Colloid Polym Sci (2002) 280: 929–935
DOI 10.1007/s00396-002-0710-3

ORIGINAL CONTRIBUTION

Masahiro Manabe
Asako Tokunaga
Hideo Kawamura
Hajime Katsuura
Masaki Shiomi
Koichi Hiramatsu

The counterion releasing effect and the partition coefficient of branched alkanols in ionic micellar solution

Received: 25 February 2002
Accepted: 2 April 2002

M. Manabe (✉) · A. Tokunaga
H. Kawamura · H. Katsuura · M. Shiomi
Department of Applied Chemistry
and Biotechnology, Niihama National
College of Technology, Niihama,
Ehime 792–8580, Japan
E-mail: manabe@chem.niihama-nct.ac.jp

K. Hiramatsu
Department of Biomolecular Science,
Faculty of Engineering, Gifu University,
Gifu 501–1112, Japan

Abstract In the micellar solution of SDS, the partition coefficient (K_x) of following branched alkanols at infinite dilution was determined by applying a differential conductivity method: the alkanols used were i-$C_mH_{2m+1}OH$ ($m=4$–9, $i=1$–5) in which the position of OH group (i) shifts from an end to the center of a hydrocarbon chain. The method provides two significant quantities, $d\alpha/dX_{am}$ and dC_{sf}/dC_{af} in addition to K_x. The following results have been obtained. (1) The dependence of K_x on i indicates that the hydrophobicity of alkanol is weakened with increasing i, whereas the increase in m strengthens the hydrophobicity. (2) The degree of counterion disossiation of micelles (α) is accelerated by the solubilized alkanols in micelles (mole fraction: X_{am}) and the acceleration rate, $d\alpha/dX_{am}$ ($=0.17$), depends on neither m nor i. (3) In the bulk water, the monomerically dissolved alkanols (concentration: C_{af}) depresses the concentration of free monomer surfactant (C_{sf}), and the depressing rate, dC_{sf}/dC_{af}, in micellar solution is identical with the corresponding quantity, $(\Delta CMC/\Delta C_a)_o$ at CMC.

Keywords Surfactant · Micelle · Partition coefficient · Mixed micelle · Ionization degree · Charge density · Surface charge density · Alkanol · Isomeric alcohol · Conductivity · Hydrophobic interaction

Introduction

The main factors controlling ionic micelle formation are hydrophobic effect [1] and electrostatic interaction [2]. The micellar aggregate bears a number of ionic groups and a certain fraction of the counter-ion is released [3] When an amount of nonionic amphiphiles are solubilized in micelles the ionization is enhanced [4] because the nonionic head groups located in the ionic surface region of micelles are considered to reduce the surface charge density. In general, for various colloid electrolytes, the correlation between the surface charge density and the degree of counterion dissociation is an important factor of the colloid stability. However, few studies have been carried out on the experimental determination of the quantitative relation, whereas there is an exceptional case that for the polyelectrolytes in rod-like form, the relation was revealed, theoretically and experimentally, by Manning [5]. In order to make an experimental study on the relation, ionic micelles are a profitable colloid electrolyte system since the surface charge density can be altered continuously with an amount of a nonionic amphiphile solubilized in the micelles.

When a nonionic amphiphile is dissolved in micellar solution, the amphiphile is distributed between the bulk water and the micelles. So far, many methods for the determination of the partition coefficient have been used [6, 7]. Manabe et al. [8] developed a novel method on the basis of conductivity data and evaluated two significant quantities, $d\alpha/dX_{am}$ and dC_{sf}/dC_{af}, in addition to the partition coefficient, at infinite dilution of the solubilizate, in the systems of SDS-1-alkanols. The $d\alpha/dX_{am}$

implies the acceleration rate of degree of counterion dissociation of micelles to the mole fraction of solubilized additives, and dC_{sf}/dC_{af} indicates the decreasing rate of monomer surfactant concentration to monomer additive one in the bulk water of a micellar solution. The validity of the conductivity method was verified by another method based on counter-ion EMF data in the same systems [4], where the values of respective quantities for each alkanol derived by two methods [4, 8] were in good agreement with each other.

