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Relationship between Solubility and Micellization of Surfactants; Micelle Temperature Range (MTR) Instead of Krafft Point

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In order to clarify the relation between the solubility and micellization of surfactants, the micellar temperature range (MTR) is proposed instead of the usually used Krafft point. The physicochemical meaning of cmc defined by Phillips was examined from a mathematical point of view. As a result, it became clear that the temperature range for MTR is based on the concentration range for cmc, which in turn results from the polydispersity of micelles. The mass-action model of multiple association can be used to explain these facts. The MTR, thus determined by solubility and by cmc, was found to be able to explain a leveling of the MTR for homologous surfactants with an increase of the alkyl chain length and its increase of sodium dodecyl sulfate with increasing concentration of added sodium chloride.

In a previous paper,[1] the authors discussed the dissolution, micellization of surfactants, and solubilization in their aqueous solution from the viewpoint of degrees of freedom based on the phase rule and reached the conclusion that the mass action model for micelle formation can perfectly elucidate the above phenomena of surfactant solutions. It was also found from a series of studies on anionic surfactants with divalent cationic gegenions[2-5] that the Krafft point is not a single point but is a diffuse temperature range which might be called the micelle temperature range (MTR) or the Krafft range.[3] That is, the MTR is a narrow temperature range over which the surfactant solubility as monomer becomes sufficiently high for monomers to start micellization notably; it is consistent with the mass-action model of micelle formation.

Up to now, two concepts have been reported concerning the Krafft point: one is a phase transition at the Krafft point and the other is a solubility increase up to the cmc for micellization at the Krafft point. Recent examples of the former concept are a melting point model of hydrated surfactant solid,[6,7] and the phase transition from a stable coagel to a composite state of gel and micelles.[8] As for the latter, the most direct approach to the Krafft point absolutely rests on the solubility and cmc measurements of surfactants with temperature, as was often pointed out in our preceding papers. From the measurements, the concept of the Krafft point can be made clear.

The authors have studied the effects of both the alkyl chain length of a surfactant ion[3] and the extent of charge separation of divalent genenion on dissolution and micelle formation[5] of surfactants and have concluded that the Krafft point should be replaced by the new term "MTR" of surfactants, which is physicochemically correct. In this study, the technical terms and concepts which had been presented in order to relate the dissolution of surfactants with their micellization are reviewed. Also, it is confirmed that the term "MTR" can be used to successfully elucidate various phenomena concerning the dissolution and micellization of surfactants, not only from a view point of the phase rule but also experimentally.

Progress of Concepts of the Krafft Point

Since 1895, Krafft and Wiglow[9] have worked with soap solutions and have used the term "Ausscheidungstemperatur" which means the temperature at which a new phase separates from the soap solutions upon cooling, colloid chemists have studied the problem with deep concern. Above all, McBain and Elford[10] have studied the potassium oleate-water system and drew a phase diagram in which the minimum temperature at which heterogeneous systems just turned into a homogeneous isotropic liquid was recorded. Also, Lawrence[11] in 1935 called this transition temperature the "Krafft point" for the first time and showed that the Krafft point represents a phase change of the adhesion between hydrocarbon chains throughout the micelle (from solid to liquid). Shinoda and Hutchinson[6]

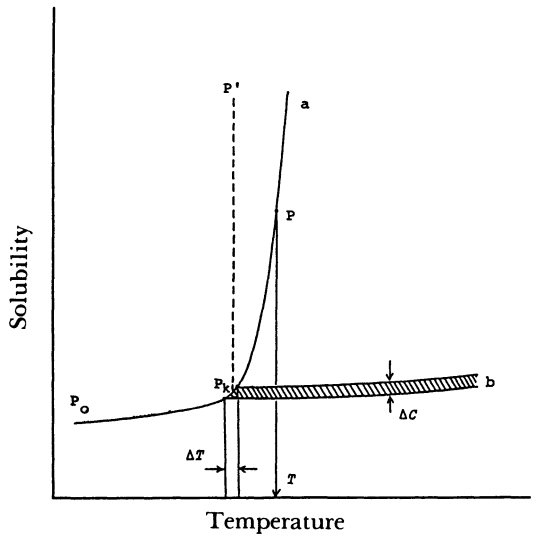

Fig. 1. Changes of solubility and cmc with temperature: (a) solubility curve, (b), cmc curve, ΔC narrow concentration range of cmc, ΔT narrow temperature range of MTR, $P_o \rightarrow P_k \rightarrow P'$ solubility for phase separation model.

presented an interpretation that the Krafft point represented a freezing of micelles or the melting point of a hydrated solid of surfactants; they said "the Krafft point now can be interpreted as a point at which solid hydrated agent and micelles are in equilibrium with monomers: in terms of phase, with two components the equilibrium hydrated solid⇄monomers⇄micelles is univariant, so that at given pressure the point is fixed."

