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Effect of pressure and temperature on adiabatic compressibility of aqueous solutions of amphiphiles with a perfluorocarbon chain☆

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Abstract

The apparent adiabatic compressibility and the apparent molar volume of sodium perfluoroheptanoate ($C_6F_{13}COONa$) were obtained from the experimental data of ultrasound velocity and density of its aqueous solutions at the concentration above and below CMC (critical micelle concentration) as functions of applied pressure (0–70 MPa) and temperature (5–35°C). Those were compared to the reported data for sodium decanoate ($C_9H_{19}COONa$) of Vikingstad et al. [J. Colloid Interface Sci. 72 (1979) 59]. It was found that the micelles of $C_6F_{13}COONa$ were more easily compressible than $C_9H_{19}COONa$ micelles under the condition studied. For the singly dispersed state below CMC, negative apparent compressibility of $C_6F_{13}COONa$ was confirmed and it approached to zero with the increase of pressure or temperature suggesting the decreased electrostriction and hydrophobic hydration with pressure or temperature rise. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Density; Sound velocity; Fluorinated surfactant; Electrostriction; Hydrophobic hydration

1. Introduction

To elucidate the thermodynamic properties of micelles and the nature of singly dispersed state of surface-active amphiphiles in aqueous environment, several investigators have measured the adiabatic compressibility of aqueous surfactant solutions [1–10]. Some of them direct their attention to temperature and/or ionic strength dependence of the compressibility [2–5], but a few studies have been performed so far on the effect of pressure [7]. Recently, we developed an apparatus which can simultaneously measure both ultrasound velocity in solution and the solution's density at high pressures [8]. Using this apparatus we had measured the ultrasound velocity and density for aqueous solutions of decyltrimethylammonium bromide ($C_{10}H_{21}N(CH_3)_3Br$), and the apparent molar volume and the apparent molar adiabatic compressibility had been estimated in the pressure range 0–40 MPa [8].

As the next step of the investigation on compressibility of aqueous surfactant solutions under high

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pressures, we adopted a surfactant having fluorocarbon as a hydrophobic part as the solute. Fluorocarbon-type surfactants have a great attraction in the field of surfactant science because of their unique properties, e.g., extreme resistance to chemical attack, great surface activity, possession of both hydrophobicity and oleophobicity, and so on. To fully understand the origin of the uniqueness of fluorinated surfactants, investigations on the hydrophobic hydration of fluoroalkyl chain are important. It is well known that surfactants having perfluorocarbon chain as a hydrophobic part exhibit a higher degree of hydrophobicity than do corresponding hydrocarbon-type surfactants with equal carbon chain length and that the critical micelle concentration (CMC) of perfluorocarbon surfactants are close to those of hydrocarbon surfactants whose carbon atoms in hydrophobic chain is 1.5 times longer [11]; this has been attributed to the difference in the transferring free energy of $–CF_2–$ and $–CH_2–$ from the aqueous environment to the micellar state. One may expect that the different properties between the two originate partly from the different nature of hydrophobic hydration around the hydrophobic part of the two types of surfactants. Adiabatic compressibility is one of the informative thermodynamic parameters to know the strength of hydration of solute molecules because hydrated water is less compressible compared to bulk water. So that, it may especially be interesting to estimate the partial molar compressibility of sodium perfluoroheptanoate ($C_6F_{13}COONa$) in both monomeric and micellar state and compare them to the corresponding data of sodium decanoate ($C_9H_{19}COONa$) reported by Vikingstad et al. [7]. In Table 1, some solution properties of $C_6F_{13}COONa$ and $C_9H_{19}COONa$ are summarized for reader's information [11–14], where ΔC_p^0 is the change in heat capacity for dissolution at an infinite dilution and $-dB/dT$ the temperature dependence of the viscosity B coefficient. Those parameters reflect the hydrophobic nature of the solutes.

In this study, we also measured the adiabatic compressibility of aqueous solutions of homologues of sodium alkanesulfonates ($C_nH_{2n+1}SO_3Na$) and sodium perfluoroalkanoates ($C_nF_{2n+1}COONa$) attempting to obtain the information concerning the group contribution of $–CH_2–$ and $–CF_2–$ to the hydrophobic hydration.