As for $d\alpha/dX_{am}$ ($=0.17$), it has little dependence on the carbon number of 1-alkanols [4, 8], and sodium alkylsulfates [9], in the systems of 1-alkaols and sodium alkylsulfates. The independence suggests that $d\alpha/dX_{am}$ is a function of the size of polar head group of solubilizates. Thus, it was attempted to elucidate the relation between $d\alpha/dX_{am}$ and the head group size for various nonionic homologues. First, in the present study, the branched alkanols have been adopted as the additives, from the following motives. The one is that compared to the terminal OH group in 1-alkanols, the branching, i.e., the shift of the group from an end toward the center, is expected to expand the effective size of polar group to increase $d\alpha/dX_{am}$. The other is how the branching weakens the hydrophobicity of alkyl-chain, which can be appreciated by the partition coefficient as well as dC_{sf}/dC_{af}. It is known that the hydrophobicity of a branched hydrocarbon-chain amphiphiles is weaker than a straight-chain ones, confirmed just for some short-chain alkanol isomers [10, 11], and some homologues of double-chain surfactants [12].

In the present study, the branching effect on the rate of ionization degree and on the hydrophobic interaction has been elucidated through the three quantities, by applying the differential conductivity method [8] to the system of isomeric alkanols from butanol to nonanol in SDS micellar solution.

Experimental

Materials

Sodium dodecylsulfate, SDS, was synthesized and purified in the same procedure as described elsewhere [13]. No minimum was detected in the surface tension – concentration curve of the SDS solution. The following isomeric alkanols (i-$C_mH_{2m+1}OH$) purchased from Tokyo Kasei Co. Ltd. (GR grade) were used without further purification: $i=1$, $m=4$–8; $i=2$, $m=5$–8; $i=3$, $m=5$–9; $i=4$, $m=7$–9, $i=5$, $m=9$ where i stands for the position of OH group from an end of a straight hydrocarbon chain consisting of m carbon atoms. The specific conductivity of deionized and distilled water was less than 2 μScm^{-1} at 298.15 K.

Procedure of conductivity measurements

The partition coefficient and related quantities for the alkanols, and the critical micelle concentration (CMC) of SDS were determined by conductometry by the following procedures, the same as in the previous studies [8]. As for the determination of partition coefficient, a micellar solution of SDS with a concentration (C_s) was prepared as a solvent. An alkanol solution with a concentration (C_a) was prepared by using a half portion of the solvent. The rest portion of the solvent was put in a conductivity cell (cell constant, 0.2638 cm^{-1}) and then small aliquot portion of the alkanol solution was successively added to the solvent put in the cell, where C_s remained constant during one experimental run.

On the other hand, for the determination of CMC of SDS in the presence of an alkanol, an alkanol solution was, contrary to above, prepared as the solvent with which a SDS solution at C_s higher than CMC was prepared.

These solutions were all prepared by weight. On each addition of the solution, a conductivity measurement was made on a conductivity meter (Fuso Seisakusyo; 361B, 2B, 3B set) at 298.15 ± 0.005 K.

For 1-alkanols, some additional measurements were carried out to those in the previous studies [8] and used for the reanalysis.

Results and Discussion

Determination of partition coefficient

When an alkanol is added in micellar solution of SDS with concentration of C_s, the specific conductivity (κ) changes almost linearly as long as the concentration of C_a is very low, as illustrated elsewhere in the system of SDS-1-alkanols [8]. The slope at infinite dilution, denoted by $(d\kappa/dC_a)_o$, is determined from the $\kappa - C_a$ curve, and plotted in Figs. 1 and 2 against C_s above CMC$_o$ (CMC of SDS itself). The $(d\kappa/dC_a)_o$ increases asymptotically from negative to positive. When i of iso-alkanols

