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Volumetric Properties of Surfactant in Water and in Mixed Solvent from Sound Velocity and Density Measurements

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A simple, automatic and economic apparatus was constructed for a precise measurement of sound velocity using a resonance method. It gives the sound velocity value with an accuracy of less than $3\times10^{-3}\%$ (± 2 cm s^{-1}). Sound velocity and density measurements were carried out in aqueous solutions of several compounds of alkyltrimethylammonium bromide (C_1TAB, C_8TAB, C_{10}TAB, C_{12}TAB, C_{14}TAB, and C_{16}TAB, where C_i is the number of carbons in straight-chain hydrocarbon groups) at 25 °C. Also, the measurements for C_{12}TAB in a mixed solvent with water and 2-propanol were performed. The critical micelle concentrations (*CMC*) were determined from the inflection point of the compressibility and electric conductivity. The partial molar adiabatic compressibility (κ_m^*) and the partial molar volume (V_m^*) for the surfactant were determined below and above *CMC* in water and in the mixed solvent from the apparent molar quantities. The partial molar quantities were also found to be dependent on the concentrations of the added alcohol. These results were interpreted from the points of view of the surfactant conditions and solvent structures.

Solvent characteristics affect various chemical phenomena, such as the reaction kinetics, organic synthesis and solubility. However, the effect of a solvent on such chemical phenomena is not sufficiently understood from the viewpoint of physicochemistry. Amphiphilic molecules exist as the monomeric form at low concentrations, and they tend to aggregate (micelle) with increasing concentration, although micelle formation is dependent not only on their hydrophobic and hydrophilic balance of molecules, but also on the environment where the surfactant exists. There are several tools to examine the characteristics of surfactants, such as conductivity, surface tension, light scattering, NMR and density.[1]

Sound velocity is also very sensitive to slight changes in the solution structure. Many research papers have been published concerning the volumetric properties of solutions using the sound velocity and density. Especially, the development of an apparatus for sound velocity measurements in liquids is remarkable. Thus, complex solution characteristics determined through compressibility data may be now examined more precisely for various systems containing biological substances.[2–5]

The present authors[6,7] have studied the dynamic characteristics of concentrated aqueous solutions of various alcohols using a sound absorption method, and have proposed how much the water structure is altered depending upon the solute structure and concentration. Also, kinetic and equilibrium studies for aqueous solutions of surfactants have been extensively carried out, and the effects of additives on the surfactant characteristics have also been examined because of the potential practical uses.[8–13]

Therefore, we have desired to investigate the properties of mixed solvents of water and alcohol through the volumetric properties of surfactants. For this purpose, we constructed a simple and convenient apparatus for a precise measurement of the sound velocity by a resonance method.[14] Using the tools for the sound velocity and density measurements, we examined the characteristic properties of concentrated aqueous solutions of alcohols, while determining the critical micelle concentration (*CMC*), the partial molar volume (V_m^*) and the partial molar adiabatic compressibility (κ_m^*) for the surfactant. The alcohol, 2-propanol, was chosen for several reasons: 1) 2-Propanol mixes with water well at room temperature; 2) this alcohol slightly promotes water structure, although ethanol has negligible effect on water structure, and 1-propanol creates hydrogen-bond network considerably;[6] 3) the results of sound absorption in aqueous solutions of 2-propanol indicate only the existence of ultrasonic relaxation due to the solute-solvent interaction, even in considerably concentrated solutions.[7] Before pursuing the main aim above, we determined *CMC*, V_m^* and κ_m^* for several alkyltrimethylammonium bromide compounds using water as a solvent, although similar experiments have been carried out by Zielinski et al.,[15] Gonzalei–Gaitano et al.[16] and Evans et al.[17] Then, the parameters, *CMC*, V_m^* and κ_m^*, were also obtained for dodecyltrimethylammonium bromide (C_{12}TAB) in a mixed solvent of water and 2-propanol given in this report.

