Properties of Dilute Aqueous Solutions of Double-Chain Surfactants, Alkyldodecyldimethylammonium Bromides with a Change in the Length of the Alkyl Chains

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A series of cationic surfactants, dialkyldimethylammonium bromides with dodecyl as the primary alkyl chain and with methyl, ethyl, propyl, butyl, hexyl, octyl, and decyl as the second alkyl chain, as well as those with symmetric alkyl chains, dioctyl, didecyl and didodecyl ones, were synthesized, and their properties were investigated through measurements of the conductivity and air–liquid surface tension for their aqueous solutions to determine their critical micelle concentrations (cmc) and surface adsorption parameters in the formulation according to a two-dimensional lattice model in the form of the Frumkin equation. The change in cmc revealed that the free energy to transfer from water to the micelle per methylene unit is significantly small for asymmetric double-chain surfactants with a shorter second alkyl chain, and it approaches as elongating the second alkyl to those for the single-chain and symmetric double-chain surfactants. The free energy to transfer to an air–solution interface decreased approximately linearly with the total length of the hydrocarbon chains for all of the species examined. The lattice area for a symmetric double-chain surfactant molecule decreased with the length of its hydrocarbons. In a series of asymmetric ones, it showed a maximum for that with hexyl in its second alkyl.

Cationic surfactants of the type of quaternary ammonium salts constitute a major class among various types of surfactants. Quaternary ammonium surfactants with a single long alkyl chain, and those carrying two long hydrophobic chains are widely applied in practical fields, such as fabric softeners and antimicrobial or antiseptic agents, besides their common properties as surface-active agents.[1,2] The class of quaternary ammonium surfactants are utilized for a variety of purposes, since their properties can be selected by controlling the chemical structures of their hydrophobic tail groups.

Single-chain surfactants of quaternary ammonium salts have been studied concerning their micellar structures; namely, transition phenomena from spherical micelles to rod-like micelles have been observed mostly for this type of surfactant.[3,4] On the other hand, double-chain quaternary ammonium salts have attracted interest owing to their properties to form bilayer structures, or vesicles,[5–12] and concerning interactions with proteins.[13] Such variations in the properties of these types of surfactants should be correlated with their chemical structures, which determine the hydrophilic–hydrophobic balance, or packing properties, in various types of molecular assemblies. It is hence important to investigate the relationship between the chemical structure and the solution or surface-active properties of the surfactants.

While some studies have been reported concerning the change of the solution properties of those surfactants with a change in the length of the hydrocarbon chain for double-chain surfactants with equal lengths of alkyl chains[7–10] and for those with unequal lengths of alkyl chains,[11,14,15] the variation in the properties of the surfactants from single-chain to double-chain ones has not been explicitly demonstrated. To understand the variation in the properties of quaternary ammonium salts, it seems to be pertinent to study the change in the properties with the length of the second alkyl chain in a systematic way.

For characterizing the variation of their properties with the length of the second alkyl chain, we prepared a series of dialkyldimethylammonium bromides with various lengths of the second alkyl chain, of which the primary alkyl is unchanged to be dodecyl, which is abbreviated as $C_{12}C_n$DMA. In the present study, the properties of aqueous solutions of eight kinds of surfactants, namely $n = 1$, 2, 3, 4, 6, 8, 10, and 12, of $C_{12}C_n$DMA surfactants, were investigated through precise measurements of the surface tensions of the air–solution interfaces as well as measurements of the conductivities of their aqueous solutions.

Experimental

Synthesis of the Double Chain Cationic Surfactants. Alkyldodecyldimethylammonium bromides were synthesized through a quaternarization reaction between dodecyldimethylamine and corresponding alkyl bromides. The reactions were performed with ethanol as a solvent under a nitrogen stream, and the resulting products were extracted by ether. The surfactants were purified by recrystallization from a mixture of acetone and ethanol. As a recrystallization solvent, ethyl acetate was occasionally used for those with hexyl and longer ones as their second alkyl chains.

Measurements of Surface Tension. The surface tension of the air–liquid interface was measured according to the drop-volume method[16] by using an automatic surface tensiometer, type YMK98, manufactured by Yamashita Giken Ltd. (Tokushima, Japan). This instrument is equipped with a photo-sensing drop counter and a precise monitor of the drop volume. The vessel ac-

Published on the web October 15, 2003; DOI 10.1246/bcsj.76.1903

commodating the drop counting apparatus was immersed into a water bath, of which the temperature was controlled to be 25 ± 0.01 °C. The surface tension (γ) was calculated according to

$$\gamma = (V\Delta dg/r)Y(r/V^{1/3}). \tag{1}$$

Here, g is the acceleration due to gravity and Δd is the difference in the density between the solution and humid air, which was approxmated to the density of water at 25.00 °C. In this equation, r is the radius of the dropping tip, which was measured with a microgauge for each of the tips used. The compensation factor, $Y(r/V^{1/3})$, was calculated according to an approximated quadratic function proposed by Lando and Oakley[17] for a given r and the measured drop volume (V).