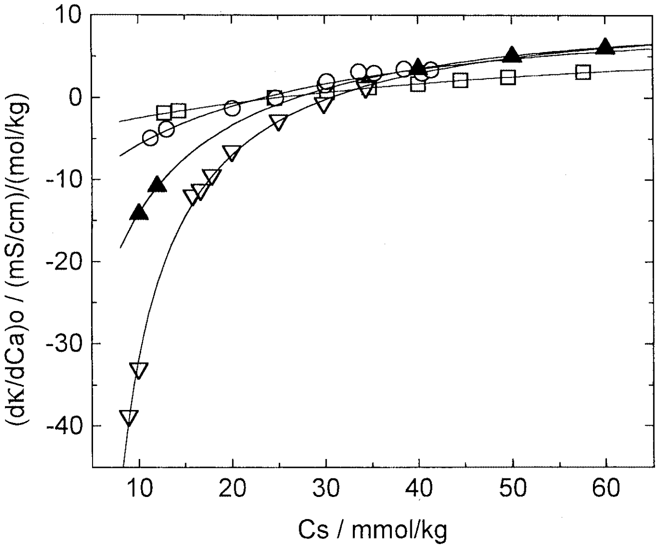

Fig. 1. Relation between the differential conductivity at limiting dilution ($(d\kappa/dC_a)_o$) of added alkanols (i-R_mOH) with a given i ($=2$) and the concentration of SDS (C_s). The *line* indicates the value calculated from resultant parameters given in Table 1; *open squares*, 2-R_5OH; *open circles*, 2-R_6OH; *filled triangles*, 2-R_7OH; *open triangles*, 2-R_8OH

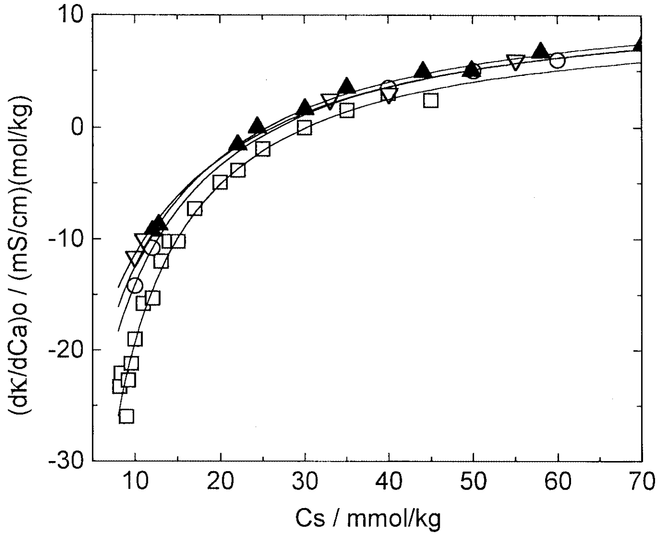

Fig. 2. Relation between the differential conductivity at limiting dilution ($(\mathrm{d}\kappa/\mathrm{d}C_a)_o$) of added alkanols ($i$-R$_m$OH) with a given m ($=7$) and the concentration of SDS (C_s). The line indicates the value calculated from resultant parameters given in Table 1; *open squares*, 1-R$_7$OH; *open circles*, 2-R$_7$OH; *filled triangles*, 3-R$_7$OH; *open triangles*, 4-R$_7$OH

is constant, the increasing tendency is more remarkable for longer chain alkanol (Fig. 1). As for a given hydrocarbon chain (m is constant), the tendency is less remarkable with increasing i, OH group shifting toward the center of chain.

The dependence of $(\mathrm{d}\kappa/\mathrm{d}C_a)_o$ on C_s allows to determine partition coefficient of alkanols between the bulk water and micelles by the differential conductivity method [8]. The equations concerning the method are briefly described in Appendix, together with notations and numerical values used for the analysis. The qualitative mechanism of it is described here.

A micellar solution of ionic surfactant is regarded to consist of two ionic phases [14, 15]: the one is the bulk water phase involving completely ionized free monomer surfactant, and the other is the phase of micelles with a definite degree of ionization (α). If a small amount of nonionic amphiphile is dissolved in a micellar solution, the additive distributes between these two phases, and the additive influences conductivity because the concentration of ionic species changes in the following manner. The solubilization fraction, J defined in Eq. A6 can be related with the conductivity change $(\mathrm{d}\kappa/\mathrm{d}C_a)_o$ by Eq. A8. The monomerically dissolved additive in the bulk water forces the monomer surfactant ion to micellize by the hydrophobic interaction. This is the conductivity decreasing factor, leading to $(\mathrm{d}\kappa/\mathrm{d}C_a)_o < 0$ in Figs. 1 and 2. At $C_s = \mathrm{CMC}_o$, entire amount of additive dissolves in the bulk water ($J \rightarrow 0$) and $(\mathrm{d}\kappa/\mathrm{d}C_a)_o$ decreases by $((\bar{\kappa}_f - \bar{\kappa}_m)\ k$ in Eq. A8. Opposite to the one, the other factor contributes to increase conductivity, $(\mathrm{d}\kappa/\mathrm{d}C_a)_o > 0$, appearing at high C_s infinite mark. When $C_s \rightarrow \infty$, the whole fraction of additive is solubilized in micelles ($J \rightarrow 1$) in the surface of which the polar head group of the additive wedges among the ionic head groups of ionic surfactant to release more counterion and, as a result, $(\mathrm{d}\kappa/\mathrm{d}C_a)_o$ increases by $(\mathrm{d}\alpha/\mathrm{d}X_{am})\ \bar{\kappa}^*_m$ in Eq. A8.