2. Experimental

2.1. Materials

Sodium perfluoroalkanoates ($C_nF_{2n+1}COONa$, n=4–6) were synthesized from perfluoroalkanoic acids (Daikin Kasei) by adding the equivalent amount of aqueous NaOH solution to the acids. The obtained salts were freeze-dried and recrystallized from ethylacetate/ethylether mixed solvent. Sodium alkanesulfonates ($C_nH_{2n+1}SO_3Na$; n=3–5, reagents for ion-pair chromatography) were purchased from Tokyo Kasei. They were recrystallized from methanol or ethanol solution. Water was passed through a Milli-Q Labo purification system (Millipore) after distillation. All sample solutions were prepared gravimetrically.

2.2. Measurements

Ultrasound velocity in solution and the solution density under applied pressure were measured simultaneously employing the apparatus reported previously [8]. Briefly, the apparatus consists of an

Table 1
Comparison of solution properties of $C_6F_{13}COONa$ and $C_9H_{19}COONa$ aqueous solutions under normal pressure at 25°C[a]

	CMC (mol dm^{-3})	Micellar aggregation number at CMC	ΔC_p^0 (J K^{-1} mol^{-1})	$-dB/dT$ (dm^3 mol^{-1} K^{-1})
$C_6F_{13}COONa$	0.0909	–	507±6[b]	0.0083[b]
$C_9H_{19}COONa$	0.0940–0.0955[c]	19[d]	~500[e]	~0.009[e]

[a] ΔC_p^0, change in heat capacity for dissolution at an infinite dilution; $-(dB/dT)$, temperature dependence of the viscosity B coefficient.
[b] Ref. [14].
[c] Ref. [12].
[d] Ref. [13].
[e] Estimated from the data in Ref. [14].

oscillating U-tube densimeter (Anton-Paar) and a 2 MHz ultrasound velocimeter. In the previous study, we used a remote cell unit (DMA 512) for the density meter, which was equipped with the sample cell made of stainless steel tube. In the present study, on the other hand, it was replaced by a special remote cell unit (DMA 512P) having the sample cell made of HASTELLOY alloy C-276 tube. The maximum operating pressure, which limits the upper end of the applied pressure of the apparatus, was improved from 40 to 70 MPa. Sample solutions were compressed by a high-pressure liquid-chromatography pump (Nihon Seimitu Kagaku, NP-AX-5S). Temperature was regulated to ±0.005°C in a PID mode by using a quartz thermometer and a microcomputer. The densimeter and the velocimeter were calibrated using the data of pressure-dependent density for water [15] and methanol [16], and the sound velocity data for water [17] and aqueous NaCl solutions [18], respectively. The accuracies of the ultrasound velocity and the density measurements in the applied pressure range of 0–70 MPa were confirmed to be $\pm 0.2\ \mathrm{m\,s^{-1}}$ and $\pm 1.5\times 10^{-4}\ \mathrm{g\,cm^{-3}}$, respectively.

For the measurements under the normal pressure, a sing-around velocimeter (UVM-2, Chou-onpa Kougyou) equipped with a concentration scanning cell system and an Anton Paar DMA 60/602 densimeter were also employed. The accuracies of the ultrasound velocity and density measurements under normal pressure were $\pm 0.1\ \mathrm{m\,s^{-1}}$ and $\pm 5\times 10^{-6}\ \mathrm{g\,cm^{-3}}$, respectively.

Apparent molar volume (ϕ_v) and apparent molar adiabatic compressibility (ϕ_K) for binary solution systems were calculated from the following equations

$$\phi_\mathrm{v} = 1000\frac{\rho_1 - \rho}{m_2\rho\rho_1} + \frac{M_2}{\rho} \tag{1}$$

$$\phi_\mathrm{K} = 1000\frac{\beta - \beta_1}{m_2\rho_1} + \beta\phi_\mathrm{v} \tag{2}$$

$$\beta = \frac{10^{-3}}{u^2\rho} \tag{3}$$

where ρ is the solution density ($\mathrm{g\,cm^{-3}}$), β the coefficient of adiabatic compressibility ($\mathrm{Pa^{-1}}$) of the solution, M_2 the solute molecular weight, m_2 the molality, and u the sound velocity ($\mathrm{m\,s^{-1}}$) in the solution. The subscript 1 and 2 refers to solvent and solute, respectively. One can readily derive partial molar volume, v_2, and partial molar compressibility, K_2 ($=-(\partial v_2/\partial P)_\mathrm{S}$), using the following equations

$$v_2 = \phi_\mathrm{v} + \left(\frac{\partial\phi_\mathrm{v}}{\partial \ln m_2}\right)_{T,P} \tag{4}$$

$$K_2 = \phi_\mathrm{K} + \left(\frac{\partial\phi_\mathrm{K}}{\partial \ln m_2}\right)_{T,P} \tag{5}$$