Measurements of Conductivity. The conductivities of the surfactant solutions at 25 °C were measured by an electric conductivity meter, CM-1DB (Toa electronics Co., Japan) with electrodes, CG-201PL, supplied by the same manufacturer. The electrodes were equilibrated with each of the surfactant solutions for 5 to 30 min before a measurement.

Results

Conductivities of Aqueous Solutions. Figure 1 shows the conductivities measured for aqueous solutions of alkyldodecyldimethylammonium bromides ($C_{12}C_nDMA$) with the second alkyl chain of methyl ($n = 1$), ethyl ($n = 2$), propyl ($n = 3$), butyl ($n = 4$), hexyl ($n = 6$), octyl ($n = 8$), decyl ($n = 10$) and dodecyl ($n = 12$) groups plotted against the surfactant concentration. For each of the surfactants, the plot shows a clear deflection, which indicates a change of the specific conductivity of the solute due to the formation of molecular assemblies. The concentration at the deflection point is hence the critical micelle concentration (cmc). The thus-determined values of cmc are given in Table 1.

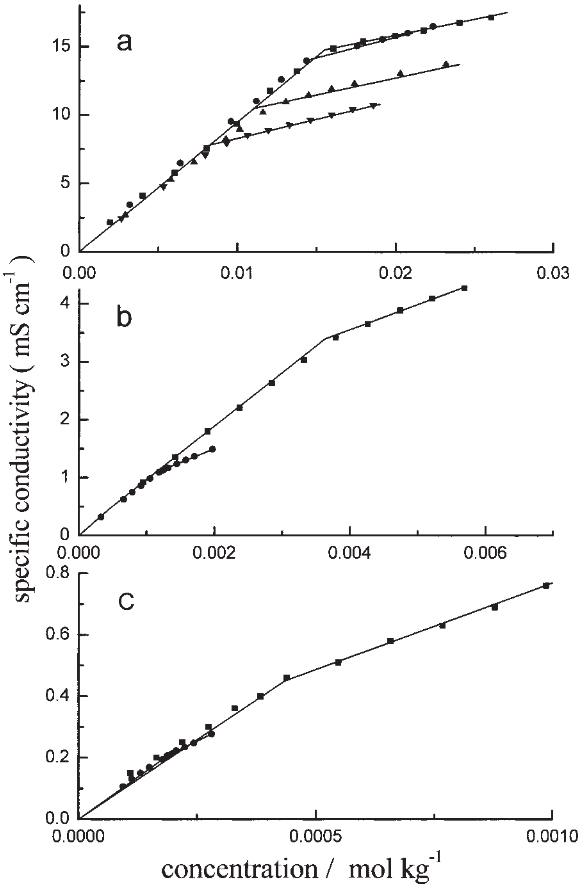

Fig. 1. Conductivities of aqueous solutions of alkyldodecyldimethylammonium bromides. $C_{12}C_1DMA$ (■), $C_{12}C_2DMA$ (●), $C_{12}C_3DMA$ (▲) and $C_{12}C_4DMA$ (▼) in (a), $C_{12}C_6DMA$ (■) and $C_{12}C_8DMA$ (●) in (b), and $C_{12}C_{10}DMA$ (■) and $C_{12}C_{12}DMA$ (●) in (c).

Table 1. Critical Micelle Concentrations and Related Properties

Surfactant species	cmc/mol kg^{-1} (Surface tension)	cmc/mol kg^{-1} (Conductivity)	β
$C_{12}C_1DMA$	1.50×10^{-2}	1.55×10^{-2}	0.24
$C_{12}C_2DMA$	1.42×10^{-2}	1.43×10^{-2}	0.32
$C_{12}C_3DMA$	1.16×10^{-2}	1.22×10^{-2}	0.29
$C_{12}C_4DMA$	9.43×10^{-3}	9.16×10^{-3}	0.32
$C_{12}C_6DMA$	3.99×10^{-3}	3.63×10^{-3}	0.50
$C_{12}C_8DMA$	1.35×10^{-3}	1.29×10^{-3}	0.54
$C_{12}C_{10}DMA$	3.50×10^{-4}	4.35×10^{-4}	0.58
C_8C_8DMA	2.22×10^{-2}	2.30×10^{-2}	0.32
$C_{10}C_{10}DMA$	1.50×10^{-3}	1.55×10^{-3}	0.53
$C_{12}C_{12}DMA$	7.0×10^{-5}	1.91×10^{-4}	0.71

While the increment of the specific conductivity below the cmc was not varied with the surfactant species, that above the cmc seemed to increase with the length of the second alkyl chain. The ratio between the slope below cmc and that above cmc (β) can be used as a measure of the degree of the counterion dissociation for the micelle. The thus-calculated values are given in Table 1. The β for $C_{12}C_1DMA$ is in good agreement with the previously reported one.[14,18] The β was observed to increase in an approximately linear way with the length of the second alkyl chain. This may be ascribed to the change in the charge density on the micellar aggregates, since the increment of the conductivity below the cmc was not significantly varied with the surfactant species.