Experimental

Chemicals. 2-Propanol, tetramethylammonium bromide (C_1TAB), octyltrimethylammonium bromide (C_8TAB), decyltrimethylammonium bromide (C_{10}TAB), dodecyltrimethylammonium bromide (C_{12}TAB), tetradecyltrimethylammonium bromide (C_{14}TAB) and hexadecyltrimethylammonium bromide (C_{16}TAB) were purchased from Wako Pure Chemicals Co., Ltd. and Tokyo Kasei Kogyo Co. Ltd. 2-Propanol distilled once at normal pressure and one without further purification gave the same sound velocity and density values. Water was distilled and purified through

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Present address: Chugai Pharmaceutical Co. Ltd., Japan

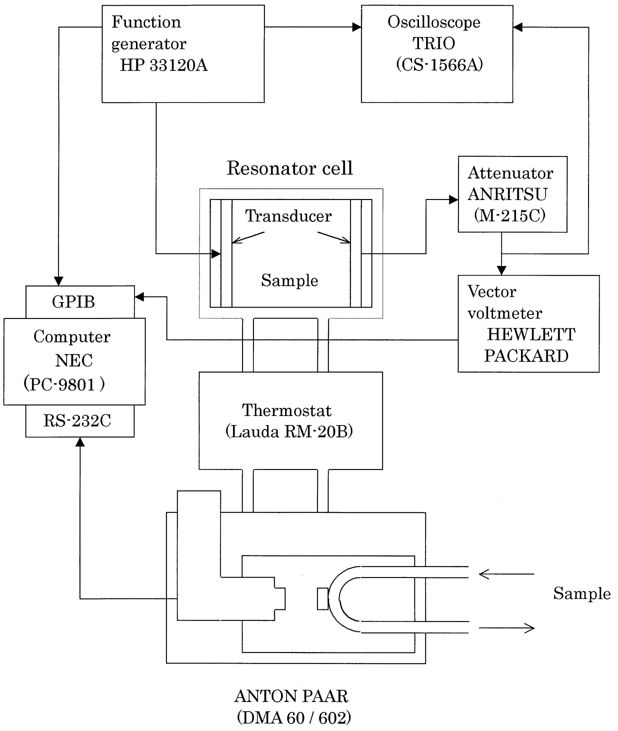

Fig. 1. The block diagram for sound velocity and density measurements.

a MiliQ SP-TOK system from Japan Millipore Ltd., and then degassed by sonication at reduced pressure. Several mixed solvents of water and 2-propanol, which were again degassed, were prepared at desired concentrations of the alcohol by a volumetric flask. The surfactants were dissolved into the mixed solvents and the solutions were diluted to the desired concentrations by the same solvents.

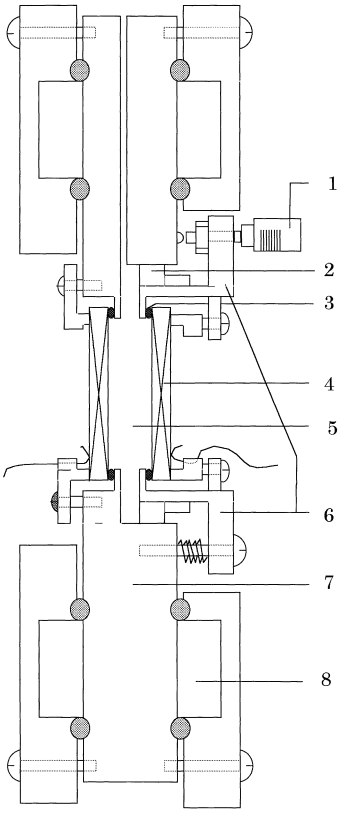

Fig. 2. Design of ultrasonic resonator cell with 5 MHz x-cut crystals.
1: micrometer, 2: teflon insulator, 3: Teflon O-ring, 4: quartz crystal, 5: sample liquid, 6: holder, 7: stainless steel, 8: water jacket.

Table 1. Comparison of the Sound Velocities Determined by the Resonator and the Interferometer at 25 °C

Chemicals	v / m s^{-1}	
	Resonator	Interferometer
Ethanol	1153.49	1154 ± 1
2-Propanol	1141.30	1142 ± 1
Acetone	1164.64	1165 ± 1
Chlorobenzene	1267.83	1269 ± 1

