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ORIGINAL CONTRIBUTION

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An electroconductivity study on degree of counterion binding or dissociation of α-sulfonatomyristic acid methyl ester micelles in water as a function of temperature

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Abstract For a sodium salt of α-sulfonatomyristic acid methyl ester (14SFNa), one of the α-SFMe series surfactants, the differential conductivity $(\partial\kappa/\partial C)_{T,P}$ vs. square root of concentration ($\sqrt{C}$) was employed in order to determine not only CMC but also the limiting molar conductance (Λ^0) and the molar conductance of micellar species (Λ^M).

Based on the data of the degree of counterion binding to micelles (β) determined previously at different temperatures ranging 15–50 °C at every 5 °C, the experimental values of the degree of dissociation (ionization) of a micelle (α_{EX}) were calculated by regarding as $\alpha_{EX} = 1 - \beta$. The ratio Λ^M/Λ^0 corresponding to the ratio of slopes below and above CMC in the curve of specific conductivity (κ) vs. concentration (C), which has been often assumed to be the degree of ionization of micelles (α), was compared with the present α_{EX}. However, the ratio Λ^M/Λ^0 ($= \alpha$) was found to have a correlationship with α_{EX} ($= 1 - \beta$) as $\alpha_{EX} \approx 0.40 \times (\Lambda^M/\Lambda^0)$, or strictly, $\alpha_{EX} = 0.40\,(\Lambda^M/\Lambda^0) + 0.08$, indicating that the simple ratio of the slopes below and above CMC in κ vs. C curve is not true for $\alpha_{EX} = 1 - \beta$. On the other hand, the method proposed by Evans gave a value closer to α_{EX} compared with the simple ratio.

Key words Electroconductivity – differential conductivity – degree of counterion binding – dissociation degree of micelles – α-sulfonato-myristic acid methyl ester

Introduction

α-Sulfonate fatty acid methyl esters (α-SFMe) have been known to show a good biodegradability [1–4] and a high detergency for fabrics [1, 5–7] in addition to their high tolerance against calcium ions [1, 8]. Since no thermodynamic analysis for α-SFMe series surfactant had been made yet, we have previously studied the thermodynamic behaviors of α-sulfonatomyristic acid methyl ester (14SFNa), as an example of α-SFMe series, in terms of critical micellization concentration (CMC), solubility and the effect of added salt concentration on CMC as a function of temperature [9]. In the previous study [9], CMC, solubility and degree of counterion binding (β) which was estimated from the Corrin–Harkins plot were determined by means of electroconductivity measurements at different temperatures ranging 15–50 °C at every 5 °C. This temperature study has enabled us to evaluate the changes in Gibbs energy change, ΔG^0_m, enthalpy, ΔH^0_m, and entropy, ΔS^0_m, upon micelle formation as a function of temperature taking the β values into consideration, showing that the contribution of entropy term to the Gibbs energy of micelle formation plays the leading part, especially in the lower temperature region (below the minimum point on the CMC-temperature curve) while the contribution from the enthalpy term increases with increasing temperature. In the CMC determination in the previous paper, the differential conductivity $(\partial \kappa/\delta C)_{T,P}$ vs. square root of concentration ($\sqrt{C}$) plot was employed; the CMC was defined at the central point of the reverse sigmoid curve. In the plot the limiting molar conductance (Λ^0) and the molar conductance of micellar species (Λ^M) were found to be easily determinable [9]. In this paper the data of Λ^0 and Λ^M are discussed in connection with utility for estimate of β or the degree of dissociation of a micelle (α), where α is regarded as being equal to $1 - \beta$; it is examined whether the α has a relation with Λ^0 and Λ^M data or not.

Further, the temperature dependence in β will come up for discussion by comparing among different counterion species.

Experimental

As for (i) *Materials and apparatus*, and (ii) *determinations of CMC and degree of counterion binding* (β), everything has been described in the previous paper [9].