Surface Tensions of Air–Aqueous Solution Interfaces. Figure 2 shows the surface tension of the air–liquid interface measured for aqueous solutions of alkyldodecyldimethylammonium bromides ($C_{12}C_nDMA$) with the second alkyl chain of methyl ($n = 1$), ethyl ($n = 2$), propyl ($n = 3$), butyl ($n = 4$), hexyl ($n = 6$), octyl ($n = 8$), and decyl ($n = 10$) groups plotted against the logarithm of the concentration.

For all of the surfactant species, the surface tension decreased monotonously with the surfactant concentration up to a deflection point. Assuming this deflection to indicate the formation of micellar aggregates, the concentration at the deflection point can be referred to the critical micelle concentration (cmc) of each of the surfactants. Here, we use the term cmc commonly for describing the concentrations at which an observed quantity changes deflectively, though the aggregates formed at the concentration may not be defined as the coventional micelle, as discussed in the Discussion section.

Above the deflection, the surface tension varied very scarcely with the surfactant concentration for those surfactants with a shorter second alkyl chain ($C_{12}C_1DMA$, $C_{12}C_2DMA$, $C_{12}C_3DMA$, and $C_{12}C_4DMA$). For those with longer second chain ($C_{12}C_6DMA$, $C_{12}C_8DMA$, and $C_{12}C_{10}DMA$), however,

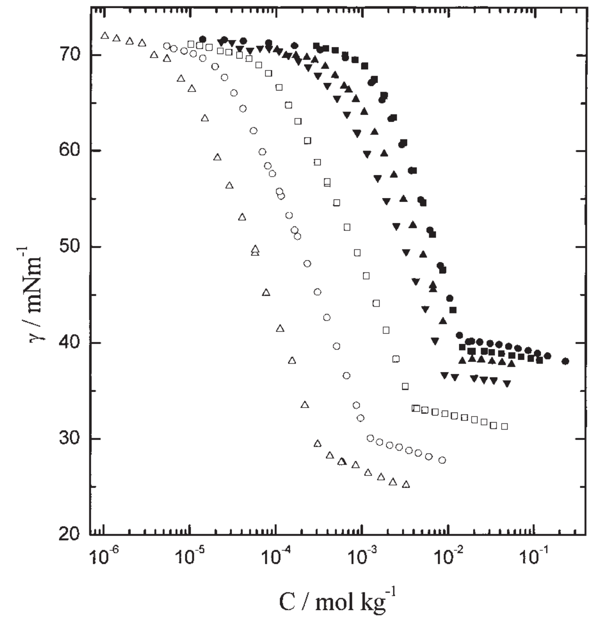

Fig. 2. Surface–tension isotherms for aqueous solutions of alkyldodecyldimethylammonium bromides. From right to left, $C_{12}C_1DMA$ (■), $C_{12}C_2DMA$ (●), $C_{12}C_3DMA$ (▲), $C_{12}C_4DMA$ (▼), $C_{12}C_6DMA$ (□), $C_{12}C_8DMA$ (○), and $C_{12}C_{10}DMA$ (△).

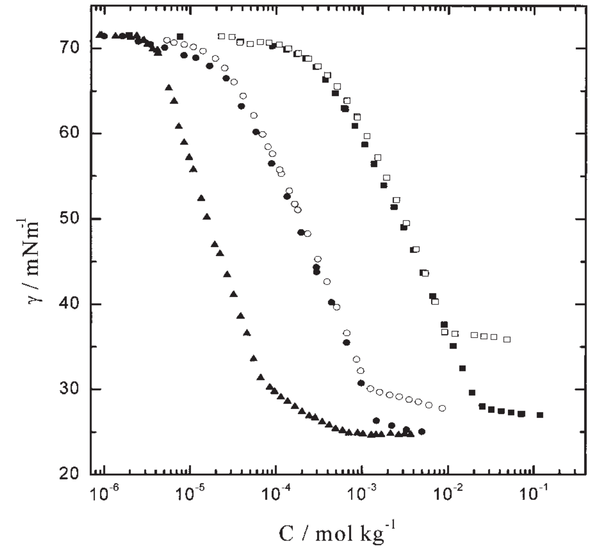

Fig. 3. Surface–tension isotherms for aqueous solutions of dialkyldimethylammonium bromides. From right to left, C_8C_8DMA (■), $C_{10}C_{10}DMA$ (●), and $C_{12}C_{12}DMA$ (▲). The data of $C_{12}C_4DMA$ (□) and $C_{12}C_8DMA$ (○), are reproduced from Fig. 2 for comparison.