On the other hand, in 1951 Eggenberger and Harwood[12] performed conductometric studies on the solubility and micelle formation of dodecylammonium chloride and found a point on the solubility curve corresponding to a very sharp break in the solubility vs. temperature curve which could be attributed to the "Krafft effect" or a solubilization of the undissociated molecule by the micelle. Significantly, the cmc vs. temperature curve intersected the precipitation curve at this point. Thereafter, a view of the Krafft point seemed to have been established as described in a paper by Phillips,[13] in which the Krafft point was defined as the temperature at which the cmc is equal to the saturation solubility. Alexander and Johnson[14] interpreted the "Krafft phenomenon" as an unusual property in that the solubility of soaps increased enormously over a small temperature range (Krafft point). Other technical terms, "critical solution temperature (cst)[15]" and "critical micellar temperature (cmt),[16]" appeared to designate this characteristic phenomenon.

As mentioned in the above review, the concept of the Krafft point can be divided into two different aspects: a phase transition of solid surfactant and a solubility increase up to cmc for micellization. Then, the Krafft point becomes a definite temperature, a point, for the former concept and a small temperature range for the latter. The existence of two different views concerning the same phenomenon is quite confusing. Therefore, it is very necessary to solve the present conflict.

Physicochemical Meaning of Critical Micelle Concentration (cmc)

The striking characteristic of a surfactant solution is the fact that monomeric surfactant molecules aggregate to form micelles above a certain concentration, leading to an abrupt change in such solution properties as the surface tension, osmotic pressure, intensity of scattered light, electrical conductivity, and so on. The narrow concentration range for these changes is called the critical micelle concentration.[17,18] There have been reported a number of methods for determining the cmc, all of which, of course, depend on abrupt changes in the concentration dependence of several properties of surfactant solutions. Taking the changes into consideration, Phillips defined the cmc as being the concentration corresponding to the maximum change in the gradient in the property-concentration (ϕ-C_t) curve:[13]

$$\left(\frac{d^3\phi}{dC_t^3}\right)_{C_t=cmc}=0 \quad (1)$$

where

$$\phi=\alpha[S]+\beta[M] \quad (2)$$

α and β are proportionality constants, and [S] and [M] are the concentrations of the monomeric surfactant and the micelle, respectively. In reality, however, the property of a solution can not be expressed so simply as in Eq. 2, although Eq. 1 is correct.

Suppose that a surfactant molecule ($G_{\nu_g}S_{\nu_s}$) is composed of ν_g counterions (G) with charge z_g and ν_s surfactant ions (S) with charge z_s. For the electrical neutrality condition to be satisfied,

$$z_g\nu_g+z_s\nu_s=0 \quad (3)$$

As is well-known, micelles are not monodisperse but polydisperse; thus, the following equilibria between counterions and surfactant ions can be given for micellization:

$$\begin{aligned} m_1G+n_1S &\overset{K_1}{\rightleftharpoons} M_1 \\ m_2G+n_2S &\overset{K_2}{\rightleftharpoons} M_2 \\ &\cdots\cdots\cdots\cdots \\ m_iG+n_iS &\overset{K_i}{\rightleftharpoons} M_i \end{aligned} \quad (4)$$