Results and discussion

The critical micellization concentrations (CMC) of α-sulfonatomyristic acid methyl ester (14SFNa) in water with and without addition of sodium chloride were measured at different temperatures by electroconductivity method, and the degrees of counterion binding (β) at the respective temperatures were determined from the plots of logarithmic CMC against logarithmic concentration of counterion (Na^+), i.e, the so-called Corrin–Harkins plot. All the resultant CMC data of 14SFNa in pure water at 5 °C and at the range 15–50 °C (at every 5 °C) together with the β values were tabulated in the previous paper (See Table 1 in Ref. [9]), but, here, for comparison with different systems the β values are again listed in Table 1. As has been described previously, the more accurate determination of CMC was found to be attained from the plot of differential conductivity $(\partial \kappa/\partial C)_{T,P}$ vs. square root of concentration in $mM(\sqrt{C})$ as compared with the conventional plot of specific conductivity (κ) vs. concentration (C). Especially, the former plot is superior to the latter in determination of CMC for the systems with addition of NaCl. In the plot of κ vs. C, otherwise, the intersection angle of the two curves of κ vs. C above and below CMC is not so sharp that the determination of the intersection point encounters with an obscurity. Comparing the two methods of κ vs. C and $(\partial \kappa/\partial C)_{T,P}$ vs. $\sqrt{\bar{C}}$, in actual treatment with CMC determination, the former results in an error of ± 20% at most (when the concentration of added salt is very high), but the latter's error ranges only ± 2%. Here it is noted that in the plot of $(\partial \kappa/\partial C)_{T,P}$ vs. $\sqrt{\bar{C}}$, $(\partial \kappa/\partial C)_{T,P}$ was assumed as being approximately equal to $\Delta\kappa/\Delta C$, where $\Delta\kappa = \kappa_{i+1} - \kappa_i$ and $\Delta C = C_{i+1} - C_i$ at ith measured point and $\bar{C} = C_{i+1} + C_i)/2$. In this text hereafter $(\partial \kappa/\partial C)_{T,P}$ and $\bar{C}$ will be expressed as $d\kappa/dC$ and C, respectively.

In Fig. 1, some examples of the plots for different systems are shown. As seen from Fig. 1, the respective curves have an abrupt fall drawing a reverse sigmoid even for systems with added NaCl.

Here it is noted that when the conductivity is measured for solutions at higher ionic concentration by using the apparatus (TOA Electric Conductivity Meter, Model CM-40S with a TOA Electrode, CG201PL), it was found that more numbers in significant figure could be read from the resistance (not the conductivity), so that the read-resistance values were converted into conductivity ones in the case of α-sulfonatomyristic acid ethyl ester (Nakamura AA et al., unpublished). But, in the present paper, the directly read data are used. Mukerjee and Yang have once employed the differential conductance to determine the CMC

Table 1 β values for variable surfactants at different temperatures

Temperature [°C]	14SFNa	DAMS[a]	DAPS[a]	DABS[a]	EdaDC[b]	EdaC[b]
10	—	0.65	0.68	0.82	0.232	0.254
15	0.716					
20	0.717	0.64	0.63	0.81	0.226	0.256
25	0.716					
30	0.715	0.66	0.61	0.78	0.220	0.266
35	0.713					
40	0.710	0.65	0.62	0.78	0.235	0.269
45	0.707					
50	0.702	0.65	0.65	0.8	0.237	0.281

[a] From [21].
[b] From [22].