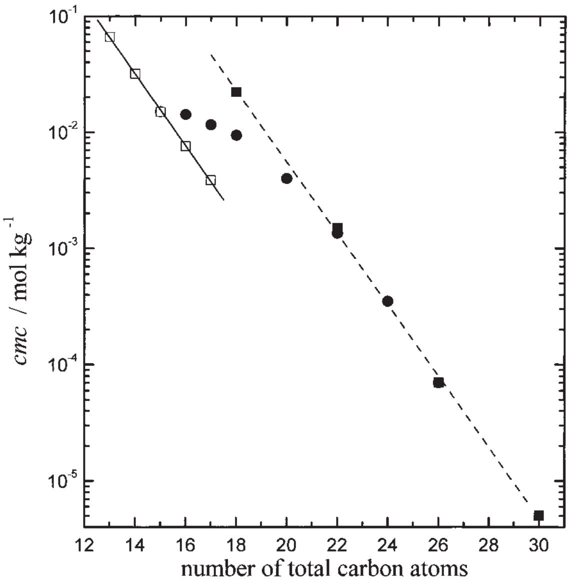

Fig. 4. Critical micelle concentrations of quaternary ammonium bromides plotted against the total number of carbon atoms in the molecule (n_C). Symbols and surfactant species: (●), alkyldodecyldimethylammonium bromides ($C_{12}C_mDMA$); (■), symmetric dialkyldimethylammonium bromides (C_nC_nDMA), among which the data of $C_{14}C_{14}$-DMA ($n_C = 30$) was adopted from Haas and Hoffmann (1996),[11] and (□), alkyltrimethylammonium bromides of which data were taken from Aoki et al. (1986).[20]

it showed a significant decrease above the deflection concentration.

Figure 3 shows surface–tension isotherms for the dialkyl surfactants with equal lengths of a couple of alkyl chains (C_8C_8DMA, $C_{10}C_{10}DMA$, and $C_{12}C_{12}DMA$ bromides). These surface–tension isotherms for symmetric double-chain surfactants were mostly in good agreement with the results reported by Svitova et al.[10] at 22 °C, except for $C_{10}C_{10}DMA$. The mode of the change of the surface tension for C_8C_8DMA, and $C_{10}C_{10}DMA$ was largely the same as that of asymmetric dialkyl surfactants shown in Fig. 2. In Fig. 3, the results for $C_{12}C_4DMA$ and $C_{12}C_8DMA$ are shown for a comparison. Apparently, the surfactants with the same carbon number have a very similar effect on decreasing surface tension, while the cmc's of the symmetric dialkyl surfactants are higher than those of the asymmetric dialkyl surfactants carrying the same carbon number. These results suggest that the magnitude of surfactant adsorption on the air–solution interface is additively determined by the total length of the hydrocarbon chains in a surfactant molecule, but the chain length inequality affects the stability of micellar aggregates (to be discussed later, see Fig. 4).

In the surface–tension isotherm of $C_{12}C_{12}DMA$, a second deflection point could be observed at a rather higher concentration. Above this point, the surface tension of its solution was observed to be constant with the surfactant concentration. Solutions of $C_{12}C_{12}DMA$ at these concentrations were slightly turbid, while the dispersion was quite stable. The second inflection point is hence presumed to be the boundary between the isotropic micellar solution and the water–liquid crystal coexisting region.

Discussion

In the present study, we obtained systematic results for quaternary ammonium bromides as double-chain surfactants carrying two elongated hydrocarbons, mainly through surface tensiometry. Here, we discuss some quantitative aspects for the change in the properties of the surfactant with varying length of the second alkyl chain.

Critical Micelle Concentrations. In Table 1, the values of cmc determined from the deflection points in the surface–tension isotherm and conductivity measurements are summarized. The values from the two methods agree well, except for $C_{12}C_{12}$DMA. The cmc for $C_{12}C_{12}$DMA was not precisely determined by a conductivity measurement, since the deflection in the concentration dependence of the conductivity was very shallow. For aqueous solutions of this kind of double-chain surfactant, the presence of two deflection points has been reported.[10–12] The presently reported values of cmc are judged to be the lower ones in the above reports. Below this (the first) cmc, the solutions involve soley monomerically dissolved surfactants.

In Fig. 4, the cmc obtained in the present study for the double chain surfactants are plotted against the total number of carbon atoms in the surfactant molecule. For ionic surfactants, the change of cmc with the hydrocarbon chain length is expressed as follows:[19]

$$\log cmc = -Am + B, \tag{2}$$

where A and B are constants for a homologous series of surfactant. In particular, the coefficient A is described by

$$A = \frac{\omega}{2.303kT(1 + K_{\mathrm{g}})}. \tag{3}$$

Here, m is the number of carbon atoms in the hydrocarbon chain(s), ω the free energy to transfer one methylene group from a hydrophobic environment to water, K_{g} the negative slope of $\ln cmc$ versus the counter-ion concentration, k the Boltzmann constant, and T the absolute temperature.