Also, the electroneutrality of a solution holds:

$$z_g[G]+z_s[S]+\sum_i(z_gm_i+z_sn_i)[M_i]=0 \quad (5)$$

where the brackets refer to the concentration of chemical species. From Eq. 4 the micellization constant can be written as

$$K_i=[M_i]/([G]^{m_i}[S]^{n_i}) \quad (6)$$

It is important at present to examine the number of degrees of freedom using Gibbs' phase rule ($f=C-P+2-r$) for the succeeding discussion. The total number of components (C) is $i+3$ (solvent, G, S, M_1, M_2, $\cdots$ M_i), the number of phases (P) is one (surfactant solution), and the number of equilibrium equations (r) is $i+1$ (Eqs. 5 and 6). Therefore, the degrees of freedom becomes three, and the total surfactant concentration (C_t) determines the concentrations of every chemical species at constant temperature and pressure. The mass balance for the counterion and surfactant ion can be expressed, respectively, as

$$\nu_gC_t=[G]+\sum_i m_i[M_i] \quad (7)$$

$$\nu_sC_t=[S]+\sum_i n_i[M_i] \quad (8)$$

From an analogy with Eq. 2 the solution property (ϕ) becomes a composite of the contributions from every chemical species:

$$\phi=\alpha_1[S]+\alpha_2[G]+\sum_i\beta_i[M_i] \quad (9)$$

where α_1, α_2, and β_i are the contribution factors of each chemical species. Their magnitudes depend on the solution properties used for a cmc determination. The solvent contribution is omitted here, since the surfac-

tant concentration is relatively small and the solution property without a solvent contribution is usually employed. Equations 8 and 9 can be rewritten in terms of the concentrations of the monomeric surfactant ion and counterion with the help of Eq. 6;

$$\nu_s C_t = [S] + \sum_i n_i K_i [G]^{m_i} [S]^{n_i} \quad (10)$$

$$\phi = \alpha_1 [S] + \alpha_2 [G] + \sum_i \beta_i K_i [G]^{m_i} [S]^{n_i} \quad (11)$$

From Eqs. 6, 7, 8, and 10, C_t and ϕ turn out to be functions of common variable [S] or [G]. The next step for a cmc determination is to obtain a solution of Eq. 1, in which the derivative of ϕ with respect to C_t can be calculated through a common variable [S]. Then, cmc (C_t) can be automatically determined from the [S] value thus determined. What must be stressed here is that the cmc value determined as a solution of Eq. 1 is a function of the contribution factors: α_1, α_2, and β_i. In other words, cmc depends on the solution property employed for a cmc determination and is naturally different, depending on a method used. Therefore, the cmc turns out to have a value with a narrow concentration range. As a matter of fact, the cmc values obtained from the solution properties mainly due to a monomeric surfactant contribution are less than those due to a surfactant micelle contribution,[17,18,19] as can be seen in Figs. 2a and 2b. In this case random errors are taken into account for the cmc determination methods. For example, the cmc from the surface tension is less than that from turbidity.[20] Contrary to the above expectation, however, the cmc has often come to be presented as a definite concentration,[21,22] especially after the appearance of a phase-separation model for micellization.[6] It is pertinent to

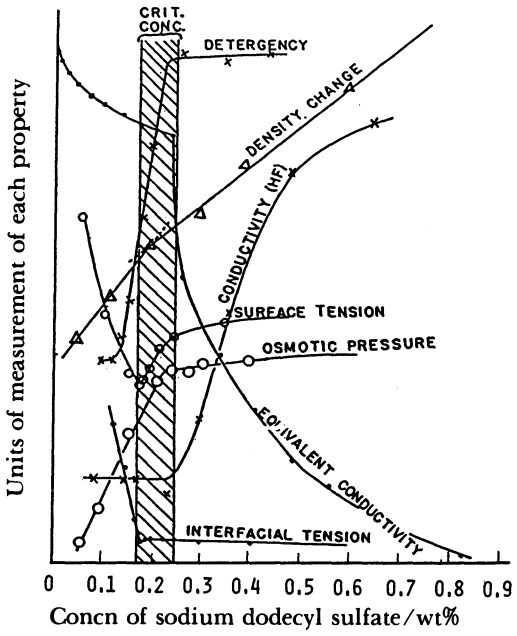

Fig. 2a. Physical property curves for sodium dodecylsulfate. Temperature=25—38°C.[17]

