

Dielectric Behavior of Aqueous Micellar Solutions of Betaine-Type Surfactants

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Dielectric behavior was examined for aqueous solutions of the betaine-type surfactants dodecyltrimethylcarbobetaine (C_{12} DCB), tetradecyltrimethylcarbobetaine (C_{14} DCB), cetyltrimethylcarbobetaine (C_{16} DCB), and oleyltrimethylcarbobetaine (OleyDCB) as a function of frequency from 1.00×10^6 to 2.00×10^{10} Hz (6.28×10^6 to 1.26×10^{11} rad s^{-1}) with changing surfactant concentration (c_D). Rotational relaxation times (τ) of the zwitterionic headgroups of the surfactants in aqueous solutions of C_{12} DCB and C_{14} DCB, which form spherical micelles, are determined to be 0.26 and 0.30 ns, respectively. Values of τ for aqueous solutions of C_{16} DCB and OleyDCB, which form threadlike micelles, are identical at 0.44 ns. The τ values of all micellar solutions are constant irrespective of c_D . The increase in τ with increasing alkyl chain length is assigned to an increase of molecular density at the micellar surface. The magnitude of the relaxation strength for the surfactant solutions increases in proportion to c_D and is not so different from that of an aqueous solution of glycine betaine (GB), which has the same chemical structure as betaine-type surfactants with zwitterionic headgroups but never forms micelles. This finding suggests that the zwitterionic headgroup rotating on the micellar surface possesses a dipole moment with a magnitude essentially the same as that of GB in aqueous solutions.

Introduction

Dielectric relaxation spectroscopy is a well-known classical method that is very sensitive to the presence of electric dipoles and can obtain information about the dynamics of dipoles existing in the system under examination.¹ Therefore, if surfactant micelles in aqueous solution include electric dipoles in their interiors or on their surfaces, dielectric measurements should provide useful information on the dynamics of micelle forming surfactant and of other additives in solution.^{2–8} Recently, it has been reported that micelles of ionic surfactants in aqueous solution possess several kinds of dipole moments, which have been detected by dielectric relaxation measurements. For example, in an aqueous micellar solution of cetyltrimethylammonium bromide (CTAB) containing only spherical micelles, distinct relatively strong dielectric relaxation modes are detected in different frequency ranges around 10^8 and 10^9 rad s^{-1} .^{2,3,5} A slow relaxation mode found around 10^8 rad s^{-1} has been assigned to the fluctuation of counterion clouds surrounding charged micelles.^{2,3,5} The other relaxation mode observed around 10^9 rad s^{-1} , of which strength is proportional to the concentration (c_D) of CTAB, has been interpreted in two ways such as the rotational motion of ion-pairs formed on the micellar surface by the cetyltrimethylammonium cation (CTA^+) and the bromide anion (Br^-), which behave as relaxing dipoles due to their rotational motion on the micellar surface,^{2,3} and the translation diffusive motion of Br^- anions bound to the charged micellar surface.^{5,6}

Ionic surfactant micelles forming other than spherical shapes in aqueous solution also exhibit remarkable dielectric relaxation. Certain cationic surfactants such as CTAB form long, stable threadlike micelles in aqueous solution with additives such as sodium salicylate (NaSal) or sodium *p*-toluenesulfonate (NapTS).^{9–12} In the cases of the threadlike micellar systems of

CTAB:NaSal/W or CTAB:NapTS/W, which also exhibited dielectric relaxation at around 10^9 rad s^{-1} , the existence of the dipole moments is attributed to the presence of ion-pairs formed on the micellar surface between CTA^+ and Sal^- or pTS^- . It is well-known that the counterion, Br^- , of CTAB is stoichiometrically replaced by Sal^- or pTS^- on the surface of micelles in threadlike micellar systems.

The idea that ion-pairs exist on the micellar surface and undergo dielectric relaxation and as a consequence contribute to the physicochemical properties of the micelles via dipole–dipole interaction between the formed ion-pairs is natural and comprehensive, but has not yet been widely accepted in the field of colloid and surface science. To confirm the validity of this idea, convincing evidence is required. For micelles formed by a zwitterionic surfactant in aqueous solution, in which the headgroups bear chemically stable positive and negative electric charges at constant separation, the surfactant can always maintain an ion-pair on the micellar surface. Moreover, the separation between opposite charges on the headgroup of the zwitterionic surfactant is not far from the estimated distance, l , between CTA^+ and Br^- for spherical CTAB micelles or CTA^+ and Sal^- (or pTS^-) for threadlike micelles in the system of CTAB:NaSal/W (or CTAB:NapTS/W); l is roughly estimated to be 0.55 nm, and as such the zwitterionic surfactant can be regarded as a suitable model surfactant for reproducing the dielectric relaxation behavior found in the aqueous CTAB and CTAB:NaSal/W (or CTAB:NapTS/W) systems. If the dielectric behavior of an aqueous micellar solution of a zwitterionic surfactant corresponds with that observed in the aqueous CTAB or CTAB:NaSal/W system (or CTAB:NapTS/W), one may conclude that the idea of ion-pair formation on the micellar surface as proposed for the ionic surfactant systems is essentially valid.

Some types of zwitterionic surfactants are commercially available, such as carbobetaine and sulfobetaine-type surfactants: $R-N^+(CH_3)_2(CH_2)_nCO_2^-$ and $R-N^+(CH_3)_2(CH_2)_nSO_3^-$,

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respectively. Several carbobetaine-type surfactants bearing different types of alkyl chains, dodecyltrimethylcarbobetaine ($C_{12}DCB$), tetradecyltrimethylcarbobetaine ($C_{14}DCB$), cetyltrimethylcarbobetaine ($C_{16}DTB$), and oleyldimethylcarbobetaine (OleyDCB), are employed in the present research. These betaine-type surfactants contain both positive and negative charges in their headgroup in the form of dimethylammonioacetate; $-N^+(CH_3)_2CH_2CO_2^-$, $n = 1$. These betaine-type surfactants are of great merit in dielectric studies of aqueous solutions for two reasons. The first reason is that the system includes large dipole moments due to constant separation being maintained between opposite charges on the zwitterionic headgroup ($l \sim 0.25$ nm), as fixed by the methylene spacer unit. Therefore, the betaine-type surfactants should be model molecules for ionic surfactants, which are considered to bear ion-pairs formed between a surfactant ion and counterion on the micellar surface. However, since the estimated length, l , between the opposite charges for the betaine-type surfactants is less than half that for the ion-pair between CTA^+ and Br^- , the magnitude of the relaxation strength for the aqueous betaine-type surfactant solution is likely to be much smaller than that for the aqueous CTAB solution at the same ion-pair concentration.