Apparatus. A simple and very economic apparatus for the sound velocity measurements was constructed based on a resonance method originally developed by Eggers.[14] The apparatus consists of a function generator (HP33120A), a resonator cell, a voltmeter (H. P. 8508A vector voltmeter), an attenuator (Anritsu M-215C), and a computer (NEC PC9801). A block diagram of the apparatus is shown in Fig. 1. The cell was home-made using stainless steel and Teflon [poly(tetrafluoroethylene)] rings, as shown in Fig. 2. The balance of the two transducers (5 MHz x-cut quartz crystals) is controlled by three micrometers (one of which is shown in the figure). It is possible to measure the sound velocity in most organic liquids. A function generator sweeps the frequency with the help of a computer, which also receives the output voltage through a voltmeter from a resonator cell, alternatively. The resonance frequency is automatically found to an accuracy of less than ±1 Hz. The home-made software ,written in N88BASIC language, is available upon request to one of the authors (SN). The resonance frequency, f_n, is related to the sound velocity[14] as $f_n = nv_n/2x$, where n is the harmonic number of the resonance peak, v_n is the sound velocity at f_n and x is the distance of the two transducers. When the two resonance frequencies are not very far apart, the dispersion of the sound velocity can be ignored in aqueous systems. The sound velocity is thus obtainable from the two different resonance frequencies by $v = v_n = 2x(f_{n+3} - f_n)/3$, where the third resonance peak, f_{n+3}, from the targeted peak, f_n, which is at around 3.8 MHz, was used. The distance between the two transducers was determined from the sound velocity value in water. In order to see how it works, several organic liquids were used to test the apparatus. The obtained sound velocity values are given in Table 1 along with those measured by an interferometer at 2.5 MHz. Another advantage of our apparatus is the small volume of the sample solution (about 3.5 cm^3) required for a measurement.

Solution densities were measured using an Anton Paar vibrating density meter (DMA 60/602) with a reproducibility of less than ±0.01 kg m^{-3} . Pure water and air were used to determine the cell constants, and methanol and ethanol were used to check the accuracy. Water was circulated around the density and resonance cells to maintain the entire measurement system at a constant temperature within ±0.01 °C using a water bath (Lauda RM 20 B). The solution density and sound velocity were measured at least three times and then averaged. Before measuring the sample solutions, the apparatus was always checked through water for the sound velocity meter and through water and air for density meter.

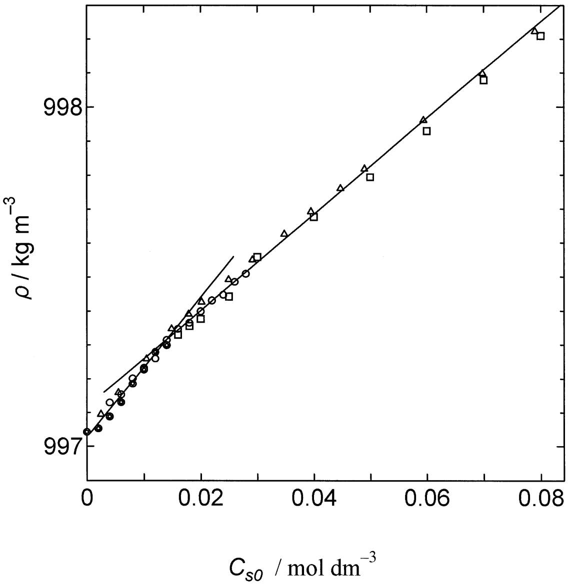

Fig. 3. Concentration dependence of the density in aqueous solution of C_{12}TAB. ○, ◎, □ data in different days, △ data in the literature from Ref. 18.

Conductivity data was collected by Digital Conduct Meter (TOA Electric Ltd. model CM-15A9).

All the measurements were performed at 25.0 °C.

Results and Discussion

Figure 3 shows representative density data as a function of the C_{12}TAB molarity, C_{s0}, and the results in the literature[18] are also presented for comparison where the molality has been converted to the molarity using the solution density. As can be seen, the present and reported values are in very good agreement with each other. The critical micelle concentration (*CMC*) for C_{12}TAB in water was estimated from the inflection point to be 15.0 mmol dm^{-3}, which is the same as the reported value.[9,18]

The adiabatic compressibility, κ_s, was obtainable by Laplace equation with the help of the solution density, ρ, and the sound velocity, v,

$$\kappa_s = 1/(\rho v^2). \tag{1}$$

Figures 4 and 5 show the concentration dependence of the adiabatic compressibility for six solutions. The *CMC* values for the individual surfactants were determined from the inflection points of these plots, while the inflection concentration was not found in a solution of C_1TAB as shown in Fig. 4. Such determined *CMC* values are the same as those obtained from the density data. It is well known that the plots of *ln* (*CMC*) vs the number of alkyl-carbon atoms, *N*, fall on a straight line, which is shown in Fig. 6 along with those from the literature.[15–17] All of the obtained *CMC* are very close to the literature values, indicating that the surfactants used were purified reasonably well.