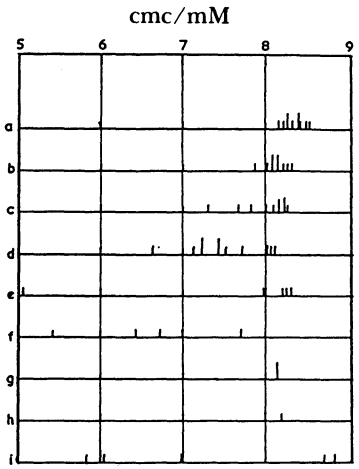

Fig. 2b. Variation of cmc of sodium dodecyl sulfate at temperature between 20 and 30°C by various experimental methods.[19] a) Specific conductivity, b) equivalent conductivity, c) other conductance, d) surface tension vs. logarithm of concentration, e) other relationships between surface tension and concentration, f) absorbance, g) solubilization of OT dye, h) light scattering, i) other methods such as refractive index, emf, vapor pressure, sound velocity, and viscosity.

demonstrate in this paper, therefore, the fact that the cmc can vary for a narrow concentration range in terms of the above discussion.

Monodisperse Micelle of Nonionic Surfactant. The most simplified example is monodisperse micelle of a nonionic surfactant, in which $\nu_g=0$, $z_s=0$, and $n_i=n$. Then, Eqs. 10 and 11 become, respectively,

$$C_t = [S] + nK_n[S]^n \quad (12)$$

and

$$\phi = \alpha[S] + \beta K_n [S]^n. \quad (13)$$

The third derivative of ϕ with respect to C_t becomes

$$\frac{d^3\phi}{dC_t^3} = (\beta - \alpha n)\, n(n-1) K_n [S]^{n-3} \times \{(n-2)(1+n^2K_n[S]^{n-1}) - 3n^2(n-1)K_n[S]^{n-1}\} / (1+n^2K_n[S]^{n-1})^5. \quad (14)$$

The solution of $d^3\phi/dC_t^3=0$ gives

$$[S] = \left\{\frac{n-2}{(2n^3-n^2)K_n}\right\}^{1/(n-1)} \quad (15)$$

and

$$C_t = \left\{\frac{n-2}{(2n^3-n^2)K_n}\right\}^{1/(n-1)} \times \frac{2n^2-2}{2n^2-n}. \quad (16)$$

The two important implications of the above are (1) cmc (C_t) does not depend on the contribution factors and (2) the micellization constant (K_n) can be estimated in terms of the values of cmc and the aggregation number of the micelle. The former clear-cut result

Table 1. Micellization Constant (K_n) of Nonionic Surfactants of Oxyethylene Type Based on Monodisperse Micelle

Lipophile	Oxyethylene unit	cmc / μmol dm^{-3}	n	log K_n
1-Dodecanol[24]	8	110	123	478
	12	93	81	318
	18	83	51	200
	23	91	40	154
Nonylphenol[25]	15	110	80	309
	20	140	62	231
	30	185	44	157
	50	280	20	65
1-Tridecanol[26]	10	125	88	335
	15	150	38	138
	22	196	28	97

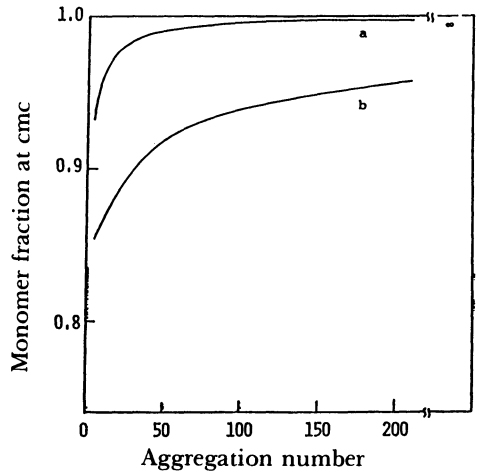

Fig. 3. Monomer fraction at cmc with aggregation number for monodisperse micelle of nonionic surfactant: a Eq. 17, b Eq. 18.

arises from the monodispersity of micelles, and cmc becomes independent of the method used for a cmc determination. In Table 1 are given many K_n values evaluated using Eq. 16 for nonionic surfactants of the oxyethylene type whose cmc and aggregation number are known.[23-26] As expected, K_n values increase with increasing aggregation number. From Eqs. 15 and 16 the fraction of nomomeric surfactants against the total surfactant concentration at cmc becomes

$$\frac{[S]}{C_t} = 1 - \frac{n-2}{2n^2-2}. \tag{17}$$

This fraction is illustrated against n in Fig. 3. On the other hand, Desnoyers et al. have already and independently presented the monomer fraction at the cmc and obtained a different expression from the same standpoint; he derived it in terms of the second derivative of the monomer fraction with respect to the total surfactant concentration.[27] However, the reason why the cmc can be defined as the total concentration at an inflection point of the monomer fraction is not clear. The fraction by Desnoyers,

$$\frac{[S]}{C_t} = \frac{n}{n-1} \times \{1 - (1/2n)^{1/2}\}, \tag{18}$$

is also shown in Fig. 3. The monomeric fraction has been found to be more than 99% at the cmc for the usual nonionic surfactant micelles with aggregation numbers greater than 50.