These two opposing factors compete to each other. The experimentally determined asymptotic relation in Figs. 1 and 2 can be converted into the linear relation shown in Figs. 3 and 4. The linear relation of $(\mathrm{d}\kappa/\mathrm{d}C_a)_o$

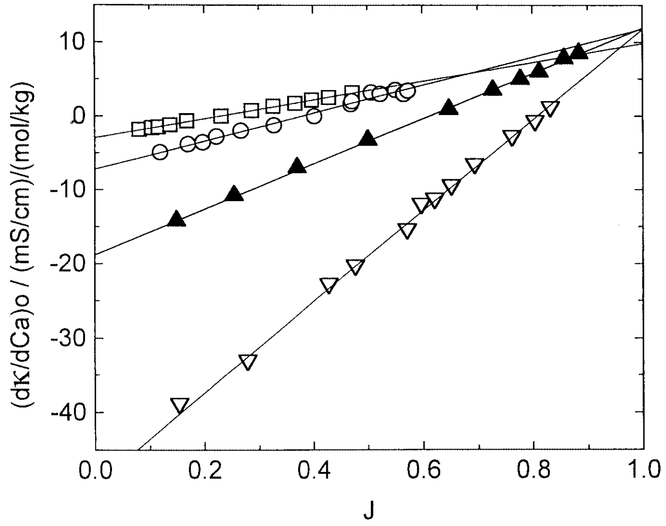

Fig. 3. Relation between $(\mathrm{d}\kappa/\mathrm{d}C_a)_o$ and solubilization fraction (J) for alkanols with a given i ($=2$). The *line* indicates the best fitting linear relation; *open squares*, 2-R$_5$OH; *open circles*, 2-R$_6$OH; *filled triangles*, 2-R$_7$OH; *open triangles*, 2-R$_8$OH

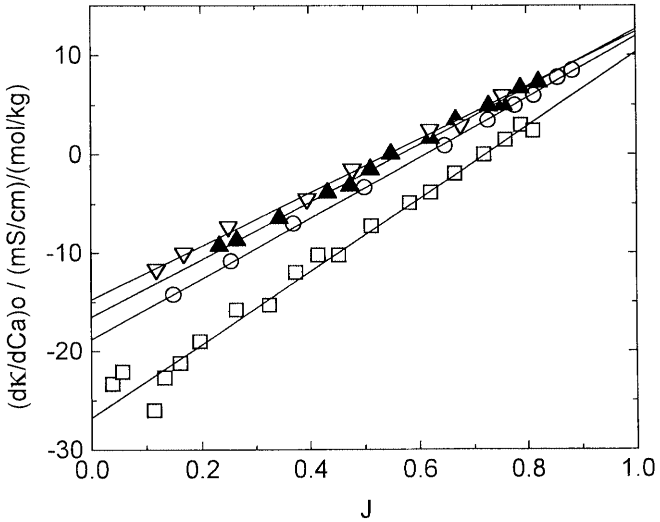

Fig. 4. Relation between $(\mathrm{d}\kappa/\mathrm{d}C_a)_o$ and solubilization fraction (J) for alkanols with a given m ($=7$). The *line* indicates the best fitting linear relation; *open squares*, 1-R$_7$OH; *open circles*, 2-R$_7$OH; *filled triangles*, 3-R$_7$OH; *open triangles*, 4-R$_7$OH

Table 1. Parameters for partitioning of iso-alkanols in SDS micellar solution at 298.15 K

i^a	m^b	$10^{-2}K_x$	$-k^c$	$-(\Delta CMC/\Delta C_a)_o$	$d\alpha/dX_{am}$	$-\Delta G^o(CH_2)^e$
1	4	3.61	0.0293	0.028	0.151	564
	5	9.44	0.0796	0.078	0.187	
	6	24.4	0.240	0.21	0.172	
	7	64.4	0.669	0.53	0.159	
	8	163	1.65	1.65	0.133	
2	5	9.99	0.0733	0.073	0.151	462
	6	22.2	0.181	0.16	0.182	
	7	46.1	0.470	0.43	0.184	
	8	104	1.24	1.19	0.181	
3	5	8.88	0.0545	0.054	0.132	445
	6	18.3	0.133	0.13	0.164	
	7	41.1	0.413	0.34	0.195	
	8	84.4	0.928	0.87	0.181	
	9	148	2.23	3.58	0.293	
4	7	36.1	0.368	0.32	0.191	402
	8	71.0	0.720	0.73	0.193	
	9	123	1.31	2.44	0.175	
5	9	116	1.29	2.30	0.201	
					0.17^d	