The apparent molar volume, ϕ_v, for a solution is defined as

$$\phi_v = (V - n_0V_0)/n, \tag{2}$$

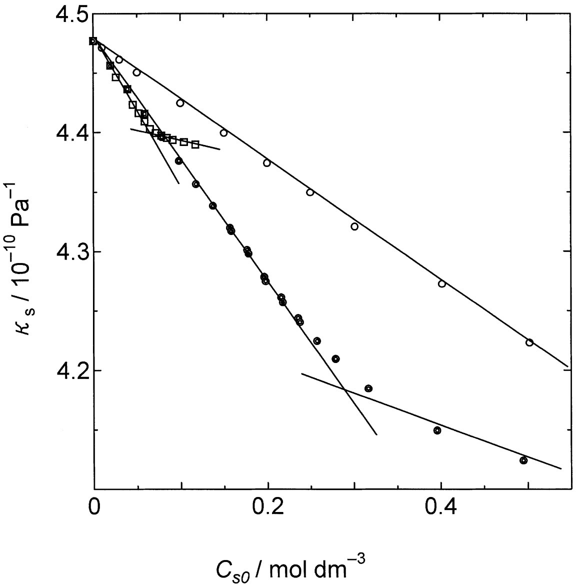

Fig. 4. Concentration dependence of the solution compressibility at 25 °C. ○: C_1TAB, ◎: C_8TAB, □: C_{10}TAB.

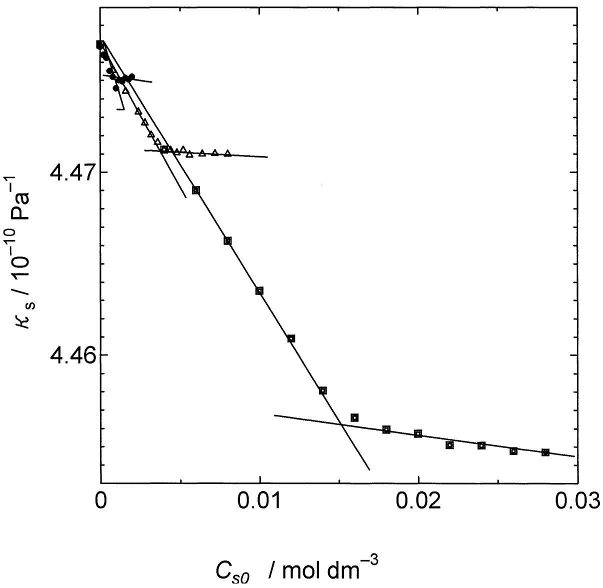

Fig. 5. Concentration dependence of the solution compressibility at 25 °C. ▣: C_{12}TAB, △: C_{14}TAB, ●: C_{16}TAB.

where V is the total volume of the solution, V_0 is the molar volume of the solvent, and n and n_0 are the number of moles of the solute and solvent, respectively. Equation 2 is converted to a usable form,

$$\phi_v = M_s/\rho + (1/m)(1/\rho - 1/\rho_0) \tag{2$'$}$$

where M_s is the molecular mass of the solute, ρ and ρ_0 are the density of the solution and the solvent, and m is the molality of the solute, which can be calculated from the molarity using the solution density. The apparent molar compressibility, ϕ_κ, is also defined in a similar fashion as

$$\phi_\kappa = (V\kappa_s - n_0V_0\kappa_{s0})/n, \tag{3}$$

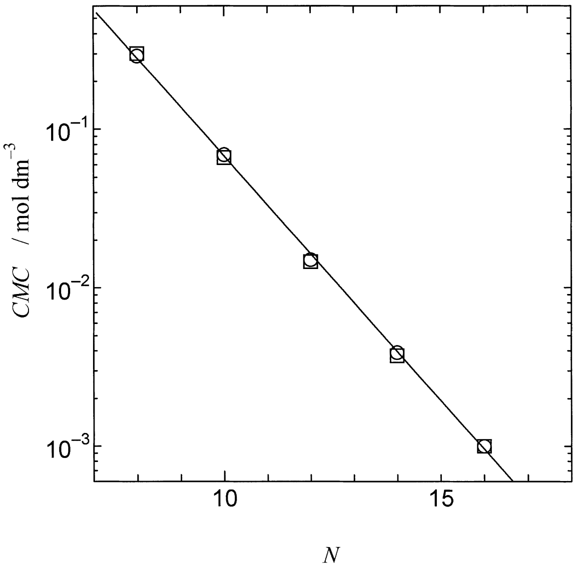

Fig. 6. Dependence of ln (*CMC*) on the number of alkyl-carbon atoms, *N*. ○: present results, □: reported values

where κ_{s0} is the adiabatic compressibility of the solvent. This is also transformed to a convenient form to calculate the value as

$$\phi_\kappa = (M_s/\rho)\kappa_s + (1/m)(\kappa_s/\rho - \kappa_{s0}/\rho_0). \qquad (3')$$