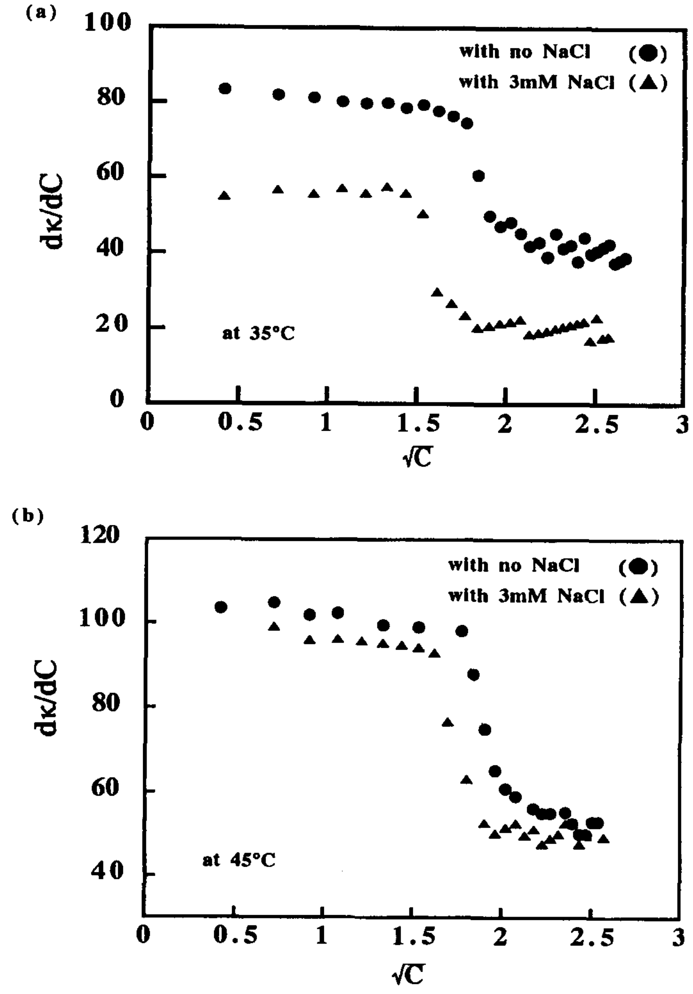

Fig. 1 Plots of $d\kappa/dC$ vs. $\sqrt{C}$ for different systems (noNaCl (●) and 3 mM NaCl (▲)) at 35 °C and 45 °C. Each CMC is determined at the central point of the reverse sigmoid

for the systems of fluorocarbon/hydrocarbon surfactant mixtures which have a trend to draw a large curvature around CMC in κ vs. C plot [10]. Subsequently, Manabe et al. have also applied appropriately this type of plot [11, 12]. But in their application ($d\kappa/dC$) was plotted against C [10, 11] and Manabe et al. have determined CMC at the shoulder point of the $d\kappa/dC$ vs. C plot curve [11, 12]. In the present study, the center of the reverse sigmoid was regarded as the point giving CMC [9], based on the definition by Philips [13, 14]. Here it is noted again that the present method enables us to determine more accurately CMC by one order than the κ–C plot method. Further, not only for drawing more clearly the reverse sigmoid but also for utilizing the conductivity data to determine the limiting molar conductance Λ^0, strictly describing, $(d\kappa/dC)^0$ determined by extrapolation to the zero concentration) in addition to micellar conductance (Λ^M), the differential conductivity was plotted against $\sqrt{C}$ as has been applied in another previous work [15].

Comparing between the curves with and without NaCl at the same temperature, the $d\kappa/dC$ curve of added salt system is located at the lower side, and accordingly Λ^0 and Λ^M are lower than those in pure water. Although the molar conductance Λ and the differential conductivity $d\kappa/dC$ have the same dimension, needless to say, both are not the same (Λ is defined as κ/C^*, here C^* is in molarity SI unit, $\mathrm{mol\,m^{-3}}$ and Λ has a dimension of $\mathrm{S\,m^2\,mol^{-1}}$. However, in the present paper, C is expressed in $\mathrm{mmol\,dm^{-3}}$ and the dimension of $\Lambda = \kappa/C$ or $d\kappa/dC$ is presented in $\mathrm{S\,cm^2\,mol^{-1}}$).

The experimental relationship between the molar conductivity and the concentration of an electrolyte solution is known to be best brought out by plotting Λ against $C^{1/2}$, especially in the lower concentration there is a linear relationship between Λ and $C^{1/2}$ (Kohlrausch's law):

$$\Lambda = \Lambda^0 - AC^{1/2}\,, \tag{1}$$

where the intercept is the molar conductivity at infinite dilution, Λ^0, and the negative slope of the straight line, $-A$, is a constant [16]. If the left-hand side of Eq. (1) is replaced with κ/C and rewritten, the following expression is obtained.

$$\kappa = \Lambda^0 C - AC^{3/2}\,. \tag{2}$$

Further, the differentiation with C leads to

$$\frac{d\kappa}{dC} = \Lambda^0 - \frac{3}{2}AC^{1/2}\,. \tag{3}$$

This equation indicates that the $d\kappa/dC$ at infinite dilution corresponds to Λ^0 and the slope of the curve below CMC in Fig. 1 does to $-(3/2)A$.