Monodisperse Micelle of Ionic Surfactant. Next, we consider the monodisperse micelle of an ionic surfactant. From the electroneutrality of a solution (eq. 5), the micelle concentration $[M_n]$ becomes

$$[M_n] = K_n[S]^n[G]^m = -x[S] - y[G] \tag{19}$$

where

$$x = z_s/(z_g m + z_s n) \tag{20}$$

and

$$y = z_g/(z_g m + z_s n) \tag{21}$$

Then, the equations corresponding to Eqs. 10 and 11 read, respectively, as

$$\nu_s C_t = (1-nx)[S] - ny[G] \tag{22}$$

and

$$\phi = (\alpha_1 - \beta x)[S] + (\alpha_2 - \beta y)[G] \tag{23}$$

The third derivative of ϕ with respect to C_t can likewise be obtained as

$$\frac{1}{\nu_s^3}\frac{d^3\phi}{dC_t^3} = (\alpha_2 - \beta y - \alpha_2 nx - \alpha_1 ny + 2\beta nxy) \times \{G'''(1 - nx - nyG') - 3nyG''^2\} / (1 - nx + nyG')^5 \tag{24}$$

where G′, G″, and G‴ are, respectively, the first, second, and third derivatives of [G] with respect to [S]. The solution then becomes

$$G'''(1 - nx + nyG') - 3nyG''^2 = 0 \tag{25}$$

In this case, too, the monomer concentration at the cmc turns out not to include any contribution factor at all. Hence, it becomes evident that the cmc theoretically does not depend on the method of cmc determination, regardless of whether an ionic or nonionic micelle is considered, as long as micelles are monodispersed. Experimentally, however, there must be random errors for the cmc values. In other words, the cmc values coincide with one another, independent of the cmc determination method, whether it is based on a solution property due to the surfactant monomer or due to the micelle. In reality, however, cmc's have been determined within a narrow concentration range.[18] This experimental fact means that the micelles formed in a surfactant solution are not monodisperse but, rather, polydisperse.

Polydisperse Micelle of Nonionic Surfactant. Now

that monodisperse micelles have been considered, the succeeding discussion should be about polydisperse micelles. Consider the simplest example in which micelles having only two kinds of aggregation numbers (n_1 and n_2) are formed in a solution. In this case, Eqs. 10 and 11 become, respectively,

$$C_t=[S]+n_1K_1[S]^{n_1}+n_2K_2[S]^{n_2} \quad (26)$$

and

$$\phi=\alpha_1[S]+\beta_1K_1[S]^{n_1}+\beta_2K_2[S]^{n_2} \quad (27)$$

Thus, from Eqs. 26 and 27,

$$\frac{d^3\phi}{dC_t^3}=N/(1+n_1^2K_1[S]^{n_1-1}+n_2^2K_2[S]^{n_2-1})^5, \quad (28)$$

where the numerator is given by

$$\begin{aligned}N &=(\beta_1-\alpha_1n_1)n_1(n_1-1)K_1[S]^{n_1-3}\times\{n_1-2\\ &+n_1^2(1-2n_1)K_1[S]^{n_1-1}\\ &+n_2^2(1+n_1-3n_2)K_2[S]^{n_2-1}\}\\ &+(\beta_2-\alpha_1n_2)n_2(n_2-1)K_2[S]^{n_2-3}\times\{n_2-2\\ &+n_1^2(1-3n_1+n_2)K_1[S]^{n_1-1}+n_2^2(1-2n_2)K_2[S]^{n_2-1}\}\\ &+n_1n_2(n_1-n_2)(\beta_1n_2-\beta_2n_1)K_1K_2[S]^{n_1+n_2-4}\\ &\times\{n_1+n_2-3+n_1^2(-2n_1+n_2)K_1[S]^{n_1-1}\\ &+n_2^2(n_1-2n_2)K_2[S]^{n_2-1}\} \quad (29)\end{aligned}$$