The second reason is that the system includes no dissociated highly conducting counterions such as Br^- , therefore, the system is completely free from high conductance, which is a serious problem for precise dielectric measurements. Because the zwitterionic headgroup of betaine-type surfactants in aqueous solution has a dipole moment estimated to be greater than 7 D, the rotational motion of the zwitterionic headgroups on the micellar surface would be precisely detected by using dielectric relaxation measurements. The dependence on concentration of the relaxation strength and time determined in aqueous micellar systems would provide important information reflecting differences in *micro- to nano-dynamics* of the zwitterionic headgroup of the betaine-type surfactants depending on the shape of micelles; the shape of $C_{12}DCB$ and $C_{14}DCB$ micelles in aqueous solution is spherical, while that of $C_{16}DCB$ and OleyDCB micelles is long and threadlike as will be discussed later.

Dielectric behavior already has been investigated for aqueous solutions of glycine betaine (*N,N,N*-trimethylglycine (GB)), which has an identical chemical structure to that of the zwitterionic headgroup of the betaine-type surfactants dealt with in this research and which never forms micelles at any concentration.¹³ A single relaxation mode is observed at a relaxation time of 0.04 ns, which has been attributed to the rotational relaxation mode of GB bearing two tightly hydrated water molecules in the bulk water phase. The magnitude of the dipole moment (μ) of GB tightly hydrated by two water molecules has been roughly evaluated to be 8.0 D. Data obtained for GB in aqueous solution using dielectric measurements is enlightening as the behavior of GB molecules rotating in the bulk water phase with the same dipole moment as that of the betaine-type surfactants is a useful model for discussion on the dynamics of the zwitterionic headgroup of surfactants on the micellar surface.

In this study, the dielectric relaxation strength and time attributed to zwitterionic headgroups on the micellar surface are investigated in detail and compared with those of GB in aqueous solution. Effects of differences in the alkyl chain length of the betaine-type surfactants on determining the micellar shape, spherical or threadlike, are discussed in relation to changes in the dynamics of the surfactant headgroups on the micellar surface. Furthermore, evidence for ion-pair formation in aqueous micellar systems of conventional ionic surfactants such as CTAB

is discussed with comparison to aqueous micellar systems of betaine-type surfactants.

Experimental Section

Materials. Concentrated aqueous $C_{12}DCB$ and $C_{14}DCB$ solutions, ca. 20 wt %, were kindly gifted by the New Japan Chemical Co., Ltd. (Osaka, Japan). First, the concentrated aqueous solutions were lyophilized, and then the obtained powder-like substances containing $C_{12}DCB$ and $C_{14}DCB$ were added to a large amount of ethanol to remove unnecessary inorganic salts as precipitates. After filtration of the precipitate, ethanol was removed with a rotary evaporator. Then, the obtained white powders were dissolved into water, and ion-exchange resins (IR120B-H-Ag, IRA400-OH-Ag, Organo Co., Tokyo, Japan) were added to the aqueous solutions to further eliminate ionic impurities. The ion-exchange resins were prepared by washing in a large amount of water and were kept standing in water for more than a day. After removing the ion-exchange resins by filtration, the aqueous solutions containing $C_{12}DCB$ and $C_{14}DCB$ at concentrations of about 0.2 M and at pH ~ 8 were lyophilized to obtain purified substances in the form of a white powder. Finally, the obtained $C_{12}DCB$ and $C_{14}DCB$ were recrystallized from a mixture of methanol and acetone.

Cetyltrimethylamine for $C_{16}DCB$ synthesis was purchased from Tokyo Kasei Co. Ltd. (Tokyo, Japan), and oleyldimethylamine for OleyDCB synthesis was gifted by Lion Akzo Co. Ltd. (Tokyo, Japan). Sodium chloroacetate was purchased from Wako Pure Chemical Ltd. (Osaka, Japan). The two amines were dissolved in ethanol, and then aqueous sodium chloroacetate solution was added to each ethanol solution of the amine at a final sodium chloroacetate concentration three times as high as that of the amine to ensure quaternization. The mixed solution was kept at 80 °C for 8 h to complete the reaction. After the reaction, the ethanol and water were evaporated and solid products including $C_{16}DCB$ or OleyDCB were lyophilized. The products were then dissolved into ethanol to remove by precipitation most of the residual salts such as NaCl produced in reaction and unreacted sodium chloroacetate. Finally, the products were dissolved into water including ion-exchange resins to remove the remaining ionic impurities. The $C_{16}DCB$ obtained by lyophilization was recrystallized from a mixture of methanol and acetone. Since the obtained OleyDCB did not crystallize even at high concentrations, recrystallization was unable to be used for purification. As such, unreacted oleyldimethylamine remaining in the obtained OleyDCB was washed out with *n*-hexane.

The purity of the obtained betaine-type surfactants $C_{12}DCB$, $C_{14}DCB$, $C_{16}DCB$, and OleyDCB was confirmed by using NMR and electromotive force measurements with a chloride ion selective electrode. The ratio of unreacted amine to product was less than 1%, and chloride ions were present at less than 0.1% for each sample.