The partial molar volumes, $V_m{}^*$ and $V_{mi}{}^*$, and the partial molar compressibilities, $\kappa_m{}^*$ and $\kappa_{mi}{}^*$, for the monomer and micellar forms, respectively, are obtained from the slopes of the linear relation of ($\phi_v m$) vs m and ($\phi_\kappa m$) vs m, above and below the *CMC*. However, these thermodynamic parameters for a $C_{16}TAB$ solution could not be determined by Eqs. 2′ and 3′, because the changes in the density and sound velocity with the concentration were too small. Table 2 tabulates the partial molar quantities, and it can be seen that the obtained values are close to the literature ones, except the partial molar compressibility below *CMC*. This may arise because the differences in the density and sound velocity values between the solution and solvent are very small. It should be noticed that the partial molar volume of the surfactants increases linearly with the number of alkyl-carbon atoms, *N*. Our results are well expressed as $V_m{}^* = (15.6\times N + 100.4)\times10^{-6}$ m^3 mol^{-1} below *CMC* and $V_{mi}{}^* = (16.8\times N + 93.7)\times10^{-6}$ m^3 mol^{-1} above *CMC*. The interpretation of the dependence of the partial molar volume or molar compressibility on the number of carbon atoms has been given theoretically by Endo.[20]

Similar experiments for $C_{12}TAB$ were carried out in a mixed solvent of water and 2-propanol. The reason why $C_{12}TAB$ was selected is that the compressibility is quite sensitive in the appropriate concentration range, as can be seen in Fig. 5. *CMC* in a mixed solvent was also determined from the inflection points of the compressibility as a function of the $C_{12}TAB$ concentration. Some of the results are shown in Fig. 7. It should be noticed that the slope values below *CMC* at concentrations less than 2.0 mol dm^{-3} of 2-propanol are smaller than those in the range more than that of 2-propanol. The *CMC* values for the surfactant were obtained from the intersection of the straight lines, except that at 2.0 mol dm^{-3} of 2-propanol. At this concentration, the distinction of two straight lines was not very clear and the *CMC* was estimated graphically. Above this concentration, the intersection again becomes clear, although the slope values below *CMC* are opposite. In order to confirm the *CMC* values for $C_{12}TAB$, the electrical conductivity was measured in a mixed solvent with 2-propanol, some results of which are shown in Fig. 8. Such obtained *CMC* values are considered to be close to those from the compressibility data, as can be seen in Table 3.

For the determining the apparent molar quantities, Eqs. 2′ and 3′ should be slightly rearranged, because the solvents are mixtures of water and 2-propanol. They are expressed by the following relations:[16]

$$\phi_v = M_s/\rho + ((1 + m_aM_a)/m)(1/\rho - 1/\rho_0), \qquad (2'')$$

$$\phi_\kappa = (M_s/\rho)\kappa_s + ((1 + m_aM_a)/m)(\kappa_s/\rho - \kappa_{s0}/\rho_0), \qquad (3'')$$

where m_a and M_a are the molality and the molecular weight of 2-propanol, respectively. Figures 9 and 10 show some repre-

Table 2. Partial Molar Volume and Partial Molar Compressibility of Alkyltrimethylammonium Bromide Compounds in Liquid Water at 25 °C

The number of alkyl-carbon Atoms	below *CMC*		above *CMC*	
N	$V_m{}^*$ / 10^{-6} m^3 mol^{-1}	$\kappa_m{}^*$ / 10^{-15} Pa^{-1} m^3 mol^{-1}	$V_{mi}{}^*$ / 10^{-6} m^3 mol^{-1}	$\kappa_{mi}{}^*$ / 10^{-15} Pa^{-1} m^3 mol^{-1}
1	116	1.23	—	—
	(114.2–115.2)	(−0.80–0)		
8	225	3.06	228	64.3
	(225.0–223.7)	(−38–−72)	(227.5–228.8)	(79–81)
10	258	−0.832	262	96.7
	(255.0–258.2)	(−14–−15)	(262.2–265.0)	(98–99)
12	288	−9.90	295	120
	(278.1–287.0)	(−42–−43)	(295.5–298.4)	(115–120)
14	319	−6.50	328	144
	(309.6–320.6)	(−81.1–−75.2)	(309.6–320.6)	(137–138)

The values in the parenthesis are from Ref. 15 and therein also with Ref. 26.