It turns out from Eq. 29 that the monomer concentration [S] satisfying $d^3\phi/dC_t^3=0$ depends on the contribution factors: α_1, β_1, and β_2. That is, the cmc value (C_t) obtained from the monomer concentration depends on a method for cmc determination. Thus, the cmc difference due to the method of determination is a systematic difference, just as systematic errors are different from random errors. The micelle aggregation number in a real system is much more dispersed than in the present case: two kinds of aggregation numbers.[28-33] Therefore, as a matter of fact, the cmc depends on the method used for a cmc determination and the cmc value should be defined as a narrow concentration range. From the above discussion, the relationship between the solubility and the cmc can be schematically illustrated (Fig. 1). The solubility is determined only by the temperature at atmospheric pressure and the cmc is given by a narrow concentration range, even at a specified temperature. As for the phase rule on a solubility curve, an excess surfactant phase coexists in the system and the number of phases becomes two. Thus, the number of degrees of freedom turns out to be two, as should be clear from the above discussion. The temperature determines the concentration of every chemical species at a specified pressure. This fact is in total agreement with the experimental fact that the solubility is determined only by the temperature at atmospheric pressure. For more details, reference to the literature[1] is recommended. The cmc change with temperature, on the other hand, is due to the variation of K_n, α, and β with temperature. As a result, the micelle temperature range (MTR) must be defined as the temperature within a narrow temperature range, for which the solubility vs. temperature curve intersects the cmc range vs. temperature curve although a single temperature within the MTR can be obtained from one cmc determination method. In other words, MTR is determined by balancing between the cmc range and the solubility and by their dependence on the temperature. In this sense, MTR is a phenomenological temperature range rather than a strict physical quantity.

Elucidation of MTR Changes

At present, it is very important to show that some experimental facts can be elucidated by the above definition of MTR, since the validity of the definition should be examined by this approach. The following are two typical examples of MTR changes.

Leveling of MTR for Homologous Surfactants with an Increase in Their Alkyl Chain Length. The Krafft point of homologous ionic surfactants has been reported to increase with an increase in the alkyl chain length of a surfactant ion.[3,34-36] The important feature is that MTR does not increase linearly with the carbon number of an alkyl chain, but with gradual leveling. On the other hand, the logarithms of both the solubility and the cmc decrease linearly with an increase in the carbon number.[3] Of course this applies for cases in which the logarithm of the solubility is less than that of the cmc at low temperature. In addition, the heat of dissolution below MTR becomes more positive with an increasing carbon number of surfactant ions; the rate of solubility increase with temperature is more rapid for a surfactant ion with a longer alkyl chain.[3] On the contrary, the cmc change with temperature is relatively small, irrespective of the alkyl chain length (Fig. 4). From the definition of MTR, in which solubility and cmc curves should intersect each other,

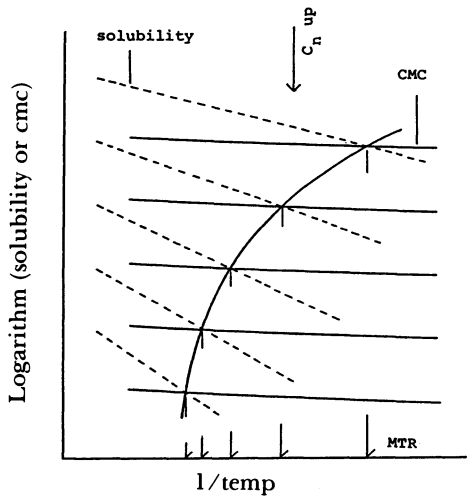

Fig. 4. Schematic illustration of MTR change with increase of carbon number of surfactant ion.

the leveling of MTR is easily understood from the figure.