Highly deionized water with a specific resistance higher than 18 M Ω cm obtained by a Milli Q system (Nihon MilliPore, Tokyo, Japan) was used as solvent. The concentration, c_D , of each betaine-type surfactant ranged from 10 to 430 mM. Because the values of the critical micelle concentrations (cmcs) of $C_{12}DCB$, $C_{14}DCB$, and $C_{16}DCB$ have been reported to be 1.9 ± 0.1 mM, 0.186 mM, and 20.1 μ M, respectively,^{14–17} the c_D values for all the prepared aqueous solutions were much higher than the cmcs and micelles were formed. Although the cmc of OleyDCB has not been reported, the value seems to be much less than 1 mM from conjecture based on the behavior of $C_{16}DCB$.

Methods. Dynamic Viscoelastic Measurements. Dynamic viscoelastic measurements were carried out in an angular frequency range from $\omega = 1.0 \times 10^{-2}$ to $1.0 \times 10^2 \text{ rad s}^{-1}$ using a stress-controlled rheometer (Reologica DAR-100, Lund, Sweden) equipped with a cone and plate geometry for the aqueous OleyDCB and C₁₆DCB systems. The storage and loss moduli (G' and G'') were determined as functions of ω under the condition of a linear viscoelastic response.

Dielectric Relaxation Measurements. An RF LCR meter (Agilent Technologies, 4287A) equipped with a homemade electrode cell was operated to determine dielectric relaxation spectra for the sample solutions in a frequency range from 1.00×10^6 to $3.00 \times 10^9 \text{ Hz}$ (6.28×10^6 to $1.88 \times 10^{10} \text{ rad s}^{-1}$ in angular frequency, ω). Dielectric measurements were carried out at 25 °C. Data were collected in the parallel mode of capacitance, C , and conductivity, G , as functions of frequency, ω . The real and imaginary parts of the complex electric permittivity, ϵ' and ϵ'' , respectively, were calculated by using the standard relations of $\epsilon' = CC_0^{-1}$ and $\epsilon'' = GC_0^{-1}\omega^{-1}$, where C_0 is the capacitance of a vacant electrode cell.¹⁻³

Dielectric spectra, ϵ' and ϵ'' , for sample solutions in a frequency range from 5.00×10^7 to $2.00 \times 10^{10} \text{ Hz}$ (3.14×10^8 to $1.26 \times 10^{11} \text{ rad s}^{-1}$) were determined by using a dielectric material probe system (Hewlett-Packard, 85070B) consisting of a network analyzer (Hewlett-Packard, 8720ES) at 25 °C. In this case, ϵ' and ϵ'' were automatically calculated via a program supplied by Hewlett-Packard. The detailed measuring procedure has been published elsewhere.³

To determine the exact dielectric contribution, $\Delta\epsilon'$ and $\Delta\epsilon''$, of the presence of micelles to the total dielectric parameters, ϵ' and ϵ'' , the real and imaginary parts of complex permittivity for pure water, ϵ'_w and ϵ''_w , were subtracted in the following manner: $\Delta\epsilon' = \epsilon' - f\epsilon'_w$ and $\Delta\epsilon'' = \epsilon'' - f\epsilon''_w - G_{dc}C_0^{-1}\omega^{-1}$, where f represents the fractional contribution of pure water, and G_{dc} is the direct current conductivity due to ionic impurities.

Density Measurements. Densities of sample solutions were measured at 25.0 °C with a density meter (DMA5000, Anton Paar, Graz, Austria) to evaluate the partial molar volume for each betaine-type surfactant in aqueous solution.

Results

Viscoelastic Behavior. The dependencies of G' and G'' on ω for an aqueous OleyDCB system at varying c_D are shown in Figure 1. The relaxation behavior at a c_D higher than 100 mM is well described by a Maxwell element with only one set of relaxation time, τ_M , and plateau modulus, G_N (eq 1), as frequently observed in threadlike micellar systems.^{9,10}

$$G' = \frac{G_N \omega^2 \tau_M^2}{1 + \omega^2 \tau_M^2} \quad G'' = \frac{G_N \omega \tau_M}{1 + \omega^2 \tau_M^2} \quad (1)$$

The values of ω where the G'' curves are maximum, which perfectly correspond to the reciprocals of relaxation times for the Maxwell element-type viscoelasticity, shift toward lower ω with increasing c_D as seen in Figure 1. The relationship between G_N , or the reciprocal of the steady-state compliance (J_e^{-1}), for a solution at 50 mM, at which G_N is not observed clearly in Figure 1, and c_D is shown in Figure 2 on a double-logarithmic scale. The relationship G_N (or J_e^{-1}) $\propto c_D^2$ is obtained over a wide c_D range from the slope of the solid line in Figure 2. The same relationship is well-known between the plateau modulus and polymer concentration in fully entangled polymer

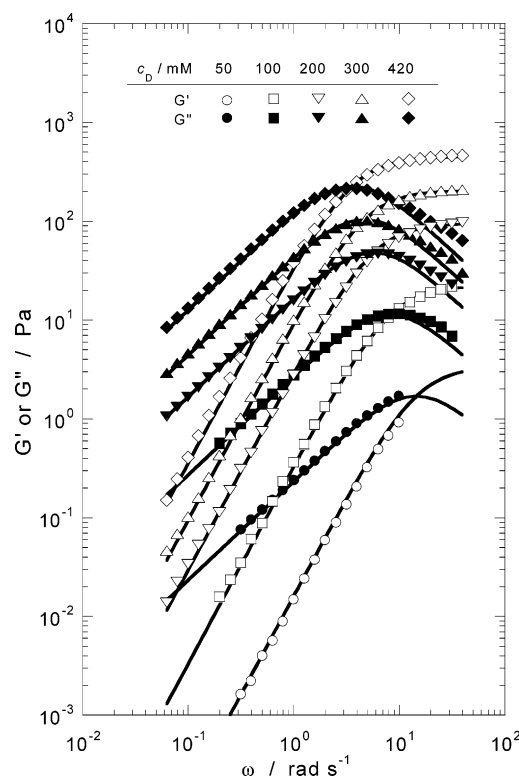


Figure 1. Dependencies of the storage and loss moduli, G' and G'' , on ω for an aqueous OleyDCB system and various concentrations, c_D .