3. Results and discussion

3.1. *Effect of pressure on volume, compressibility, and CMC of $C_6F_{13}COONa$ at 25°C*

Fig. 1 shows the pressure dependence of density and sound velocity for $C_6F_{13}COONa$ aqueous solutions as a function of concentration. As the pressure increases, both density and sound velocity are shifted upward. Under each pressure, the data points can be fitted well with two straight lines having different slopes to give a break at the CMC. The estimated CMC values are plotted as a function of applied pressure in Fig. 2. Under normal pressure, the CMC of $C_6F_{13}COONa$ was 90.9 mM which is somewhat higher than the reported value (85 mM) by Guo et al. [19]. In the applied pressure range of 0–70 MPa, the smooth increase of CMC has been confirmed. The increase of CMC with pressure may be interpreted on the basis of the Le Chatelier–Braun principle. An increase in pressure causes the monomer-micelle equilibrium to proceed in the direction in which the volume of the system is decreased. Since the molar volume of surfactant in micelle is larger than that of the monomeric form under the present condition, the application of pressure suppressed the micelle formation. It is to be noted that the effect of pressure on the CMC of $C_6F_{13}COONa$ is almost the same on a fractional basis as compared to published data on sodium perfluorooctanoate ($C_7F_{15}COONa$) in the pressure range 0–70 MPa [20].

From Eqs. (1)–(3), apparent molar volume, ϕ_v, and apparent molar adiabatic compressibility, ϕ_K, are calculated and plotted in Fig. 3. (In Fig. 3a, data below $0.05\ \mathrm{mol\,kg^{-1}}$ are omitted because of the lack of sufficient accuracy in density measurement which leads enormous errors to ϕ_v in the dilute region.) We can see that apparent molar volume of the surfactant increases more steeply with concentration in post-

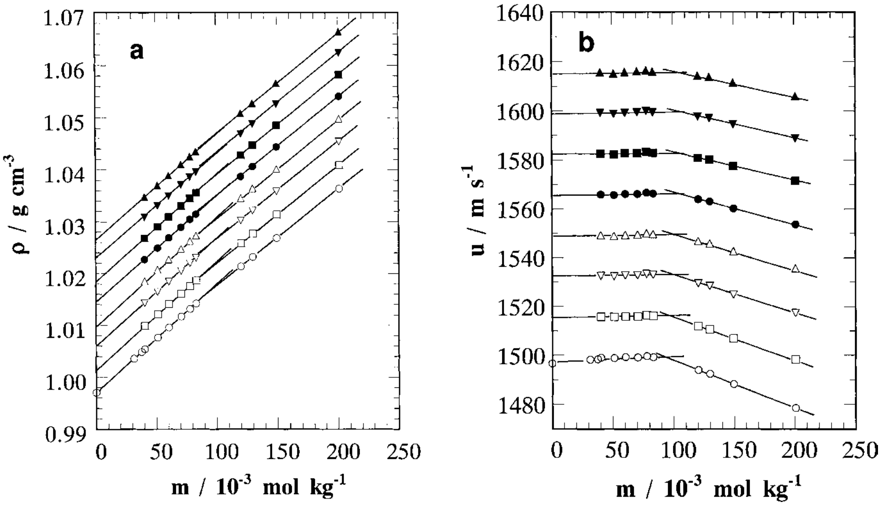

Fig. 1. Plots of density (a) and sound velocity (b) against molality of aqueous solutions of sodium perfluoroheptanoate ($C_6F_{13}COONa$) under various applied pressures at 25°C. Applied pressures are 0 (○), 10 (□), 20 (▽), 30 (Δ), 40 (●), 50 (■), 60 (▼), and 70 MPa (▲).

micelle than in pre-micelle concentration region irrespective of the pressure. Because of the long-range Coulombic force, concentration dependence of ϕ_V in pre-micelle region becomes slightly positive [21]. It is interesting that while ϕ_V increase with pressure in the pre-micelle region, it decreases with pressure in the post-micelle region. Similar behavior of pressure dependence can be confirmed for ϕ_K as seen in Fig. 3b.