MTR Increase of Sodium Dodecyl Sulfate (SDS) with Increase of Counterion Concentration. The addition of a salt having an ion in common with a counterion into an ionic surfactant solution leads to both a decrease in the cmc and an increase in the aggregation number of micelles. The presence of excess counterions also leads to a solubility decrease of the surfactant due to the constant solubility product of the counterion and the surfactant ion, as long as an excess surfactant phase coexists in the system, even when the surfactant concentration is above the cmc. Then, an MTR change is expected from an addition of excess salt into the system. In fact, the MTR of sodium dodecylsulfate increases with an increase in the concentration of sodium chloride in the solution. The aim of this section is to elucidate the movement of the MTR to higher temperature from the viewpoint of the present concept as to MTR and to compare the evaluated results with the reported ones.[16]

Let us suppose a monodisperse micelle formation, sicne the mass-action model of a single micellar size has been well applied to ionic surfactants.[37] The relation between the cmc and the counterion concentration then, according to Eq. 6, becomes

$$\ln \text{cmc} = -\frac{m}{n}\ln[\text{G}] - \frac{1}{n}\ln K_n + \frac{1}{n}\ln[\text{M}_n] \qquad (30)$$

since the concentration of the monomeric surfactant ion at the cmc can be replaced by the total surfactant concentration with more than 99% confidence, according to Phillips' definition of cmc.[37] In the usual case ($n > 50$; $K_n \gg [\text{M}_n]$) the last term on the right-hand side is less than a few percent of the constant term of association constant, and Eq. 30 can be well approximated by

$$\ln \text{cmc} = -\frac{m}{n}\ln[\text{G}] + \text{constant}. \qquad (31)$$

Here, m/n is the association degree of gegenion to the micelle. The linear relataionship between ln cmc and ln [G] has been ascertained from a number of experiments; this indicates that the above approximation is correct. The cmc of SDS is 8.4×10^{-3} mol dm^{-3} and m/n was extrapolated to be 0.72—0.75[38] at its MTR (9 °C).[39] The value of the constant was evaluated to be −8.22 and −8.36 for 0.72 and 0.75 of m/n, respectively. On the other hand, the solubility of SDS decreases with an increase in the counterion concentration, while maintaining the solubilty product constant at 9 °C;

$$C(C + C_{\text{Na}^+}) = (8.4\times10^{-3})^2, \qquad (32)$$

where C is the concentration of the surfactant or the solubility. From Eqs. 31 and 32 the difference between ln cmc and ln C at 9 °C can be evaluated at different C_{Na^+} concentrations. A cmc change with temperature

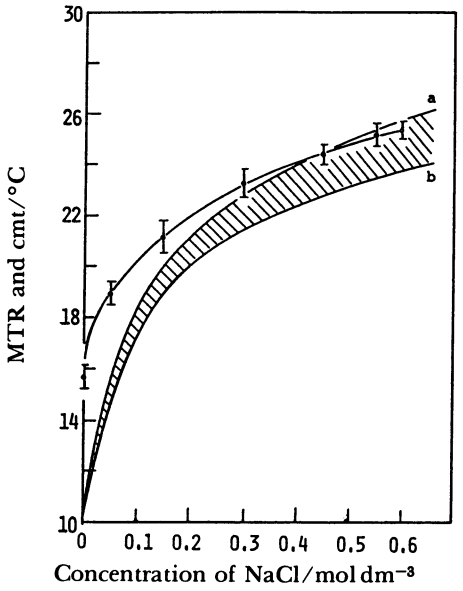

Fig. 5. MTR increase of sodium dodecylsulfate with increase of sodium chloride concentration: ⊖ cmt change, a m/n=0.72, b m/n=0.75.

is negligibly small compared with a solubility change. Then, it can be presumed that the difference ln cmc—ln C can be made zero only by a solubility increase with temperature. Then, MTR is the temperature at which the above difference becomes zero. The heat of dissolution (Δh) is necessary for the present calculation; Δh was estimated to be 50 kJ mol^{-1} from the solubility data of Nakayama and Shinoda.[40] The range of MTR thus obtained from two m/n values, 0.72 and 0.75, is shown in Fig. 5 together with the experimental results. The difference is less than a few degrees between the MTR and the critical micellar temperature (cmt)[16] by Mazer and Benedek; this is quite reasonable, judging from the definition of cmt. In spite of the difference between MTR and cmt, the present agreement can be said to be excellent.

The conclusions reached from the above discussion are (1) the micelle temperature range (MTR) is a better technical term than the Krafft point for expressing the relation between the solubility and micelle formation, (2) MTR can be determined only by balancing between the cmc range and the solubility and their dependence on temperature, and (3) these can be well explained by the mass-action model of micelle formation and the size distribution of micelles.

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