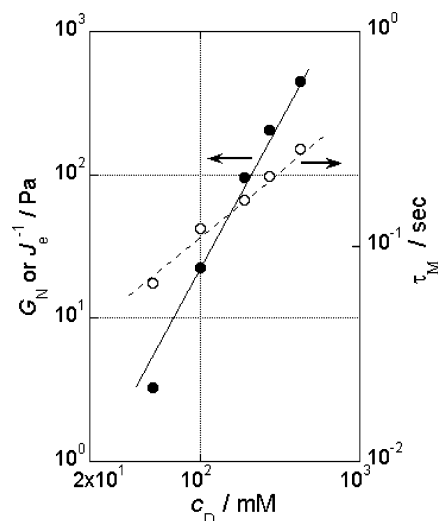


Figure 2. Relationship between the plateau modulus, G_N , or the reciprocal of the steady-state compliance, J_e^{-1} , and the mechanical relaxation time, τ_M , on c_D for the aqueous OleyDCB system.

solutions.¹⁸ Figure 2 also contains the relationship between τ and c_D on a double-logarithmic scale. The equation of $\tau \propto c_D \sim 0.6$ is obtained from the slope of the dashed line.

The viscoelastic behavior of the aqueous OleyDCB system showing Maxwell-type viscoelastic behavior with G_N proportional to the square of c_D strongly suggests that enormously long threadlike micelles are formed in the system, and that these threadlike micelles form a concentrated entanglement network as well, as observed in the elastic behavior owing to entanglements in fully entangled polymer systems.^{18,19} Because the proportionality constant of G_N , i.e. G_N (or J_e^{-1}) $\propto c_D^2$, for previously investigated threadlike micellar systems such as CTAB:NaSal/W and CTAB:NaP/TS/W is three times as large as that for the aqueous OleyDCB system, the micellar contour

length for CTAB:NaSal/W is considered to be slightly longer than that for the OleyDCB system at the same c_D . Such a difference in the value of G_N at the same c_D also has been found in another threadlike micellar system formed by amineoxide-type surfactants²⁰ which bear small zwitterionic headgroups.

Such a small value of 0.6 for the exponent relating τ and c_D does not match well with any theoretical predictions, nor with empirical relationships obtained for fully entangled polymer systems, but does not contradict with the phantom crossing model⁴ that was proposed to explain the unique viscoelastic behavior of threadlike micellar systems. A living polymer model,²¹ which also has been proposed for the viscoelastic behavior of threadlike micellar systems, predicts an exponent of 1.2–1.7, which is greater than that obtained in the OleyDCB system by a factor of 2–3, therefore, the living polymer model is not a successful representation of this system. It should be pointed out that exponents for viscoelastic parameters theoretically predicted by the living polymer model²¹ are based on an idea that micellar contour length is proportional to the square root of surfactant concentration, c_D , assuming the mean-field theory of linearly self-assembling systems; however, recent experiments^{22,23} and also theoretical works^{22,24} have shown that the micellar contour length is not proportional to the square root of c_D over a wide c_D range. Because the phantom crossing model does not predict an exact exponent, the applicability of this model is still expectative.

Although an aqueous C_{16} DCB system has a much higher viscosity relative to aqueous C_{12} DCB and C_{14} DCB systems at any concentration, the viscoelasticity of the system is obviously lower than that observed in the aqueous OleyDCB system described above. The crossing of the G' and G'' curves is not observed, nor is a plateau observed for G' in the ω range examined, even at 430 mM. Moreover, since J_e^{-1} at 430 mM for the aqueous C_{16} DCB system is half that of the OleyDCB system at the same concentration, the length of formed threadlike micelles in the C_{16} DCB system is likely not long enough to develop fully entangled networks as formed in the OleyDCB system.

Aqueous C_{12} DCB and C_{14} DCB systems show Newtonian flow behavior with low viscosities. The values of the relative viscosities for both systems at 100 mM have been evaluated to be 1.15.¹⁶ The aggregation number of C_{12} DCB has been determined to be 80 irrespective of c_D .¹⁷ These indicate that spherical micelles are formed in both the aqueous C_{12} DCB and C_{14} DCB systems.

Ultimately, it is considered that micelles formed in aqueous solution are spherical for C_{12} DCB and C_{14} DCB, and threadlike for C_{16} DCB and OleyDCB.

Dielectric Behavior. Dielectric spectra of ϵ' and ϵ'' versus ω for an aqueous C_{14} DCB solution at 430 mM are shown in Figure 3 as typical examples. The figure also contains the ω dependence of ϵ'_w and ϵ''_w for pure water, and $\Delta\epsilon'$ and $\Delta\epsilon''$ evaluated assuming $f = 0.80$. The solid lines drawn in Figure 3 represent the ω dependence of the best fit curves for $\Delta\epsilon'$ and $\Delta\epsilon''$ calculated with the Debye-type relaxation functions¹ as given in eq 2 with only one set of relaxation strength and time, $\Delta\epsilon = 15.7$ and $\tau = 0.30$ ns, respectively.

$$\Delta\epsilon' = \frac{\Delta\epsilon}{1 + \omega^2\tau^2} \quad \Delta\epsilon'' = \frac{\Delta\epsilon\omega\tau}{1 + \omega^2\tau^2} \quad (2)$$

Because the agreement between experiments and calculations looks reasonable, as seen in Figure 3, all other $\Delta\epsilon'$ and $\Delta\epsilon''$ data are also analyzed by calculating best fit curves based on