From the data below CMC, partial molar volume and partial molar compressibility for the singly dispersed state (designated as v_s and K_s, respectively) may be evaluated using Eqs. (4) and (5). Also, the experimental ϕ_V and ϕ_K in the pre-micelle region can usually be fitted in molality m_2 by the equation

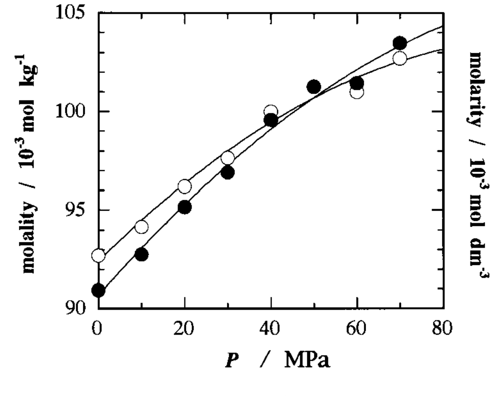

Fig. 2. Relation between CMC of $C_6F_{13}COONa$ and applied pressure at 25°C using molality (○) and molarity (●) scale.

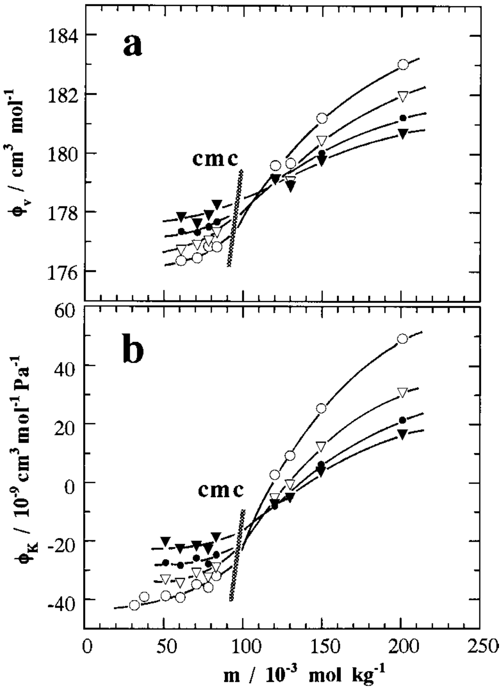

Fig. 3. Concentration dependence of apparent molar volume, ϕ_V (a), and apparent molar compressibility, ϕ_K (b), for aqueous solutions of $C_6F_{13}COONa$ under various applied pressures at 25°C. Applied pressures are 0 (○), 20 (▽), 40 (●), and 60 MPa (▼). The CMC under each applied pressures are indicated by the thick line.

$$\phi_Y = \phi_Y^0 + A_Y m_2^{1/2} + B_Y m_2 \tag{6}$$

where Y stands for V or K, A_Y are the limiting slopes calculated from the Debye–Hückel theory, and B_Y are equivalent to the second virial coefficients. The values at infinite dilution, ϕ_Y^0, are equal to the partial molar quantities, v_s^0 or K_s^0. When the concentration is above CMC, however, Eq. (6) cannot be used for data fitting. Unfortunately, we could not estimate the partial molar quantities with a satisfactory precision in the post-micelle region using Eqs. (4) and (5), and an approximate method was employed alternatively to evaluate the change of partial molar quantities during micellar formation based on the pseudo-phase model for micellar formation [3,8].

For a dilute surfactant solution containing 1 kg of solvent, in which m_s mol of solute is dissolved as singly dispersed state and m_m mol as micelles, the total volume of solution, V_t, may be expressed as

$$V_t = \frac{10^3 + M_2 m_2}{\rho} = \frac{10^3 v_1}{M_1} + \phi_{v,s} m_s + \phi_{v,m} m_m \tag{7}$$

where M_1 and M_2 are the molecular weight of solvent and solute, respectively, v_1 the molar volume of the solvent and $\phi_{v,s}$ ($\phi_{v,m}$) is the apparent molar volume of solute in monomeric (micellar) form, respectively. By differentiating Eq. (7) with respect to pressure at constant entropy, one obtains

$$V_t \beta = \frac{10^3 v_1 \beta_1}{M_1} + \phi_{K,s} m_s + \phi_{K,m} m_m \tag{8}$$

where the adiabatic compressibility of solvent, β_1, and the apparent molar adiabatic compressibility of solute in monomeric (micellar) state, $\phi_{K,s}$ ($\phi_{K,m}$), are defined by

$$\beta_1 = -\frac{(\partial v_1/\partial P)_S}{v_1} \tag{9}$$

$$\phi_{K,s} = -\left(\frac{\partial \phi_{v,s}}{\partial P}\right)_S \tag{10}$$

$$\phi_{K,m} = -\left(\frac{\partial \phi_{v,m}}{\partial P}\right)_S \tag{11}$$

In the pseudo-phase model of micelle formation, the following approximation is made for the solutions below and above CMC:

$$m_s = m_2, \quad m_m = 0 \quad (m_2 < \mathrm{CMC}) \tag{12}$$

$$m_s = \mathrm{CMC}, \quad m_m = m_2 - \mathrm{CMC} \quad (m_2 > \mathrm{CMC}) \tag{13}$$