Table 3. Partial Molar Compressibility and Partial Molar Volume of $C_{12}TAB$ in the Mixed Solvents with 2-Propanol at 25 °C

2-Propanol	*CMC*		below *CMC*		above *CMC*	
C_{a0}/ mol dm^{-3}	mmol dm^{-3} Compressibility	mmol dm^{-3} Conductivity	κ_m^*/ 10^{-15} Pa^{-1}(mol m^{-3})$^{-1}$	V_m^*/ 10^{-6} m^3 mol^{-1}	κ_{mi}^*/ 10^{-15} Pa^{-1}(mol m^{-3})$^{-1}$	V_{mi}^*/ 10^{-6} m^3 mol^{-1}
0	15.3	15.0	−9.90	288	120	295
1.00	11.3	12.7	0.166	280	167	296
1.50	9.58	13.4	46.8	298	182	297
2.00	~20	17.0	200	296	212	302
2.50	20.7	17.4	308	301	226	303
3.00	24.4	25.6	364	313	228	304

The concentration and *CMC* are expressed by the conventionally used units.

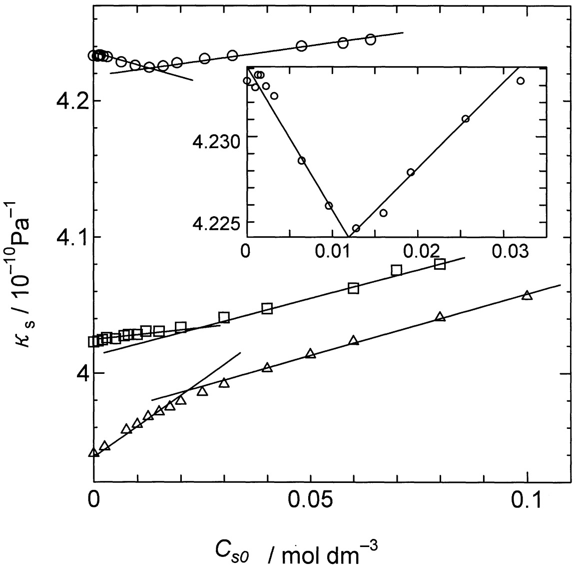

Fig. 7. $C_{12}TAB$ concentration dependence of the compressibility at different concentrations of 2-propanol.
○: 1.0 mol dm^{-3} of 2-propanol, □: 2.0 mol dm^{-3} 2-propanol, △: 3.0 mol dm^{-3} 2-propanol.

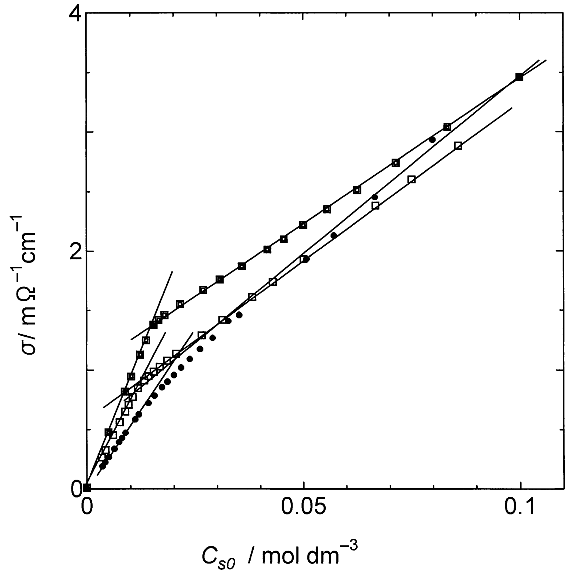

Fig. 8. Representative $C_{12}TAB$ concentration dependence of the conductivity at several 2-propanol concentrations.
⊡: in water, □: in the mixed solvent with 1 mol dm^{-3} 2-propanol, ●: in the mixed solvent with 2.5 mol dm^{-3} 2-propanol.

sentative plots of ($\phi_v m$) and ($\phi_\kappa m$) as a function of the molality, m, for determining the partial molar volume and the partial molar compressibility of $C_{12}TAB$. Again, good linear portions were observed above and below *CMC*. The obtained partial molar quantities are tabulated in Table 3.