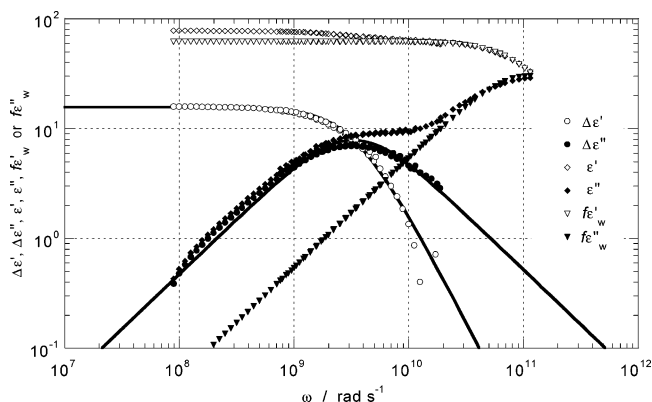


Figure 3. Frequency, ω , dependencies of dielectric spectra, ϵ' , ϵ'' , $\Delta\epsilon'$, $\Delta\epsilon''$, ϵ'_w , and ϵ''_w , for an aqueous C_{14} DCB system at 430 mM. For the evaluation of $\Delta\epsilon'$ and $\Delta\epsilon''$, the value of $f = 0.80$ is assumed.

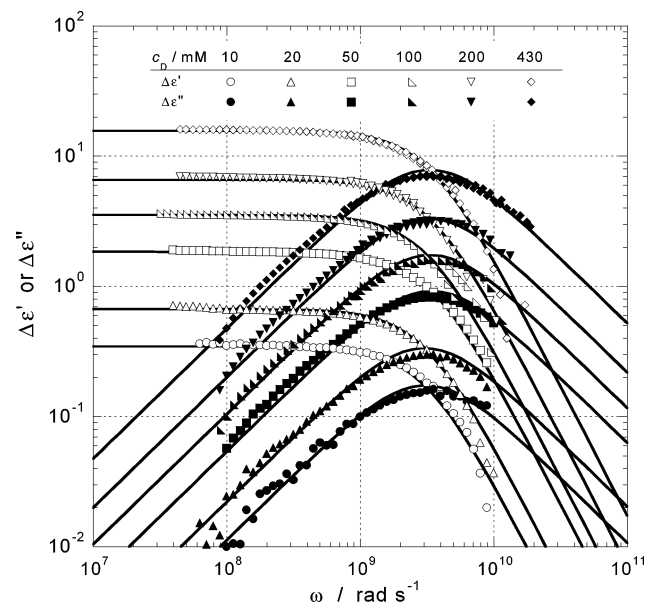


Figure 4. Dependence of $\Delta\epsilon'$ and $\Delta\epsilon''$ on ω for an aqueous C_{14} DCB system at various c_D values. Solid lines represent the best fit curves for experiments calculated with eq 2.

eq 2, allowing determination of the values of $\Delta\epsilon$ and τ for each sample solution.

The dependence of $\Delta\epsilon'$ and $\Delta\epsilon''$ on ω for an aqueous C_{14} DCB system at various c_D values is shown in Figure 4. Dielectric parameters such as f , $\Delta\epsilon$, and τ determined by using the fitting procedure based on eq 2 are summarized in Table 1 for all solutions. The dielectric relaxation mode found in the aqueous systems of betaine-type surfactants should be assigned to the rotational motion of the zwitterionic headgroups of the surfactants since other possible mechanisms that provide significant dielectric relaxation modes do not exist in these systems.

The dependence of the f value on c_D for the aqueous C_{14} DCB system is shown in Figure 5 as a typical example. The f value decreases almost in proportion to c_D in the region examined. The solid line in this figure predicts the dependence of f on c_D according to eq 3.²⁵ Equation 3 is an approximation of Wagner's equation,²⁶ which predicts the electric permittivity (ϵ_b) of systems consisting of dispersed particles with volume fraction v and permittivity ϵ_p , ca. 2 for hydrocarbon chains, in a medium with permittivity ϵ_m , ca. 78 for water. In this case, f corresponds to $\epsilon_b\epsilon_m^{-1}$ and eq 3 is obtained assuming $\epsilon_m \gg \epsilon_p$. Another theoretical model proposed by Bruggeman²⁷ to predict the dependence of ϵ_b on v has been widely accepted in

TABLE 1: Concentration, c_D , Dependencies of Dielectric Relaxation Parameters Such as Relaxation Time, τ , Relaxation Strength, $\Delta\epsilon$, Determined by Using a Debye-Type Equation, Eq 2, and Fractional Contribution of Pure Water, f (the upper part), and Summaries of τ , the Concentration Reduced Dielectric Relaxation Strength, $\Delta\epsilon c_D^{-1}$, Partial Molar Volume, V_m , and Number of Water Molecules Tightly Hydrated to a Surfactant Molecule, m , for Each Surfactant (the lower part)

	c_D/mM	τ/ns	$\Delta\epsilon$	f
C ₁₂ DCB	10.01	0.254	0.277	0.995
	20.46	0.261	0.601	0.991
	27.34	0.258	0.917	0.988
	49.32	0.247	1.74	0.977
	97.44	0.270	3.50	0.958
	190.0	0.265	7.13	0.917
	277.9	0.249	10.2	0.880
C ₁₄ DCB	440.2	0.255	16.8	0.810
	9.711	0.330	0.347	0.993
	20.06	0.330	0.670	0.989
	26.00	0.302	0.896	0.984
	49.10	0.295	1.85	0.975
	96.69	0.300	3.48	0.951
	188.3	0.303	6.60	0.911
C ₁₆ DCB	274.2	0.308	10.1	0.871
	437.2	0.302	15.7	0.800
	9.915	0.457	0.350	0.994
	19.79	0.412	0.722	0.989
	29.42	0.419	1.08	0.985
	49.34	0.434	1.75	0.975
	96.83	0.433	3.54	0.950
OleyDCB	186.7	0.450	7.36	0.897
	270.5	0.442	9.75	0.862
	427.2	0.425	15.7	0.782
	9.909	0.481	0.338	0.992
	19.85	0.450	0.674	0.987
	29.64	0.422	1.09	0.983
	49.07	0.433	1.95	0.973
GB ^a	96.28	0.418	3.65	0.947
	187.2	0.423	7.00	0.893
	271.8	0.438	10.4	0.849
	424.5	0.453	15.7	0.769
	τ/ns	$\Delta\epsilon(c_D)^{-1}/\text{M}^{-1}$	$V_m/\text{cm}^3 \text{mol}^{-1}$	m
C ₁₂ DCB	0.26 ± 0.01	37.6	281.5	1.7
C ₁₄ DCB	0.30 ± 0.01	36.5	315.2	1.0
C ₁₆ DCB	0.44 ± 0.02	36.1	347.1	1.4
OleyDCB	0.44 ± 0.02	37.4		
GB ^a	0.040	33.3	99.2	2.0