Therefore, the values of $\phi_{v,s}$, $\phi_{v,m}$, $\phi_{K,s}$, and $\phi_{K,m}$ can be estimated from the slopes of Eqs. (7) and (8) in the concentration range below and above CMC. We obtained two straight lines having different slopes to give a break at CMC (not shown here) indicating that $\phi_{v,s}$, $\phi_{v,m}$, $\phi_{K,s}$, and $\phi_{K,m}$ thus estimated were approximated as the partial molar quantities of surfactant in monomeric and micellar form around the CMC [8]. It was also confirmed that thus estimated $\phi_{v,s}$ ($\phi_{K,s}$) values were comparable with those of partial molar quantities from Eqs. (4) and (5), i.e., $\phi_{v,s}$ ($\phi_{K,s}$)$\cong v_s$ (K_s) at CMC. Fig. 4 shows the pressure dependence of the apparent molar quantities of $C_6F_{13}COONa$ in monomeric and micellar state. The corresponding data for $C_9H_{19}COONa$ reported by Vikingstad et al. [7] are also plotted.

Fig. 4a indicates that (1) the apparent molar volume of the micellar surfactant, $\phi_{v,m}$, is larger than that of monomeric surfactant, $\phi_{v,s}$, in the measured pressure range for both $C_6F_{13}COONa$ and $C_9H_{19}COONa$, (2) the difference of apparent molar volumes between $C_6F_{13}COONa$ and $C_9H_{19}COONa$ is ca. 14 $cm^3\ mol^{-1}$ for both $\phi_{v,s}$ and $\phi_{v,m}$ under normal pressure and it decreases to ca. 11 $cm^3\ mol^{-1}$ at 70 MPa, and (3) the change of partial molar volume during micellization, ΔV ($=\phi_{v,m}-\phi_{v,s}$), decreases with pressure since $\phi_{v,m}$ steeply decreases with the increase of pressure for both surfactants. The decrease in $\phi_{v,m}$ can be ascribed to the loss of free space between the molecules in the interior of the micelles when the pressure increases.

Fig. 4b shows the pressure dependence of $\phi_{K,s}$, $\phi_{K,m}$, and the apparent molar compressibility at infinite dilution, ϕ_K^0, estimated by extrapolation to zero concentration in Fig. 3b. Since micellar aggregates are easily compressed by the application of pressure, $\phi_{K,m}$ has positive values. However, ϕ_K^0 and $\phi_{K,s}$ are negative because of the strong electrostrictive effects of Na^+ and the hydrophobic hydration around the alkyl chain of monomeric state of the amphiphiles in solution. The increase of ϕ_K^0 and $\phi_{K,s}$ with pressure can be explained by the changes in electrostriction of water molecules around Na^+ ions; at higher pressures where the water structure is already somewhat compressed, the introduction of Na^+ ion has a smaller hardening effect to the surrounding water structure [22]. The marked