First, the newly constructed resonator is proved to be a simple and convenient tool to monitor the characteristics of a solution. The temperature fluctuation of the solutions can also be monitored using the density meter. The determined *CMC*'s for several alkyltrimethylammonium compounds are in good agreement with those in the literatures.[15–18]

Second, the effects of alcohols on the surfactant characteristics have been examined by various methods.[9,11,19,21–24] *CMC* and the aggregation number of surfactants increase or decrease depending upon the structures of the surfactants and the concentrations of added alcohols. A notable feature was found in the $C_{12}TAB$ concentration dependence of the compressibility, as shown in Fig. 7. Below *CMC*, the slope of the plots of the compressibility vs the concentration of $C_{12}TAB$ gives a negative value in a mixture with 2-propanol less than 2.0 mol dm^{-3}, while it is positive when the alcohol concentration is higher than 2.0 mol dm^{-3}(2.3 mol kg^{-1}). This means that the circumstance of $C_{12}TAB$ changed at around 2.0 mol dm^{-3} of the alcohol. In determining the partial molar volume and the partial molar compressibility of the surfactant, very clear linear relationships in the plots of ($\phi_v m$) and ($\phi_\kappa m$) as a function of the molality of the surfactant, m, were found below and above *CMC* at several concentrations of 2-propanol. This indicates that these partial molar quantities are constant over a quite wide concentration range of $C_{12}TAB$ up to around 100 mmol dm^{-3}, although they depend upon the 2-propanol concentration, m_a, as shown in Figs. 11 and 12. Vikingstad and Kvammen[24] have reported on the effects of alcohols on the partial molar quantities of sodium decanoate; their results for the partial molar volume are shown in Fig. 11 for a comparison. The reference values are given by the molality, and thus our results are also indicated by the same scale. Although they considered the apparent molar quantities, we prefer to focus on the partial molar quantities. In the concentration range lower than 2.0 mol dm^{-3} of 2-propanol, the partial molar volume for micellar form is greater than that for the monomeric form, and

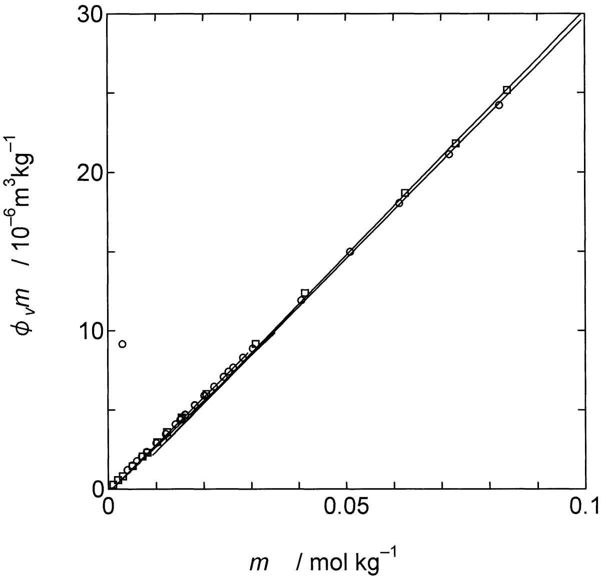

Fig. 9. Representative plots of $\phi_v m$ as a function of C_{12}TAB molality, m. ○: in water, □: in the mixed solvent with 2.5 mol dm^{-3} 2-propanol.

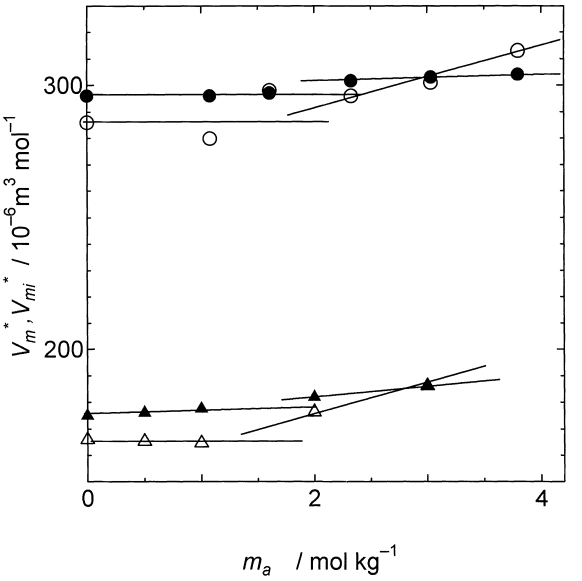

Fig. 11. The dependence of the partial molar volume of C_{12}TAB on 2-propanol molality, m_a. ○: below *CMC* and ●: above *CMC* for C_{12}TAB, △: below *CMC* and ▲:above *CMC* for sodium decanoate.