The curves including those not shown here, in general, demonstrate that (i) the values of A for the systems in pure water are larger than for those in the presence of added salt and (ii) Λ^0 values in pure water systems are also greater than those of added salt systems, indicating that these factors mainly result from enhanced viscosity of medium, as suggested from the Stokes–Einstein relation and the change of the dielectric constant in the Debye–Hückel reciprocal length [16]. Here, the NaCl solution at a given concentration used as a solvent was assumed to be the medium dissolving the surfactant. The minimum ($d\kappa/dC$) value may be regarded as the molar conductance of micelle-forming species (Λ^M). The Λ^M is determined from the curve of ($d\kappa/dC$) vs. $\sqrt{C}$ as is shown in Fig. 1; the tangential line drawn from the minimum of the curve gives the Λ^M at the intersect with ordinate (drawn at CMC), or in most cases, the curves attain an almost constant value at the higher concentration range so that the value itself corresponds to Λ^{M}. The lower (Λ^{M}) values for the added salt systems may reflect the growth of micellar size due to increase in aggregation number caused by the addition of salt.

Here, we would like to draw attention to the correlationship of the degree of dissociation of micelles (α) or that of association of counterion (counterion binding to micelles, β) with the differential conductivity $(\partial\kappa/\partial C)_{T,P}$. In the previous work we have shown that the differential conductivity at the range sufficiently higher than CMC, Λ^{M}, can be related to the dissociation degree of micelles [15, 17]. That is

$$\left(\frac{\partial\kappa}{\partial C}\right)_{T,P} = \Lambda^{\mathrm{M}} = \alpha(Fu_{\mathrm{mic}} + \lambda_{+}) \quad (C \gg \mathrm{CMC}) \tag{4}$$

in which the most left-hand side is the slope of specific conductance curve above the CMC, λ_{+} is the conductance of counterion (Na^{+}); u_{mic}, the electrophoretic mobility of micelles and F, the Faraday constant [17]. And the limiting conductance of the given ionic surfactant is considered to be determined by extrapolating to zero concentration in the region below CMC:

$$\left(\frac{\partial\kappa}{\partial C}\right)^{0}_{T,P} = \Lambda^{0} = Fu_{s}^{0} + \lambda_{+}^{0} \quad (C = 0), \tag{5}$$

where u_{s}^{0} denotes the mobility of a singly dispersed surfactant species at infinite dilution. Λ^{M} and Λ^{0} are functions of pressure P and temperature T. If Eqs. (4) and (5) are expressed simply as $\Lambda^{\mathrm{M}} = \alpha S(T,P)$ and $\Lambda^{0} = S'(T,P)$, respectively, and the ratio $\Lambda^{\mathrm{M}}/\Lambda^{0}$ is taken, the following relation is obtained:

$$\frac{\Lambda^{\mathrm{M}}}{\Lambda^{0}} = \alpha\frac{S(T,P)}{S'(T,P)} = \alpha k\,, \tag{6}$$

where $S(T,P)/S'(T,P)$ is denoted as k. Although k is not yet known to be a constant, Eq. (6) indicates at least that the ratio involves the dissociation degree of micelles. From the curves as shown in Fig. 1, the Λ^{0} and Λ^{M} were read and the ratio was calculated at each temperature. The data are listed in Table 2. Regrettably, the Λ^{M} values have a wider error width compared with Λ^{0} values because of scattering of measured points. Therefore, the significant figure number must be restricted at most to two. However, the averaged value was obtained from more than ten measured points. Figure 2 shows the plots of Λ^{M} and Λ^{0} against temperature. As for Λ^{0} and Λ^{M}, a monotonously increasing curve was, respectively, obtained as has been observed previously [17]. From the data shown in Fig. 2 the ratio $\Lambda^{\mathrm{M}}/\Lambda^{0}$ was calculated.