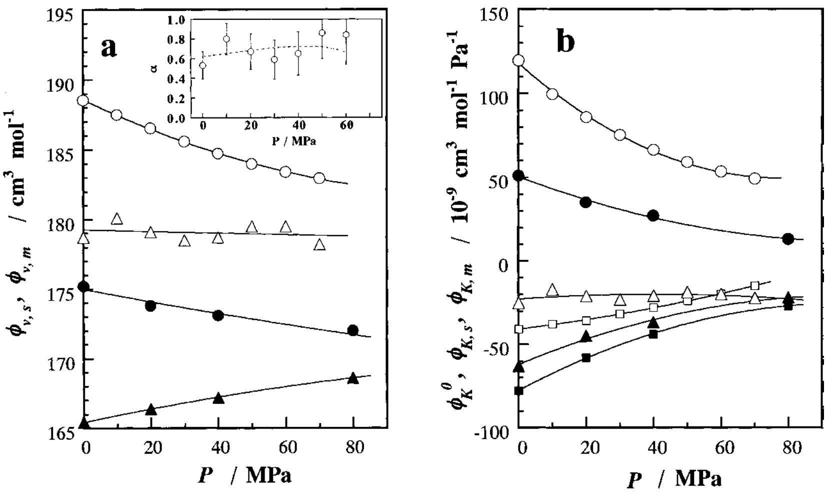

Fig. 4. Plots of apparent molar volume (a) and apparent molar compressibility (b) against applied pressure for aqueous solutions of $C_6F_{13}COONa$ (open symbols) and $C_9H_{19}COONa$ (filled symbols) at 25°C. (a) Triangle and circle indicate the data around the CMC for singly dispersed state ($\phi_{v,s}$) and the micellar state ($\phi_{v,m}$), respectively. In the inset, degree of dissociation of the counterion (Na^+) for $C_6F_{13}COONa$ micelle, α, is plotted as a function of pressure. (b) Square, triangle, and circle indicate the data for infinite dilution (ϕ_K^0), the data around the CMC for singly dispersed state ($\phi_{K,s}$) and the micellar state ($\phi_{K,m}$), respectively. Data for $C_9H_{19}COONa$ were adopted from Vikingstad et al. [7].

differences in behavior of the compressibilities between $C_6F_{13}COONa$ and $C_9H_{19}COONa$ are as follows: (1) $\phi_{K,m}$ of $C_6F_{13}COONa$ is quite larger than that of $C_9H_{19}COONa$ suggesting that the micelles of perfluorinated surfactant are more easily compressible than the hydrocarbon-type surfactant and (2) ϕ_K^0 (or $\phi_{K,s}$) of $C_6F_{13}COONa$ is less negative than that of $C_9H_{19}COONa$ in the pressure range studied. The first difference corresponds to the larger compressibility of perfluorocarbon than hydrocarbon. (The reported values of isothermal compressibility for n-C_7F_{16}, n-C_6H_{14}, and n-C_8H_{18} are 29.98, 16.27, and 12.14×10^{-5} atm^{-1} at 25°C, respectively [23].) The second difference is an unexpected result since the solution properties reflecting the hydrophobic nature of $C_6F_{13}COONa$ and $C_9H_{19}COONa$ are quite similar as indicated in Table 1. Negative values of ϕ_K^0 are ascribed to the effect of hydration of the monomers,

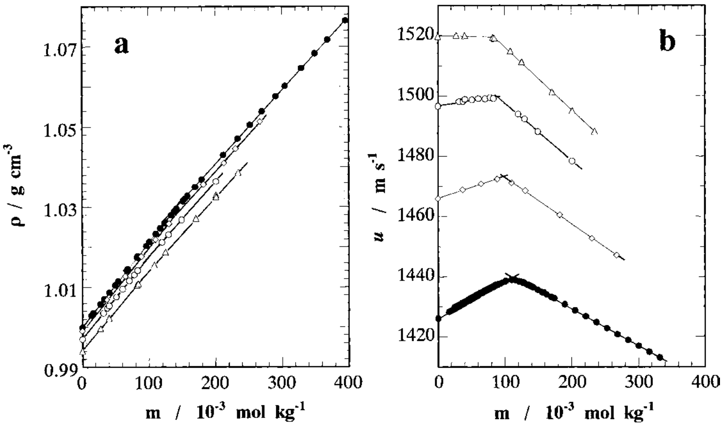

Fig. 5. Plots of density (a) and sound velocity (b) against molality of aqueous solutions of $C_6F_{13}COONa$ at 5 (●), 15 (◇), 25 (○), and 35°C (Δ) under normal pressure.

this result may be attributed to the weaker hydrophobic hydration of C_6F_{13} group than C_9H_{19} from the view point of adiabatic compressibility.

3.2. Effect of pressure on dissociation of counter ion of $C_6F_{13}COONa$ micelles

According to the charged pseudo-phase separation model for the micelle formation of ionic surfactants, the change in partial molar volume during micelle formation, ΔV, can be expressed as

$$\Delta V = (2-\alpha)RT\left[\frac{\partial \ln(\mathrm{CMC})}{\partial P}\right]_T \tag{14}$$

where α is the degree of dissociation of counter ion for surfactant in micelles, R the gas constant, and T the absolute temperature, respectively [24]. Employing the pressure dependence of CMC (Fig. 2), the degree of dissociation of the counter ion for $C_6F_{13}COONa$ micelles is calculated (see the inset of Fig. 4a). Although the estimated error of α is rather large, the obtained data clearly indicate that α for $C_6F_{13}COONa$ is considerably higher than that of typical hydrocarbon-type surfactants, e.g., α=0.22 for sodium dodecyl sulfate [25]. For $C_7F_{15}COONa$ micelles, comparable values were reported; α=0.44 under normal pressure and 0.45 when pressure became 1000 kgf cm^{-2} (=98 MPa) [20].