As shown in the figure, the log *cmc* for the single-chain surfactant decreases linearly with the total number of carbons, or with the length of its hydrocarbon chain.[20] Such a linear relation is shown to also hold for a series of double-chain surfactants with equal length of the alkyl groups. It is also noted that the change for the equal-length double-chain surfactants is parallel with that for single-chain surfactants. This fact has been shown by Kunieda and Shinoda[7] for those quaternary ammonium chlorides. In this respect, an elongation of the alkyl chain length additively affects the stabilization of micelle formation for both types of surfactants. This aspect thus indicates that both types of surfactants are equivalent in terms of A, but distincted in B.

In the results of the present series of surfactants carrying unequal lengths of two alkyl chains, the points are shown to deviate from the line of the single-chain species and approach to that of the equal-length double-chain species as the carbon number increases. The change of cmc with the hydrocarbon chain length can be compared with the effect of the position of the ionic group in a long hydrocarbon chain.[21,22] The resulting compound can be regarded as a series of double-chain surfactants of the type of sodium 1-alkylalkyl sulfates (RR′$CHSO_4$Na).

It has been pointed out that the elongation of the shorter alkyl chain in the above type of surfactants carrying another longer alkyl chain also linearly decreases ln *cmc*, but does not do so as effectively as that of the longer one.[23] For the present results for dialkyldimethylammonium bromides, the linear relation with respect to the second alkyl chain length appears to hold only for those of which the chain length is very short.

As summarized in the literature,[19] shifting the position of a sulfate group has been shown to increase cmc to shift the log *cmc* versus *m* line for the homologous series of surfactants. Those changes of cmc are quite similar to the present results. In the expression of Eq. 2, the difference in the length of the second chain is reflected by that of the constant, B. This can be regarded as a change in the properties of the hydrophilic head group. In the results for RR′$CHSO_4$Na surfactants, the relation of Eq. 2 has been shown to hold for the length of one (primary) alkyl chain for each series of surfactants which has same the length as another (second) chain. This indicates that the additional second hydrocarbon chain attaching to a head group acts to modify the original properties of the hydrophilic group, or generates a new series of surfactants of which cmc varies systematically with the length of the primary hydrocarbon.

For the present series of asymmetric double-chain surfactants, the change in the hydrophilic head group in terms of B can be estimated, provided that the cmc of each series of surfactants with the same length of the second chain changes as Eq. 2 or Eq. 4 with same slope, A as a function of the chain length of the primary alkyl. Figure 5 shows the variance in the intercept (B) with the length of the second chain. In this result, B changes linearly with the length of the second chain for carbon numbers up to 4, and further elongation of the chain has an effect similar to that in the series of symmetric double-chain surfactants.

Here, the change in cmc for the present double-chain surfactants can be discussed in terms of the balance between their hydrophilic and hydrophobic contributions to the energetics of micelle formation. The value of cmc is correlated with the change in the Gibbs free-energy upon micelle formation, $\Delta\bar{G}_{\mathrm{m}}^{\circ}$. The relation may be assumed to be described by the following equation for ionic surfactants:[24]

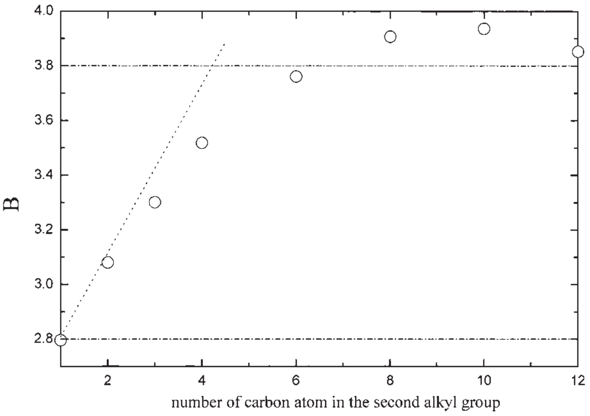

Fig. 5. Variation in B for asymmetric double-chain surfactants, alkyldodecyldimethylammonium bromides ($C_{12}C_m$DMA) with the number of carbon atoms in the second alkyl group. The dashed line is the level for the single-chain surfactants (lower line) and that for symmetric double-chain surfactants (upper line). The dotted line shows the line with the slope corresponding to the common A to the single-chain surfactants and the symmetric double-chain ones.

$$\Delta \bar{G}_{\mathrm{m}}{}^{\circ} = \mu_{\mathrm{m}}^{\circ} - \mu_{1}^{\circ} = (1 + K_{\mathrm{g}})RT \ln X_{\mathrm{cmc}}, \tag{4}$$

where μ_{m}° and μ_{1}° are the standard chemical potential for the surfactant species in a micellar environment and that for a monomeric species in an aqueous environment; X_{cmc} is the mole fraction of the surfactant at cmc. Combined with Eq. 2, the change in the Gibbs free energy can be described as

$$\Delta \bar{G}_{\mathrm{m}}{}^{\circ}(m) = -\omega' m + \bar{G}_{\mathrm{w}}. \tag{5}$$

Here, $\omega' = 2.303RTA(1 + K_{\mathrm{g}})$ is the increment of the free energy per one mole of methylene group, and $\bar{G}_{\mathrm{w}} = 2.303RT[B(1 + K_{\mathrm{g}}) + \ln \Omega_{\mathrm{w}}]$, where Ω_{w} is the molality of water, and can be regarded as a constant term for a series of surfactants carrying the same hydrophilic head group.