The $\Lambda^{\mathrm{M}}/\Lambda^{0}$ ratio being plotted against temperature, the curve obtained decreases slightly and then changes the trend via minimum around 28 °C with increasing temperature. (The curve is not shown here, but known from Table 2.) If the $\Lambda^{\mathrm{M}}/\Lambda^{0}$ ratio could be directly related to the α and if k were a constant, the ratio could be used for estimate of α. We have experimentally determined the β values at the respective temperatures (Table 1), so the β value may be related to the α value, assuming $\alpha + \beta = 1$. Thus, if we examine the correlationship between $\Lambda^{\mathrm{M}}/\Lambda^{0}$

Table 2 Electroconductivity data for 14SFNa at discrete temperatures: Limiting molar conductivity Λ^{0}, micellar conductivity Λ^{M} and ratio $\Lambda^{\mathrm{M}}/\Lambda^{0}$

Temp. [°C]	15	20	25	30	35	40	45	50
Λ^{0} [S cm^2 mol^{-1}]	53.5	63.0	70.0	77.5	85.5	96.0	105.0	116.0
Λ^{M} [S cm^2 mol^{-1}]	27.5	32.0	35.0	38.5	43.0	50.0	55.1	62.0
$\Lambda^{\mathrm{M}}/\Lambda^{0}$	0.514	0.508	0.500	0.496	0.503	0.520	0.524	0.535

Table 3 The data of CMC and slope ratio above and below CMC (S^{M}/S^{1} or $\Lambda^{\mathrm{M}}/\Lambda^{0}$) for different aqueous surfactant systems at 25 °C

Surfactant	CMC [mM]	S^{M}/S^{1} ($\Lambda^{\mathrm{M}}/\Lambda^{0}$)	Ref.
α-sulfonatomyristic acid methylester Na (14SFNa)	3.15	0.50	Present work
perfluorooctanosulfonate Li ($C_8F_{17}SO_3Li$)	6.9	0.61	18
perfluorooctanosulfonate Me_4N ($C_8F_{17}SO_3Me_4N$)	1.9	0.22	18
perfluorohexanosulfonate Et_4N ($C_6F_{13}SO_3Et_4N$)	8.4	0.24	18
p-(1-propylnonyl benzensule Na (4DPS)	1.75	0.69	19
dodecylammonium trifluoroacetate (DAPA)	7.7	0.15 (at 40 °C)	20

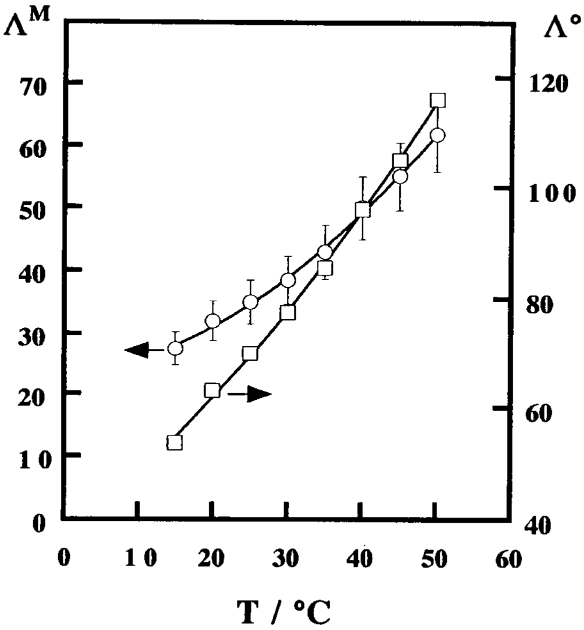

Fig. 2 The limiting molar conductivity of singly dispersed species Λ^0 and the molar conductivity of micellar species Λ^M as a function of temperature