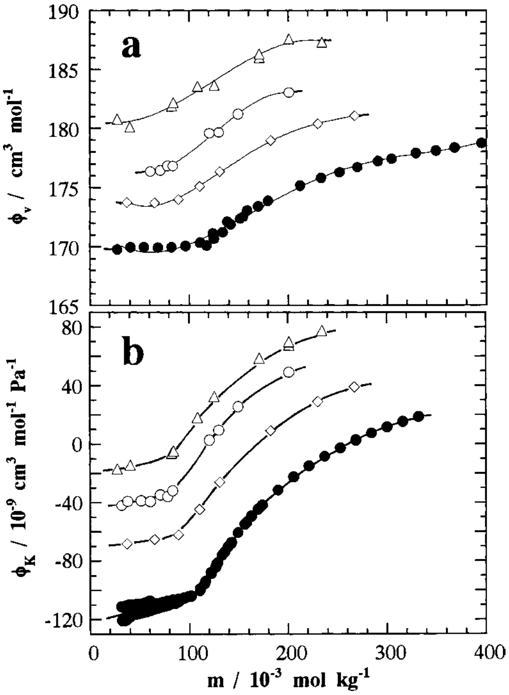

Fig. 6. Concentration dependence of apparent molar volume, ϕ_v (a), and apparent molar compressibility, ϕ_K (b), for aqueous solutions of $C_6F_{13}COONa$ under normal pressure at 5 (●), 15 (◇), 25 (○), and 35°C (Δ).

3.3. Effect of temperature on volume, compressibility, and CMC of $C_6F_{13}COONa$

We measured density and sound velocity of $C_6F_{13}COONa$ solutions at various temperatures under

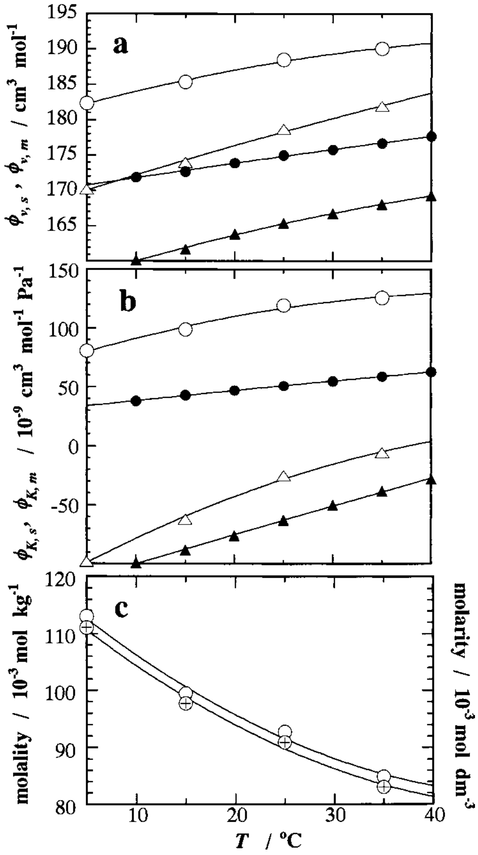

Fig. 7. Relation between apparent molar volume (a), apparent molar compressibility (b), and the CMC (c) against temperature for aqueous solutions of $C_6F_{13}COONa$ (open symbols) and $C_9H_{19}COONa$ (filled symbols) under normal pressure. Data for $C_9H_{19}COONa$ were adopted from Vikingstad et al. [7]. (a, b) Triangle and circle indicate the data for singly dispersed state and the micellar state, respectively. (c) The CMC in molality (○) and molarity (⊕) scale.