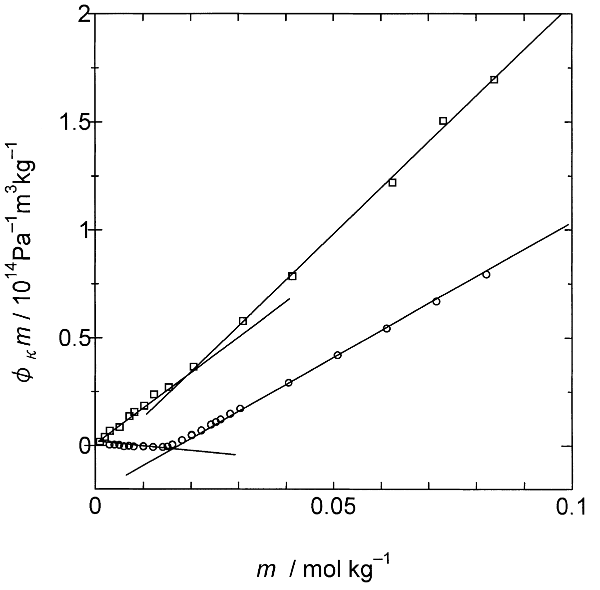

Fig. 10. Representative plots of $\phi_\kappa m$ as a function of C_{12}TAB molality m. ○: in water, □: in the mixed solvent with 2.0 mol dm^{-3} 2-propanol.

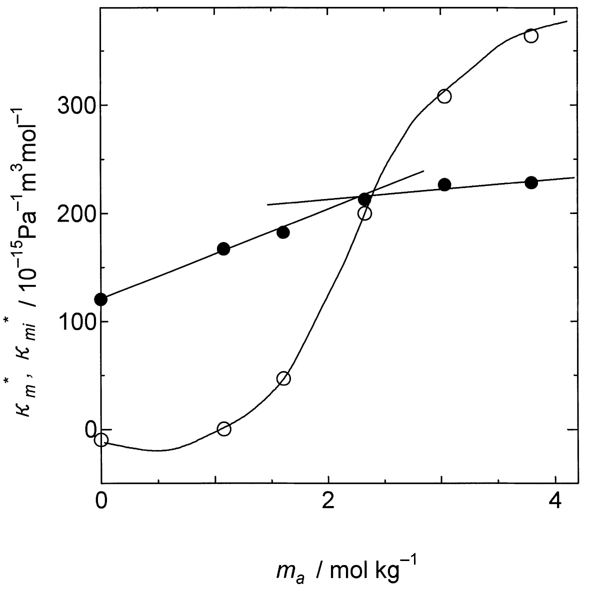

Fig. 12. The dependence of the partial molar compressibility of C_{12}TAB on 2-propanol molality, m_a. ○: below *CMC* and ●: above *CMC*.

the volumes are close to each other, or slightly greater for the monomer in both surfactants above that 2-propanol concentration. There seems to be a structural change in the solution at around 2.0 mol dm^{-3} of 2-propanol. Discontinuous trends are remarkably found in the concentration dependence of the partial molar compressibility, as can be seen in Fig. 12. In the micellar form, the inflection concentration is found at 2.3 mol kg^{-1}, while a sharp increase is observed in the partial molar compressibility for the monomer form. Similar trends for the monomer and micelle forms for sodium decanoate have been reported.[24] In our previous study using ultrasonic absorption measurements in aqueous solution of 2-propanol,[7] the relaxation associated with the water-alcohol interaction was observed from around 3 mol dm^{-3}, and the structural change in the solution was proposed to yield the promoted water structure. Also, this relaxation phenomenon is very much affected by the addition of salt.[25] Therefore, in a ternary system with a surfactant, it is considered that the structural change may start with a slightly lower concentration. It has been generally recognized that the partial molar quantities reflect the hydrophobic and hydrophilic hydrations to solute molecules. When the water structure still remains as the pure state, the hydration to the surfactant may be the same and the partial molar volume remains the same up to around 2.0 mol dm^{-3} of 2-propanol. Above this concentration, water hydrogen-bond networks are promoted by 2-propanol, and the space occupied by the surfactant increases. Also, parts of 2-propanol molecules penetrate into the micelles, which causes an increase in the compressibility. The smaller increment in the compressibility profile above 2.0 mol dm^{-3} 2-propanol indicates that the micelles are less compressive because of a further increase in the water hydrogen-bond networks around the micelles. A steep increase in the partial molar compressibility for the monomer form may arise from the existence of the surfactant in the sufficient cavities of the water hydrogen-bond network.

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