^a Reference 13.

concentrated dispersion systems; however, the dependence of f ($=\epsilon_b\epsilon_m^{-1}$) on v of the model under the condition of $\epsilon_p = 2$ and $\epsilon_m = 78$ completely agrees with that of eq 3 in a v range less than 0.15. Consequently, eq 3 accurately describes the contribution of the volume fraction, v , of solute molecules to f in the system examined.

$$f = \frac{1 - v}{1 + \frac{1}{2}v} \quad (3)$$

The value of v can be evaluated from the product between the partial molar volume (V_m) and c_D ; $v = V_m c_D$. The value of V_m is determined via the dependence of solution density on c_D . Since the experimental f values deviate below the solid line of eq 3, the contribution of the volume effect of the solute to the dielectric behavior does not appear sufficient to describe the dependence of f on c_D . This strongly suggests that a few water molecules tightly hydrate to the surfactants forming micelles. Equation 4 includes the contribution to f of water molecules tightly hydrated to surfactant molecules in addition to the

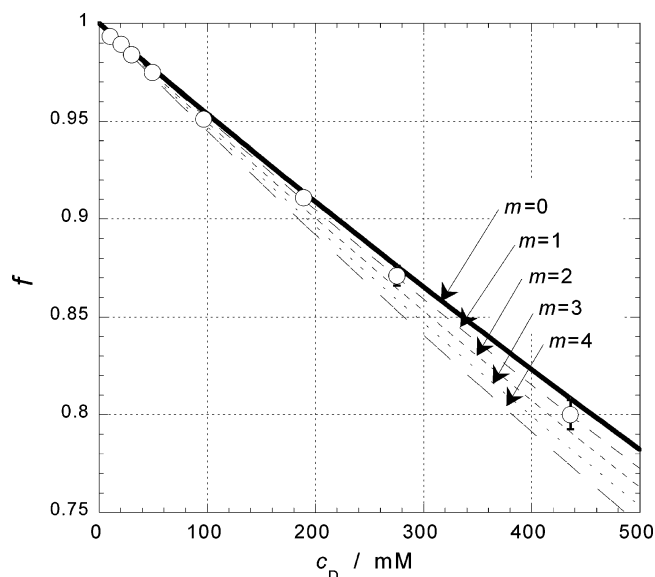


Figure 5. Relationship between the fractional contribution of water molecules, f , to the dielectric relaxation behavior and c_D for the aqueous C₁₄DCB system at 25 °C.

contribution of the volume effect of solute molecules given by eq 3.

$$f = \frac{1 - v}{1 + \frac{1}{2}v} - \frac{m c_D}{55.6} \quad (4)$$

where m represents the number of water molecules tightly hydrated to a surfactant molecule. The dependence of f on c_D calculated by eq 4 is also shown in Figure 5 assuming m to be from 1 to 4. The experimental f value for the aqueous C₁₄DCB system is in good agreement with lines calculated assuming 1 for the m value irrespective of c_D , as seen in Figure 5. Similar agreement between the values of experimental and calculated f assuming $m = 1$ or 2 is obtained for the other aqueous betaine-type surfactant systems, as summarized in Table 1. The fact that reasonably reproducible f curves can be described by eq 4 assuming an m value from 1 to 2 in all experimental systems, irrespective of the surfactant used, strongly suggests that 1 to 2 water molecules are tightly hydrated to the betaine-type surfactant in both spherical and threadlike micelles.

Furthermore, it is likely that few water molecules are incorporated in the micellar interior since the m value of 1 to 2 is similar to that found in an aqueous solution of GB,¹³ which has the same chemical structure as that of the zwitterionic headgroup and which never forms micelles. According to the results of ab initio quantum chemical calculations, two water molecules are hydrated to each oxygen of the carboxyl group of GB through hydrogen bonding.¹³ Consequently, we may conclude that the zwitterionic headgroup of the betaine-type surfactant molecules in the micelles has a hydrated structure identical with that of GB in aqueous solution, and that very few water molecules are included in the micellar interior irrespective of micellar shape.

Discussion

Relaxation Strength. The dielectric relaxation strengths, $\Delta\epsilon$, evaluated for aqueous betaine-type surfactants are shown as a function of c_D in Figure 6. In this figure, $\Delta\epsilon$ for aqueous solutions of GB¹³ is also plotted for comparison between the behavior of the surfactant systems and a freely rotating small molecule with the same chemical structure as that of the

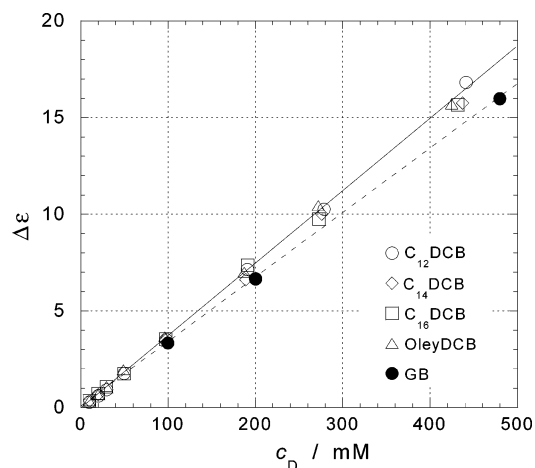


Figure 6. Dependence of dielectric relaxation strength, $\Delta\epsilon$, on c_D for aqueous betaine-type surfactant and GB systems.

zwitterionic headgroup. The dependences of $\Delta\epsilon$ on c_D are identical for all the surfactant systems examined, as seen in Figure 6. The value of $\Delta\epsilon$ is clearly proportional to c_D for all systems and the slope between $\Delta\epsilon$ and c_D is evaluated to be 37.5 M^{-1} , which is not so different from that for the GB system, ca. 33.3 M^{-1} . These findings strongly suggest that the tightly hydrated zwitterionic headgroup rotates on the micellar surface with a dipole moment, μ , not very different in magnitude from that of GB in aqueous solution.