[a] Position of OH group in hydrocarbon chain of iso-alkanols (i -$C_mH_{2m+1}OH$)

[b] Total carbon number in alkanol

[c] $k = dC_{sf}/dC_{af}$ above CMC_o

[d] Mean value of $d\alpha/dX_{am}$ for all alkanols except nonanols

[e] Mean value at a given i except nonalols, in cal/mol unit

with J along Eq. A8 is obtained by the regressive analysis for K_x included in J (Eq. A7) as a adjustable parameter. In addition to K_x, significant quantities k and ($d\alpha/dX_{am}$) can be obtained from respective intercepts at $J = 0$ and 1. These values are listed in Table1, together with $\Delta CMC/\Delta C_a$ estimated as the limiting slope of CMC vs. C_a plot.

Dependence of K_x on m and i

The relation between $\log(K_x)$ and m is shown in Fig. 5. At a given i, $\log(K_x)$ increases with increasing m, which can be attributed to strengthening of hydrophobicity. It is apparent that the slope of the plot becomes less steeper with increasing i. The free energy of transfer of alkanol from the bulk water to micelles is a useful measure of hydrophobicity and it is evaluated as $\Delta G^o = -RT\ln(K_x)$, where R and T are the gas constant and absolute temperature, respectively. In addition, the contribution of a methylene group, $\Delta G^o(CH_2)$, can be estimated on the basis of the increment of K_x between the nearest neighbor alkanols in Fig. 5. By approximating the plot in Fig. 5 to be linear, a mean value of $\Delta G^o(CH_2)$ for each homologue with a given i can be estimated (except nonanol) as given in Table 1. The decrease of $\Delta G^o(CH_2)$ in magnitude indicates that the shift of OH group from an end to the center of an hydrocarbon weakens its hydrophobicity, as reported for isomeric alkanols [10, 11].

It is noticeable in Fig. 5 that the lines cross to each other around $m = 5$. The result is compatible with the following facts observed in the system of SDS–1-alkanols: a linear relation of $\log(-(\Delta CMC/\Delta C_a)_o)$ with m deviates for lower alkanols than butanol [16], and no difference was found between the partial molar volumes of these short chain alkanols below and above CMC [17]. Accordingly, the little dependence of K_x on i for the short-chain alkanols may be ascribed to their original low hydrophobicity even without isomerization.

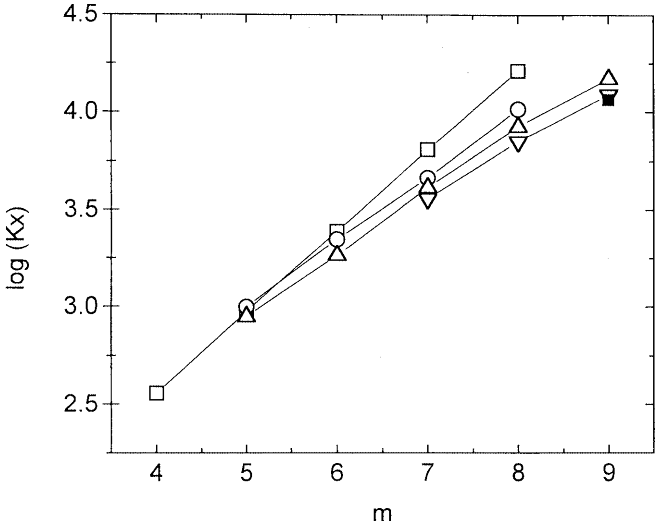

Fig. 5. Relation between the partition coefficient (K_x) and the carbon number (m) of iso-alkanols (i-R_mOH). *open squares*, $i = 1$; *open circles*, $i = 2$; *open upper triangles*, $i = 3$; *open lower triangles*, $i = 4$; *filled squares*, $i = 5$

The rate of counterion releasing, $d\alpha/dX_{am}$

It has been generally considered that the dilution of surface charge density induced by incorporated nonionic moiety in the ionic surface of micelles enhances the counter-ion releasing. So far, however, no experimental study has been carried out on the relation between the surface charge density and the ionization degree of micelles, whereas such a quantitative relation was evidenced by Manning [5], concerning with simple linear rod shape of polyelectrolytes. The present quantity, $d\alpha/dX_{am}$, can be connected straightforward to the relation on a plane surface, since X_{am} is directly correlated to the surface charge density if each cross sectional area of head groups of surfactant and additive can be assigned.