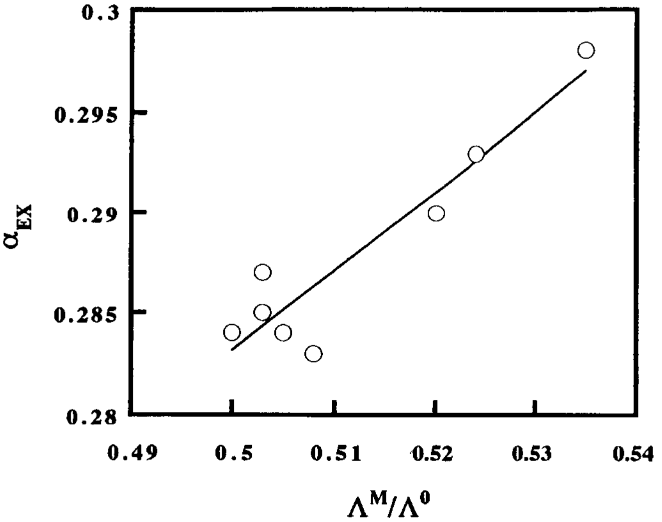

Fig. 3 The correlationship between α_{EX} and Λ^M/Λ^0

and experimentally estimated α (here, denoted as α_{EX}), the applicability of the ratio should be confirmed. In fact, a good correlationship (with a regression value = 0.94) was found to hold between Λ^M/Λ^0 and α_{EX} ($= 1 - \beta$) as is demonstrated in Fig. 3. Here, the correlation of α with ratio Λ^M/Λ^0 is expressed as

$$\alpha_{EX} = 0.40(\Lambda^M/\Lambda^0) + 0.08\,. \tag{7}$$

This indicates that α_{EX} corresponds roughly to 40% of Λ^M/Λ^0 over the range of temperature studied here and at the same time k in Eq. (6) is not a constant.

Very recently, Tamaki et al. [18] reported an electric conductivity study on CMC and dissociation (ionization) degree of micelles of perfluoroalkanesulfonate salts as a function of chain length in aqueous solution, in which they have indicated the ratios of slopes above and below CMC in κ vs. concentration curves (S_M/S_1) by regarding as a measure of dissociation degree of micelles based on the literature of Lianos and Lang (L&L) [19]. According to the literature, L&L supposed that k in Eq. (6) might be unity, meaning that the slope ratio itself is the ionization degree of micelles. Evans had demonstrated that the degree of micellar ionization could be estimated from the conductivity data as early as 1956, but his method requires the knowledge of the micellar aggregation number [20].

On the other hand, previously we have suggested that Λ^M itself could be related to the micellar ionization degree [15], being also derived from Eq. (6) as

$$\Lambda^M = \left(\frac{\partial \kappa}{\partial C}\right)^0_{T,P} = \alpha k \Lambda^0 = \alpha k' \quad (C \gg \mathrm{CMC}). \tag{6'}$$

This means that the factor k' corresponds to the slope of κ vs. concentration curve below CMC, according to L&L [19] or Evans [20].

Based on Evans' idea we calculated the α value at 25 °C by employing the aggregation number 80 (determinated from the previous light scattering measurement [8]) and obtained as $\alpha = 0.154$. This value is much different from our result of $\Lambda^M/\Lambda^0 = 0.50$ (see Table 2) or (S_M/S_1) defined by L&L [19]. This marked difference should be discussed.

When the ionization degree is calculated from the relation of $\alpha_{EX} = 1 - \beta$, where β is the experimental value (shown in Table 1), we obtained $\alpha_{EX} = 0.28$. As was described above, we found that α_{EX} approximates to 40% of the slope ratio in the present system; 40% of $\alpha_{EX} = 0.50$ is 0.20. From the empirical relation (Eq. (7)), α_{EX} at 25 °C is calculated as 0.28. The value 0.20 is in between Evans' 0.15 and our actual results 0.28 ($= 1 - 0.72$). This disagreement may come from a certain limitation of Evans' assumption and our simple supposition that $\alpha + \beta = 1$ or $\alpha_{EX} = 1 - \beta$. In fact, it has been observed that the Corrin–Harkins plot in some cases results in a value of larger than unity or unity, although micelles have electric charges to a small extent [15]. This fact is also suggested from the intercept in Eq. (7) and from the previous paper [17]. In addition, even if the experiment of added salt effect on CMC is very carefully performed, a few percent of error is unavoidable. These facts mentioned above imply that the determination