If the dielectric interaction between the dipoles on the zwitterionic headgroups of the betaine-type surfactants, and that between the headgroup and water molecules are not strong, the concentration reduced dielectric relaxation strength, $\Delta\epsilon c_D^{-1}$, is proportional to the square of the magnitude of the dipole moment, μ^2 , as given by eq 5,³

$$\frac{\Delta\epsilon}{c_D} = \frac{AN_A\mu^2}{2\epsilon_v k_B T} \quad (5)$$

where A is a numerical factor representing the magnitude of interaction between dipoles in the system as described by eq 6,²⁸ N_A is Avogadro's number, ϵ_v is the electric permittivity of a vacuum, and $k_B T$ is the product between Boltzmann's constant and the absolute temperature. In eq 5, the correction taking into account the cmc value is neglected because each sample solution possesses a c_D much higher than the cmc. Oncley^{29,30} first derived eq 5 for aqueous solutions of dipolar molecules such as water-soluble protein particles. In the case of aqueous systems of molecules dissolved without micelle formation such as GB, the last term of A (eq 6) is not necessary because it expresses the contribution of the interaction between zwitterionic headgroups on the micellar surface, as follows

$$A = 1 + \frac{|\mu_w|z \cos\gamma}{|\mu|} + z_s \cos\gamma_s \quad (6)$$

where $|\mu_w|$ represents the magnitude of the dipole moment of a water molecule, ca. 1.85 D, z is the number of first neighbor water molecules tightly hydrated to the zwitterionic headgroup, and γ is the average angle between the total dipole of the tightly hydrated zwitterionic headgroup and the dipoles of the first neighbor water molecules. Parameters z_s and γ_s represent the number of surfactant headgroups surrounding the surfactant headgroup considered and the average angle between the dipole of this headgroup and surrounding dipoles, respectively.

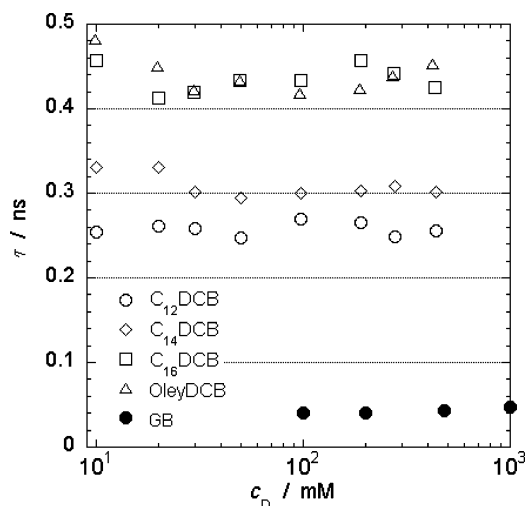


Figure 7. Relationship between dielectric relaxation time (τ) and c_D for aqueous betaine-type surfactant and GB systems.

In a study of an aqueous system of the zwitterionic surfactant dodecyltrimethylammoniumoxide (DDAO),²⁸ the parameters $z_s = 12$ and $\gamma_s = 54.7^\circ$ were used based on z_s as the sum of the first and second neighbor surfactant headgroups on the micellar surface assuming the random orientational condition, $3\langle\cos^2\gamma\rangle \sim 1$. Moreover, a value one-third of z for an aqueous system of trimethylamineoxide (TMAO),³¹ which has an identical chemical structure to that of the headgroup of DDAO, was employed as z for the DDAO micellar system, and the value of γ was again assumed to be 54.7° . The conclusion obtained in the latter study³¹ was that the $|\mu|$ of the DDAO headgroup is essentially the same as that of TMAO in aqueous solution. Here, we adopt the same assumption, taking into account the parameters determined in the previous study on GB¹³ and obtaining eq 7, the same result as in the study for DDAO.

$$A = 8.0 + \frac{11}{|\mu|} \quad (7)$$

In the previous study on the aqueous GB system,¹³ the parameters $z = 31$ and $\gamma \sim 54.7^\circ$ were employed and the value $|\mu| = 8.0 \text{ D}$ was obtained. Substituting eq 6 and $\Delta\epsilon c_D^{-1} = 37.5 \text{ M}^{-1}$ into eq 5 gives a $|\mu|$ value of 6.5 D for the micelle forming zwitterionic headgroup of the betaine-type surfactants examined in this study. The $|\mu|$ value obtained for the betaine-type surfactants is only smaller than that of GB by 15%.

Because the size of the headgroup of the surfactants in this study is slightly greater than that of DDAO, the value of z_s is possibly smaller than 12 as assumed in the DDAO system. If one accepts the number of the first neighbor headgroups, 6, as z_s , the first numerical constant of eq 6 changes from 8.0 to 4.5. Then, by the same procedure, the value $|\mu| = 8.4 \text{ D}$ is obtained for the zwitterionic headgroup. Thus, the actual value of $|\mu|$ for the zwitterionic headgroup seems to be in the range of 6.5 to 8.4 D. Consequently, it is likely that the magnitude of the dipole moment, μ , for the headgroup is essentially the same as that of GB in aqueous solution. Moreover, the magnitude of the dipole moment of the headgroup is not influenced by the type of surfactant or the micellar shape.