The values of $d\alpha/dX_{am}$ shown in Table 1 are positive, reflecting that the counter-ions are set free from micelles by the solubilized alkanols. In Table 1, it is apparent that $(d\alpha/dX_{am})$ are close to each other (averaged value, 0.17) for all alkanols studied, as also seen in Figs. 3 and 4 where the lines cross around a common point at $J=1$. The fact suggests that only the OH group virtually contributes to the acceleration of counterion releasing, against the expectation that the branching expands the effective cross sectional area of the polar moiety compared to 1-alkanols. It is significant that $d\alpha/dX_{am}$ is independent of both *m* and *i*, whereas $\Delta G^{o}(CH_2)$ is dependent on *i*. A plausible explanation for the results is that the branching affects the dissolved state of alkanols not in micelles but substantially in the bulk water.

Independence of $d\alpha/dX_{am}$ from *m* and *i* suggests that an effective size of polar group in solubilized state can be estimate if a series of $d\alpha/dX_{am}$ with the size of polar group is accomplished for comprehensive groups. Determination of values of $d\alpha/dX_{am}$ for various polar groups is under study.

The relation between k and $(\Delta CMC/\Delta C_a)_o$

The value of *k* calculated from the intercept at $J=0$ in Figs. 3 and 4 is shown in Table 1. From the definition, *k* implies that the relation between concentrations of monomerically dissolved surfactant and additive in the bulk water in micellar solution. The negative value of *k* indicates that C_{sf} is reduced by the addition of alkanols dissolved in monomerical form. The decreasing tendency is in line with the well known fact that CMC decreases with an increase in the concentration of organic additives [18, 19]. In order to compare *k* with the CMC decreasing rate, the CMC in the presence of all alkanols studied was determined as a function of C_a, and then the limiting slope $(\Delta CMC/\Delta C_a)_o$ at $C_a \rightarrow 0$ in the curve of CMC vs. C_a was estimated as listed in Table 1. It is obvious that the values of *k* estimated above CMC and of $(\Delta CMC/\Delta C_a)_o$ estimated just at CMC are in good agreement with each other for each alkanol. The agreement reveals that the hydrophobic interaction between different monomer species of SDS and alkanols remains same at infinite dilution of alkanols because C_{sf} remains low and constant (close to CMC_o) even in the presence of micelles at high C_s.

Relation between $(\Delta CMC/\Delta C_a)_o$ or k and K_x

Manabe et al. [20] described about the relation of $(\Delta CMC/\Delta C_a)_o$ with K_x.

$$-(\Delta CMC/\Delta C_a)_o = \theta(CMC_o/n_w)K_x \qquad (1)$$

where θ is a parameter participating in the interactions among all species of surfactant and additive, and it involves, in particular, the electrostatic contribution as discussed for its physical meaning [20, 21, 22]. The values of θ, 0.69 [20], 0.82 [21] independent of *m* were reported in the system of SDS–1-alkanols. The constancy of θ is examined through Eq. 1 for the present data of both $(\Delta CMC/\Delta C_a)_o$ and *k* and K_x, except nonanols, in Table 1. The linear relation is obtained: $\log(-(\Delta CMC/\Delta C_a)_o, -k) = 1.128\log(K_x) - 4.500$ with correlation factor of 0.9951. The slope is close to unity and $\theta = 0.23$ is calculated from the intercept. The good linearity reflects that Eq. 1 holds and θ is constant for all isomeric alkanols studied.

Finally, the independence of θ as well as $d\alpha/dX_{am}$ from *m* and *i* at infinite dilution leads to the conclusion that the electrostatic interaction on mixed micelle formation is little different from each other for all alkanols studied. In other words, the reduction of surface charge density due to solubilization may be cancelled by counterion releasing. surface potential remaining constant.