The parallel relation for the single-chain species and the equal-length double-chain ones in Eq. 2 is interpreted as that both of them have almost the same values for ω', while the former has a smaller value of $\bar{G}_{\mathrm{w}}$ than the latter. This indicates that the formation of micelles by an equal-length double-chain surfactant is unstabilized compared with that by a single-chain surfactant carrying the same total carbon number in its tail group; namely, the former shows a higher cmc than the latter. This difference is largely ascribed to that in the energetic contribution of their hydrophilic parts upon transfer from water to the molecular assemblies formed by each of surfactant species.

An elongation of an alkyl chain in a surfactant molecule is supposed to increase unfavorable interactions between monomerically dissolved species and surrounding water molecules, namely to increase μ_{1}°. This usually yields a decrease of cmc, when the elongation would not alter the micellar state to keep μ_{m}° unchanged. In the case of an elongation of the second alkyl chain, it should also certainly contribute to the destabilization of the monomeric state in water, even for the unequal-length species. The fact that the elongation yields not so much depression of cmc implies that the chemical potential in the micellar state (μ_{m}°) should be increased concomitantly by an elongation of the second alkyl chain.

It is to be noted that the initial slope of the plot in Fig. 5 closely coincides with the value of A. This coincidence indicates that the magnitude of the increase in μ_{m}° is equal to that of the increase in μ_{1}° by an elongation of the second alkyl chain. This suggests that the elongated hydrophobic part in the second chain is scarcely embedded into the internal environment of the micellar aggregates, but is mostly protruded into the aqueous environment, especially when the second chain is relatively short. This could make the micellar state rather unstable to increase μ_{m}°. The effect seems less pronounced with increasing the length of the second alkyl chain. This is plausible, because some of the hydrophobic part of the second chain can be hidden from the aqueous medium upon the formation of micellar aggregates.

Properties in Air–Solution Interfaces. According to the Gibbs equation for a binary solution, the surface excess of the surfactant (Γ_2) is related to the change in the surface tension with the activity of the surfactant,

$$\Gamma_2 = -\left(\frac{\partial \gamma}{\partial \mu_2}\right)_{T,P} = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln a_2}\right)_{T,P}, \tag{6}$$

where μ_2 and a_2 are the chemical potential and the activity of the solute, respectively. For aqueous solutions of an ionic surfactant, its activity is given by $a_{\pm} = a_{+}a_{-} = (f_{+}C_{+})(f_{-}C_{-})$, where f_{+} and f_{-} are the activity coefficients for the cation and the anion, respectively. For a monomeric surfactant solution with a concentration of $C_2^{(1)}$, $C_{+} = C_{-} = C_2^{(1)}$. In the present study, regarding each of the activity coefficients to be unity, we estimated the surface excess by

$$\Gamma_2 = -\frac{1}{2RT}\left(\frac{\partial \gamma}{\partial \ln C_2^{(1)}}\right)_{T,P}. \tag{7}$$

The surface excesses thus estimated from the surface–tension isotherms are shown in Fig. 6 against the logarithm of the surfactant concentration.

In a simple theoretical treatment for the surface adsorption by using the Bragg–Williams approach,[25] the following relation between the surface excess and the solute concentration in a bulk solution is derived:

$$C_2 = \frac{A_0\Gamma_2}{K(1 - A_0\Gamma_2)} \exp(WA_0\Gamma_2). \tag{8}$$

Here, A_0 is the surface area per lattice site, and W represents the magnitude of the preferential interaction among the adsorbed molecules. In the above equation, K is an elementary binding constant, which is related to the standard free-energy change per mole of the adsorbed surfactant ($\Delta G_{\mathrm{a}}^{\circ}$) by

$$\Delta G_{\mathrm{a}}^{\circ} = -RT \ln K. \tag{9}$$

The above formulation is known as the Frumkin equation.[26,27] The surface excess empirically estimated as above is known to change in a discontinuous manner in a region of low bulk concentration.[28,29] Sophisticated treatments have been made to describe the entire change of the surface tension.[30,31] In the present study, Eq. 8 was applied to the whole concentration region, while neglecting the discontinuous behavior of the surface adsorption. The empirically estimated $\Gamma_2(C_2)$ was read as $C_2(\Gamma_2)$, and the parameters in Eq. 8 were evaluated by a non-linear fitting procedure. The fitting was reasonably well made except for the discontinuous region. The results are shown as functions by the smooth lines in Fig. 6, and the thus-estimated adsorption parameters are given in Table 2. To compare the variation in the parameters with the surfactant species, those parameters are plotted against the total number of carbon atoms of the surfactant molecule in Fig. 7.