Relaxation Time. The c_D dependence of the relaxation time, τ , corresponding to the rotational relaxation time of zwitterionic headgroups on the micellar surface is shown in Figure 7. It appears that the τ values are almost independent of c_D for all systems. Figure 7 also contains the dependence of τ on concentration of GB in aqueous solution for comparison. The

τ values for all betaine-type surfactants in aqueous solution are summarized in Table 1.

The fact that τ seems independent of c_D for all systems suggests that the molecular densities of surfactant headgroups on the micellar surface depend not on c_D but on the type of surfactant. The value of τ for the zwitterionic headgroups on the micellar surface is 5 to 10 times as long as that of GB in aqueous solution as seen in Figure 7 and Table 1. This tendency can be definitely assigned to higher molecular densities on the micellar surface, which effectively depress rotation and mobility of the headgroup, where GB rotates freely only sensing the minimal viscosity due to surrounding water molecules.

The trend that τ increases with increasing alkyl chain length is recognized for methylene numbers from 12 to 16. It is known that the molecular density of headgroups on the micellar surface increases with increasing alkyl chain length when surfactants with the same headgroup form spherical micelles.³² As described above, there is a transition in micellar shape from spherical to cylindrical or threadlike between C_{14} DCB and C_{16} DCB. Threadlike micelles have higher molecular density of headgroups than spherical micelles for the same headgroup. As seen in Figure 7 and Table 1, the relaxation time, τ , for aqueous C_{16} DCB and OleyDCB systems appears identical. This strongly suggests that the molecular densities of headgroups on the micellar surface for the systems are essentially the same because both systems only involve threadlike micelles. Consequently, the τ value reflects the rate of rotational molecular motion governed by the molecular density of headgroups on the micellar surface, and therefore the value is useful in probing *micro-* to *nano-dynamics* of surfactants in micelles, especially those bearing zwitterionic headgroups such as the betaine-type surfactants.

The fact that the value of viscoelastic relaxation time, τ_M , for the aqueous OleyDCB system is much longer than that for the C_{16} DCB system although the value of τ for both the systems is identical permits us to conclude that the viscoelastic relaxation mechanism observed in the C_{16} DCB and OleyDCB systems is not directly related to the dielectric relaxation mechanism due to the rotational motion of headgroups. Such independence between a slow viscoelastic process (*macro-dynamics*) and the fast *micro-* to *nano-dynamics* observed in the micellar systems has been frequently reported.^{9,10,20,33}

Behavior as a Model System for Ionic Surfactants Bearing Ion-Pairs. The cationic surfactant CTAB forms spherical micelles above its cmc in aqueous solution and shows pronounced dielectric relaxation behavior.³ The reduced relaxation strength taking into account concentration, c_D , and the degree of dissociation (α), $\Delta\epsilon c_D^{-1}\alpha^{-1}$, and relaxation time, τ , have been evaluated to be $\sim 260 \text{ M}^{-1}$ and 0.8 ns, respectively, over a wide c_D range. Supposing the formation of an ion-pair between CTA^+ and Br^- , the magnitude of dipole moment, $|\mu|$, for the ion-pair was roughly estimated to be 18 D. Such a large dipole moment, indicating a separation, l , between the opposite charges of about 0.4 nm seems to be a reasonable value because it is slightly shorter than the sum of the ionic radius of tetramethylammonium, $\text{N}^+(\text{CH}_3)_4$, similar to the headgroup of CTA^+ , ca. 0.35 nm, with that of Br^- , ca. 0.2 nm. However, decisive evidence for the formation of an ion-pair has not been found because the formed ion-pair has not been separated from the micellar situation.

The situation for the betaine-type surfactant system investigated in this study is definitely different from that of CTAB. Because GB has the same chemical structure as that of the zwitterionic headgroup under study, GB represents an ion-pair as separated from the micelles formed with the betaine-type

surfactants. That the ω dependences of $\Delta\epsilon'$ and $\Delta\epsilon''$ for the aqueous CTAB system,^{2,3} well described with a single Debye type relaxation mode given by eq 2 for the supposed ion-pair, are essentially the same as that for the betaine-type surfactant systems strongly suggests that the ion-pair CTA^+-Br^- formed on the micellar surface rotates with a single time constant τ interacting with other ion-pairs. The reason $\Delta\epsilon c_D^{-1}\alpha^{-1}$ and τ are greater for the CTAB system than for the betaine-type surfactant systems is due to the difference in size of CTA^+-Br^- and the zwitterionic headgroup. To obtain a more realistic betaine-type model surfactant for CTA^+-Br^- , another surfactant with greater separation between the opposite charges should be employed. Cetyldimethylammoniopropanesulfonate (C_{16} DSB) is one such surfactant, and the dielectric behavior of an aqueous C_{16} DSB system⁷ forming spherical micelles exhibits obvious relaxation behavior with parameters $\Delta\epsilon c_D^{-1} = 92 \text{ M}^{-1}$ and $\tau = 0.90 \text{ ns}$, which are closer to the parameters for the aqueous CTAB system than those of the betaine-type surfactants in this study.

Concluding Remarks

In micelles formed by betaine-type surfactants such as dodecyldimethylcarbobetaine (C_{12} DCB), tetradecyldimethylcarbobetaine (C_{14} DCB), cetyldimethyl-carbobetaine (C_{16} DCB), and oleyldimethylcarbobetaine (OleyDCB), a rotational relaxation mode of the zwitterionic headgroup is clearly detected by dielectric relaxation measurements with relaxation times from 0.26 to 0.44 ns depending on the shape of the formed micelles. On the other hand, the relaxation strength, which is proportional to the surfactant concentration, does not depend on the shape of micelles. The magnitude evaluated for the dipole moment of the zwitterionic headgroup rotating on the micellar surface is a similar value to that obtained for GB in aqueous solution, which has the same structure as that of the zwitterionic headgroup and never forms micelles. The betaine-type surfactants function well as model surfactants for ionic surfactants that form ion-pairs between surfactant ions and counterions on the micellar surface such as cetyltrimethylammonium bromide.

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