Further, if the electrostatic contribution (extra-thermodynamic) to the free energy of transfer remains constant, $\Delta G^{o}(CH_2)$ can be considered to represent the thermodynamic contribution concerning with the hydrophobic interaction only. Thus, the decrease of $\Delta G^{o}(CH_2)$ with *i* is supposed to be attributed to the change of interaction even in the bulk water, not in micelles, since the interaction in micelles inside of which is non-polar is hardly affected by the branching.

Appendix

Differential conductivity method for the determination of partition coefficient of nonionic substance in ionic surfactant micellar solution [8].

Concentrations of surfactant (s) and additive(a) in free monomer (f) and micellar (m) states are related as:

$$C_s = C_{sf} + C_{sm}\ ;\ C_a = C_{af} + C_{am} \qquad (A1)$$

Differential conductivity of free monomer and micellar surfactant species of an ionic surfactant are defined by differentiating specific conductivity (κ) with concentration of respective species of the surfactant.

$$\bar{\kappa}_{\mathrm{f}} = \mathrm{d}\kappa/\mathrm{d}C_{\mathrm{sf}}\ ,\ \bar{\kappa}_{\mathrm{m}} = \mathrm{d}\bar{\kappa}/\mathrm{d}C_{\mathrm{sm}} \tag{A2}$$

where $\bar{\kappa}_{\mathrm{f}}$ and $\bar{\kappa}_{\mathrm{m}}$ are the differential conductivities below $\mathrm{CMC_o}$ and above the CMC region, respectively. Then the κ of a micellar solution can be expressed as a linear combination of differential conductivity and concentration of respective species.

$$\kappa = \bar{\kappa}_{\mathrm{f}} C_{\mathrm{sf}} + \bar{\kappa}_{\mathrm{m}} C_{\mathrm{sm}} \tag{A3}$$

When a small amount of a nonionic substance is added in a micellar solution with a given C_{s}, the rate of conductivity change represented in the form of ($\mathrm{d}\kappa/\mathrm{d}C_{\mathrm{a}}$) can be derived by differentiating Eq. A3 with C_{a} under the condition of a constant C_{s}.

$$\mathrm{d}\kappa/\mathrm{d}C_{\mathrm{a}} = \bar{\kappa}_{\mathrm{f}}(\mathrm{d}C_{\mathrm{sf}}/\mathrm{d}C_{\mathrm{a}}) + \bar{\kappa}_{\mathrm{m}}(\mathrm{d}C_{\mathrm{sm}}/\mathrm{d}C_{\mathrm{a}}) + (\mathrm{d}\bar{\kappa}_{\mathrm{m}}/\mathrm{d}C_{\mathrm{a}})C_{\mathrm{sm}} \tag{A4}$$

In the derivation, the term of ($\mathrm{d}\bar{\kappa}_{\mathrm{f}}/\mathrm{d}C_{\mathrm{a}}$) can be neglected from the experimental result.

Further, $\bar{\kappa}_{\mathrm{m}}$ is taken to be correlated with degree of counterion dissociation of micelles (α).

$$\bar{\kappa}_{\mathrm{m}} = \alpha \bar{\kappa}^{*}_{\mathrm{m}} \tag{A5}$$

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

Now, following quantities are defined: the partition coefficient (K_{x}) of additive in mole fraction unit, the decreasing rate of monomer surfactant (k), and the solubilization fraction (J).

$$K_{\mathrm{x}} = X_{\mathrm{af}}/X_{\mathrm{am}}\ ;\ k = \mathrm{d}C_{\mathrm{sf}}/\mathrm{d}C_{\mathrm{af}}\ ;\ J = \mathrm{d}C_{\mathrm{am}}/\mathrm{d}C_{\mathrm{a}} \tag{A6}$$

Under the condition of $C_{\mathrm{a}} \rightarrow 0$, the approximations can be valid.

$$J = (K_{\mathrm{x}}/n_{\mathrm{w}})(C_{\mathrm{s}} - \mathrm{CMC_o})/(1 + (K_{\mathrm{x}}/n_{\mathrm{w}})(C_{\mathrm{s}} - \mathrm{CMC_o})) \tag{A7}$$

where, n_{w} and $\mathrm{CMC_o}$ stand for the mole number of water in 1 kg of solution, and the CMC of the ionic surfactant itself, respectively. Eq. A7 allows to calculate J at any C_{s} when K_{x} can be estimated. As a result, Eq. A4 can be rewritten by using above quantities, at the infinite dilution of additive.