In Fig. 7a, the standard free-energy change upon adsorption ($\Delta G_{\mathrm{a}}^{\circ}$) decreases linearly with the number of carbon atoms. A very similar tendency of this parameter can be found in other series of compounds having a linear hydrocarbon in the data reported by Hirte and Lunkenheimer.[30] It is noted that the two symmetric double-chain surfactants, C_8C_8DMA and $C_{10}C_{10}$DMA, show nearly the same values as those for the asymmetric ones with the same carbon number, $C_{12}C_4$DMA and $C_{12}C_8$DMA, respectively. This indicates that the free energy to transfer a hydrocarbon chain from the aqueous phase to the air–liquid interface is determined additively by the length of the hydrocarbon chain, even in asymmetric double-chain surfactants. This change may be compared with the change in cmc, which varies linearly with the length of hydrocarbon

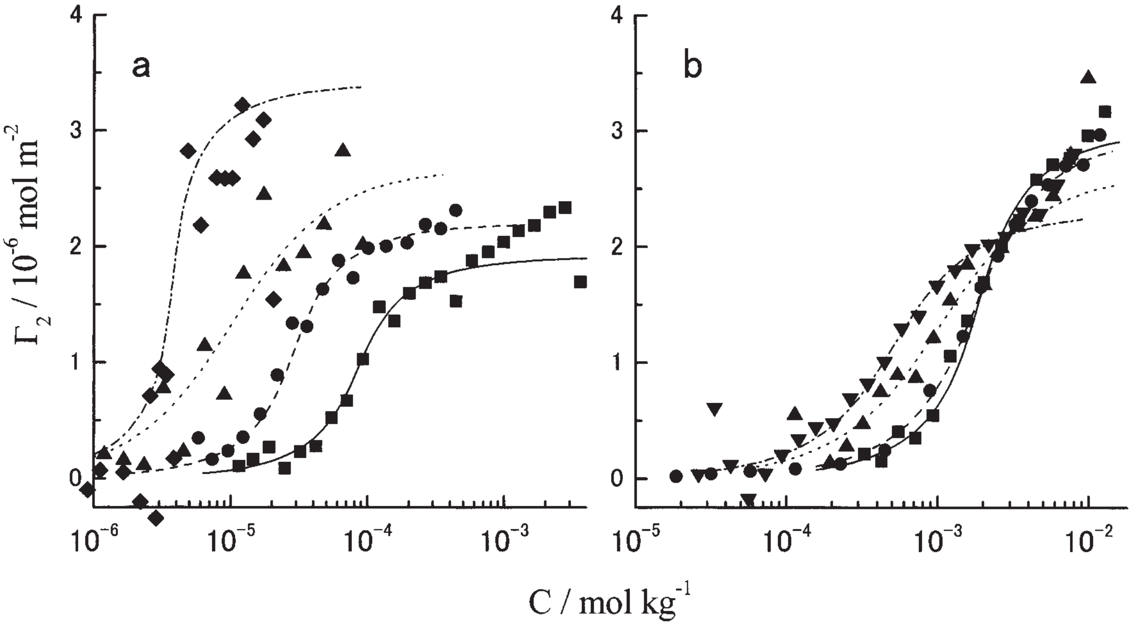

Fig. 6. Changes of surface excess (Γ_2) for aqueous solutions of alkyldodecyldimethylammonium bromides with surfactant concentration. Symbols are $C_{12}C_6$DMA (■), $C_{12}C_8$DMA (●), $C_{12}C_{10}$DMA (▲), and $C_{12}C_{12}$DMA (◆) in (a), and $C_{12}C_1$DMA (■), $C_{12}C_2$DMA (●), $C_{12}C_3$DMA (▲), and $C_{12}C_4$DMA (▼) in (b).

Table 2. Adsorption Parameters

DADMA Br	$A_0 \times 10^{16}/\mathrm{cm}^2$	$K/\mathrm{kg\,mol}^{-1}$	$\Delta G^\circ_a/\mathrm{kJ\,mol}^{-1}$	W
$C_{12}C_1$DMA	55.0	1.58×10^2	−12.5	−2.45
$C_{12}C_2$DMA	55.7	2.20×10^2	−13.4	−1.87
$C_{12}C_3$DMA	63.4	5.41×10^2	−15.6	−1.13
$C_{12}C_4$DMA	72.2	9.09×10^2	−16.8	−1.52
$C_{12}C_6$DMA	87.0	3.55×10^3	−20.3	−2.38
$C_{12}C_8$DMA	75.5	1.03×10^4	−22.9	−2.41
$C_{12}C_{10}$DMA	66.1	4.08×10^4	−26.3	−1.81
C_8C_8DMA	74.4	1.05×10^3	−17.3	−1.96
$C_{10}C_{10}$DMA	65.0	1.93×10^4	−24.5	−0.750
$C_{12}C_{12}$DMA	48.8	5.19×10^4	−26.9	−3.26

only when the length of the second alkyl chain is very similar to that of the primary chain. This indicates that the energetics for transferring a hydrocarbon chain from the aqueous phase to the air is not identical with that to the interior of a micellar aggregate for those surfactants. The difference evidently indicates that the change of cmc should be affected by the properties of the micellar or vesicular assemblies formed at the concentration reflected by μ°_m in Eq. 4. Upon adsorption to a flat air–liquid interface, the effect of elongating the chain length may be totally averaged, so that the lengths of both chains additively affect the energetics of the adsorption. These results also strongly suggest that the mode of the molecular assembly in the aggregates formed at the critical concentration could prominently vary as the second alkyl length elongated from methyl to hexyl.