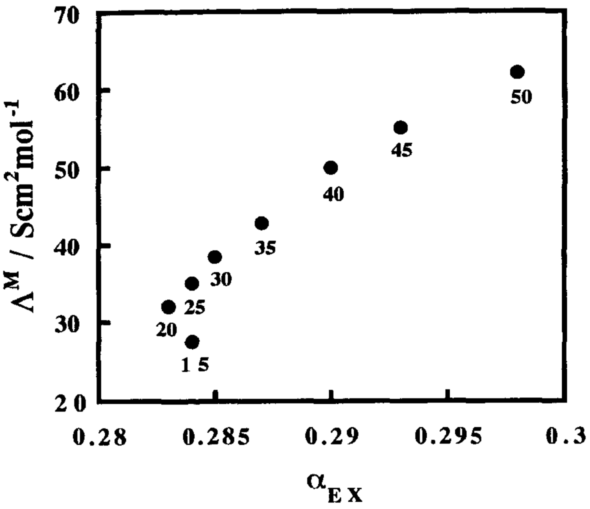

Fig. 4 The correlationship between Λ^M/Λ^0 and α_{EX}

of degree of micellar dissociation has still a difficulty. Nevertheless, our present results may tell us that the method of L&L, or taking a simple ratio of the slopes above and below CMC does not lead to a real value of degree of micellar ionization.

Concerning the relationship between Λ^M and α, another problem should be noted here. In an electroconductivity study [15] on the effect of the hydrophobicity in counterions on micelle formation for dodecyl ammonium (DA) salts having different perfluorocarboxylate and alkanesulfonate ions such as trifluoroacetate (PA), pentafluoropropionate (PP), methanesulfonate (MS) and ethanesulfonate (ES), previously to the present paper, Λ^M value was measured for each system at a constant temperature (40 °C). The paper has reported that Λ^M itself has a linear relation (starting from zero) with α (see Fig. 4 in Ref. [15]); Λ^M increases in the order DAPP < DAPA < DAES < DAMS reflecting their hydrodynamic radii. Plotting similarly Λ^M against $\alpha_{EX} = 1 - \beta$ for the present system, however, the result demonstrates a nonlinear relation, as shown in Fig. 4. In the figure, the numerical values by the respective measured points indicate the temperature in °C. Comparing the nonlinear $\Lambda^M - \alpha_{EX}$ curve in the present study with that obtained for DA salts having different counterions at 40 °C, it may be said that a linearity between Λ^M and α should hold only at a constant temperature. Anyway the result shown in Fig. 4 suggests that the trend reflects the difference in hydration state of ions or in the sign of enthalpy term.

One of the aims of the present paper was to examine the temperature dependence in β. We have investigated the temperature effects on β for different series of ionic surfactants; a collection of the β-temperature data are given in Table 1. In addition to dodecyl ammonium (DA) salts: DAMS, DAES, DAPS and DABS [15], Araki et al. have examined the degrees of counterion (Na^+) binding for a new series of cationic surfactants derived from bile acids; ethylenediammine mono cholanoic acid (EdaC), ethylenediammine monodeoxycholanoic acid (EdaDC) and so on [22]. The results are included in Table 1. The data show three main features. The first, the cationic bile acid derivatives (CBADs) have a β value as have been observed for taurine conjugate or free bile acid salts, ranging commonly around 0.25 [23–25]. This low value compared with those linear hydrocarbon type surfactants is attributed to the bulky and rigid structure of steroid skeleton to which two or three hydroxyl groups are attached. The second, the value depends much on the species of counterion, for example, β increases with increasing hydrophobicity as observed for DAMS, DAPS and DABS, and also the difference of head group (especially the difference in hydrophobicity at the part of head group) reflects on β, e.g., the present 14SFNa (α-SF Me) has a β value of around 0.72, while 15SFNa (α-SFEt) has a β of ca. 0.61 (Nakamura AA et al., unpublished data). The third, the simpler chemical structure of counterions such as Na^+ and Cl^- seems to have the less temperature dependence in β. This is also seen from comparing MS^- and PS^- or BS^- in Table 1. Above all the most hydrophobic and bulky butanesulfonate ion shows a prominent temperature dependence.

Consequently, for ionic surfactants having Na^+, K^+, Cl^- or Br^- as counterion, the use of a β value may be allowed in approximate calculation of enthalpy or entropy changes on micellization at different temperatures other than at the temperature studied.

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