$$\mathrm{d}\kappa/\mathrm{d}C_{\mathrm{a}} = (\bar{\kappa}_{\mathrm{f}} - \bar{\kappa}_{\mathrm{m}})k + \left\{\bar{\kappa}^{*}_{\mathrm{m}}(\mathrm{d}\alpha/\mathrm{d}X_{\mathrm{am}}) - (\bar{\kappa}_{\mathrm{f}} - \bar{\kappa}_{\mathrm{m}})k\right\}J \tag{A8}$$

In the right-hand side, only J is a variable. Therefore, Eq. A8 indicates that experimentally determined ($\mathrm{d}\kappa/\mathrm{d}C_{\mathrm{a}}$) at a infinite dilution of additive, expressed as $(\mathrm{d}\kappa/\mathrm{d}C_{\mathrm{a}})_{\mathrm{o}}$ in text is a linear function of J. The linear relation can be determined by a regressive analysis for the best fitting K_{x} as a parameter. Respective intercepts at $J = 0$ and $J = 1$ of the resultant relation provide k and ($\mathrm{d}\alpha/\mathrm{d}X_{\mathrm{am}}$), which indicates the acceleration rate of ionization of micelles. On the analysis concerning with SDS, the numerical values were adopted: $\bar{\kappa}_{\mathrm{f}} = 65.0$, and $\bar{\kappa}_{\mathrm{m}} = 25.0$ mS cm^{-1} mol^{-1} kg estimated from experimental data of differential conductivity curve of SDS solution, just at $\mathrm{CMC_o}$ and far above $\mathrm{CMC_o}$, respectively. In addition, $\bar{\kappa}^{*}_{\mathrm{m}}$ was postulated to be identical with $\bar{\kappa}_{\mathrm{f}}$. The value of CMCo is 7.8 mmol/kg.

References

1. Tanford C (1973) The hydrophobic effect. Wiley, New York
2. Stigter D (1975) In van Olphen H, Maysels KJ (eds) Physical chemistry: enriching topics from colloid and surface science. Theorex, La Jolla, CA, p 181
3. Moroi Y (1992) Micelles, theoretical and applied aspects. Plenum, New York, p 61
4. Manabe M, Kawamura H, Kondo S, Kojima M, Tokunaga S (1990) Langmuir, 6:1596
5. Manning GS (1975) J Phys Chem 79:262
6. Trainer C (1995) In Christian SD, Schamehorn JF (eds) Solubilization in surfactant aggregates. Dekker, New York, p 383
7. Marangoni G, Kwak CT (1995) In Christian SD, Schamehorn JF (eds) Solubilization in surfactant aggregates. Dekker, New York, p 455
8. Manabe M, Kawamura H, Yamashita A, Tokunaga S (1987) J Colloid Interface Sci 115:147
9. Manabe M, Kawamura H, Yamashita Y, Tokunaga S (1990) In Bloor DM, Wyn-Jones E (eds) The structure, dynamics and equilibrium properties of colloidal systems. Kluwer, Dordrecht, p 63
10. De Lisi R, Milioto S (1995) In Christian SD, Schamehorn JF (eds) Solubilization in surfactant aggregates. Dekker, New York, p 101
11. Matsui Y, Mochida K (1979) Bull Chem Soc Jpn 52:808
12. Evans HC (1956) J Chem Soc:579
13. Manabe M, Tanizaki Y, Watanabe H, Tokunaga S, Koda M (1983) Memoirs of Niihama Technical College (Science and Engeneering), vol 19. p 50
14. Sasaki T, Hattori M, Sasaki J (1975) Bull Chem Soc Jpn 18:1397
15. Sasaki T, Yasuda M, Suzuki H (1977) Bull Chem Soc Jpn 50:2538
16. Manabe M, Koda M (1978) Bull Chem Soc Jpn 51:1599

17. Manabe M, Shirahama K, Koda M (1976) Bull Chem Soc Jpn 49:2904
18. Shinoda K (1963) In Shinoda K, Nakagawa T, Tamamushi B, Isemura T (eds) Colloidal surfactsants. Academic Press, New York, p 69
19. Manabe M, Kawamura H, Sugihara G, Tanaka M (1988) Bull Chem Soc Jpn 61:1551
20. Manabe M, Koda M, Shirahama K (1980) J Colloid Interface Sci 77:189
21. Hayase K, Hayano S (1978) J Colloid Interface Sci 63:446
22. Abu-Handiyyah M, El-Danab C (1983) J Phys Chem 87:544