The values of A_0 for the present single-chain surfactant ($C_{12}C_1$DMA), 55×10^{-16} cm^2, is similar to the reported value, 49×10^{-16} cm^2.[32] The value for the ionic surfactant is rather large compared with nonionic surfactants having the same length of alkyl chain, 36×10^{-16} cm^2 for dodecylglucoside,[33] for example. This may be ascribed to the properties of the hydrophilic head group, which exserts significant electrostatic interactions for the present surfactants. The value is shown to decrease linearly with the alkyl chain length for symmetric double-chain surfactants. This change appears to be inconsistent with the change in the molecular size. The magnitude of A_0 is considered to correlate rather better with the properties of the hydrophilic head group of a surfactant molecule than its overall molecular size. It is presumably correlated with the magnitude of interactions among the molecules set in an array on the interface. The present results hence suggest that a change in the hydrophobic tail group significantly affects the properties of the head group interacting at the surface. The interactions among the molecules on the interface should involve a repulsive one due to an ionic interaction, and an attractive one due to van der Waals interaction between neighboring molecules. The decrease in A_0 with the length of the hydrocarbon chains can be rationalized, since the latter is generally enhanced for elongated hydrocarbon chains. The correlation between A_0 and the size of the adsorbent molecule does not seem

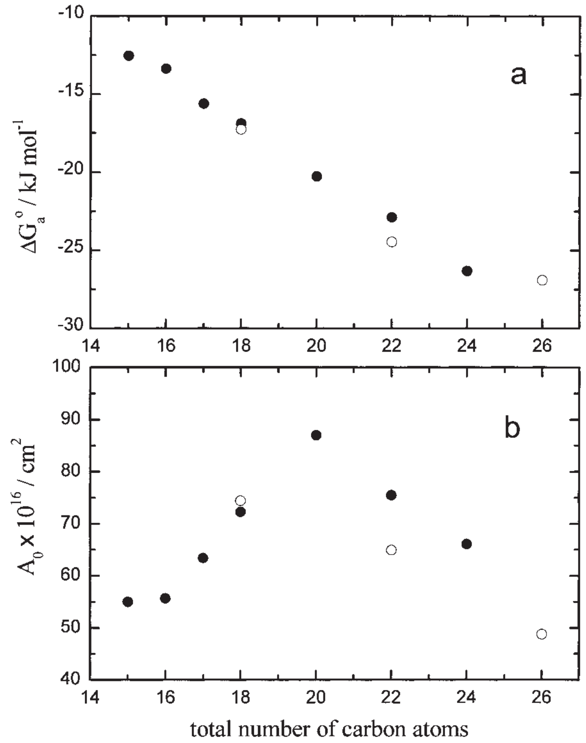

Fig. 7. Adsorption parameters for air–liquid interface of aqueous solutions of dialkyldimethylammonium bromides. ΔG_a° in (a), and A_0 in (b). The open symbols represent the data for the symmetric double chain surfactants.

to be straightforward, since the change is not even in a monotonous way for asymmetric double-chain surfactants. The value appears to have a maximum for the case that the second chain length is half that of the first chain. This indicates that additional interactions, such as steric ones, and flexibility of concerning chains, should be taken into account concerning the result for the series of asymmetric double-chain surfactants.

Concluding Remarks

Through the present study for a series of dialkyldimethylammonium bromides, the variation in their characteristics from those with a single major alkyl chain to those with two symmetric alkyl chains has been shown as a change in the critical concentration for the formation of molecular aggregates, and that in properties of air–liquid interface of their aqueous solutions in terms of the effect of the length of the second alkyl chain.

The properties of a surfactant species can be specified by its molecular characteristics, that a surfactant molecule carries a hydrophilic head group and a hydrophobic tail group. An elongation of alkyl chains in a quaternary ammonium surfactant molecule leads to an increase of its over-all hydrophobic surface. This seemingly yields an additive effect directly on the energetics for the elementary process of the adsorption of a molecule from an aqueous medium to the air–liquid interface. On the other hand, it seems to affect rather specifically the equilibrium between the monomerically dissolved state and the micellar state. The elongation in single-chain surfactants, and that in symmetric double-chain surfactants leads directly to the stabilization of micellar aggregates, due to an increase in the chemical potentials of the monomerically dissolved state. This reflects in a shift of the linear correlation between ln *cmc* and the chain length. For asymmetric double-chain surfactants with a shorter second alkyl, however, the elongation does not contribute very much to the micellar state to lead a destabilization effect of the micellar state.

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