following quantities are defined as the partition coefficient (K_x) of the additive in the mole-fraction unit, the decreasing rate of the monomer surfactant (k), and the solubilization fraction (J):

$$K_x = X_{af}/X_{am},\ \ k = \mathrm{d}C_{sf}/\mathrm{d}C_{af}\ ,\ \ J = \mathrm{d}C_{am}/\mathrm{d}C_a. \tag{A-6}$$

Under the condition $C_a \rightarrow 0$, the following approximations can be valid:

$$J = (K_x/n_w)(C_s - \mathrm{cmc_o})/(1 + (K_x/n_w)\,(C_s - \mathrm{cmc_o})), \tag{A-7}$$

where n_w and $\mathrm{cmc_o}$ stand for the mole number of water in one kg of solution, and the cmc of the ionic surfactant, itself, respectively. Eq. (A-7) allows us to calculate J at any C_s when K_x can be estimated. As a result, Eq. (A-4) can be rewritten by using the above quantities at infinite dilution of the additive,

$$\begin{aligned}\mathrm{d}\kappa/\mathrm{d}C_a = {} & (\bar{\kappa}_f - \bar{\kappa}_m)k\\ & + \{\bar{\kappa}_m{}^*(\mathrm{d}\alpha/\mathrm{d}X_{am}) - (\bar{\kappa}_f - \bar{\kappa}_m)k\}J,\end{aligned} \tag{A-8}$$

In the right-hand side, only J is a variable. Therefore, Eq. (A-8) indicates that the experimentally determined ($\mathrm{d}\kappa/\mathrm{d}C_a$) at infinite dilution of the additive, expressed as $(\mathrm{d}\kappa/\mathrm{d}C_a)_o$ in the tex, t is a linear function of J. The linear relation can be determined by a regressive analysis for the best fitting of K_x as a parameter. The respective intercepts at $J = 0$ and $J = 1$ of the resultant relation provide k and ($\mathrm{d}\alpha/\mathrm{d}X_{am}$) which indicate the acceleration rate of the ionization of micelles. In an analysis concerning SDS, the following numerical values were adopted: $\bar{\kappa}_f = 65.0$, and $\bar{\kappa}_m = 25.0$ mS cm^{-1} mol^{-1} kg, estimated from experimental data of the differential conductivity curve of an SDS solution, just at $\mathrm{cmc_o}$ and far above $\mathrm{cmc_o}$, respectively. In addition, $\bar{\kappa}_m{}^*$ was postulated to be identical to $\bar{\kappa}_f$. The value of $\mathrm{cmc_o}$ is 7.8 mmol/kg.

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