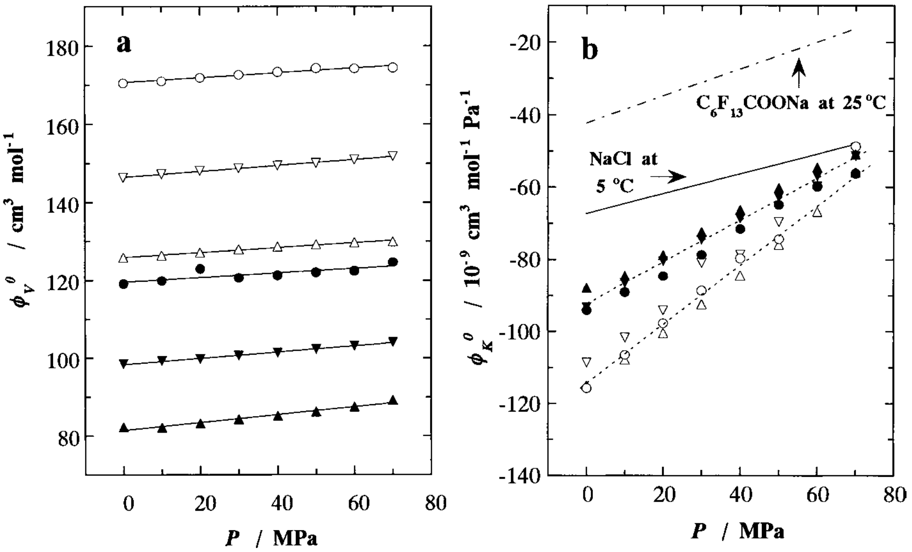

Fig. 8. Plots of apparent molar volume, ϕ_V^0 (a), and apparent molar compressibility, ϕ_K^0 (b), at infinite dilution against applied pressure for aqueous solutions of various amphiphiles at 5°C. Different symbols indicate different amphiphiles, i.e., sodium perfluoroalkanoates ($C_nF_{2n+1}COONa$, $n=4$ (Δ), 5 (▽), and 6 (○)) and sodium alkanesulfonates ($C_nH_{2n+1}SO_3Na$, $n=3$ (▲), 4 (▼), and 5 (●)). In (b), pressure dependence of ϕ_K^0 for NaCl at 5°C (full line) and for $C_6F_{13}COONa$ at 25°C (chain line) are also indicated.

normal pressure in this study. Fig. 5 shows the density and sound velocity data for $C_6F_{13}COONa$ as a function of concentration at 5, 15, 25, and 35°C. From Eqs. (1)–(3), apparent molar volume and apparent molar adiabatic compressibility are calculated and plotted in Fig. 6. One can see that both ϕ_V and ϕ_K are shifted upward with the increase of temperature. Temperature dependence of the apparent molar quantities in monomeric and micellar form was estimated using Eqs. (7)–(13), and the CMC estimated from the breaks in sound velocity data are also plotted in Fig. 7.

Fig. 7a shows that $\phi_{V,s}$ and $\phi_{V,m}$ increase with temperature for both $C_6F_{13}COONa$ and $C_9H_{19}COONa$. The increase in $\phi_{V,s}$ for amphiphilic solutes with temperature is usually ascribed to the reducing of the negative contribution to $\phi_{V,s}$ from hydrophobic hydration and electrostriction. For the increase of $\phi_{V,m}$, on the other hand, the positive contribution to $\phi_{V,m}$ from the thermal expansion of micelles should be considered. The volume of the ionic head groups at the micelle surface will also increase with temperature. The estimated values of expansion coefficient, α_T, for $C_6F_{13}COONa$ and $C_9H_{19}COONa$ micelles are 1.42×10^{-3} and 1.12×10^{-3} K^{-1}, respectively. (Note that the reported values of α_T for n-C_7F_{16}, n-C_6H_{14}, and n-C_8H_{18} are 1.56×10^{-3}, 1.39×10^{-3}, and 1.15×10^{-3} K^{-1} at 25°C, respectively [23].) Fig. 7b shows that both $\phi_{K,s}$ and $\phi_{K,m}$ linearly increase with temperature, but the increase in $\phi_{K,s}$ is much larger. This increase in compressibility with temperature can be attributed to a result of decreased electrostriction and hydrophobic hydration, as the resistance to pressure of the electrostricted water around Na^+ and ionic head group and the water structure around alkyl chain decrease with the increase of temperature [7]. Note that the difference in $\phi_{K,s}$ between $C_6F_{13}COONa$ and $C_9H_{19}COONa$ does not change so much with temperature, but the difference in $\phi_{K,s}$ becomes smaller when pressure is increased (see Fig. 4b).

3.4. *Effect of pressure on the hydrophobic hydration of fluorocarbon and hydrocarbon group*

We further measured the density and adiabatic compressibility of aqueous solutions of homologues of sodium alkanesulfonates ($C_nH_{2n+1}SO_3Na$, $n=3$–5) and sodium perfluoroalkanoates ($C_nF_{2n+1}COONa$, $n=4$–6), both are strong electrolyte salts, attempting to obtain the quantitative information concerning the difference of hydrophobic hydration around –CH_2– and –CF_2–.

In Fig. 8, indicated are the pressure dependence of the apparent molar volume and apparent molar compressibility at infinite dilution (ϕ_v^0 and ϕ_K^0) at 5°C. According to the group contribution of –CF_2– and –CH_2– to the molecular volume, the value of ϕ_v^0 increases linearly with alkyl chain length. However, the chain length dependence in ϕ_K^0 could not be detected in this experiment (see Fig. 8b); the accuracies of density and ultrasound velocity measurements have to be improved for the quantitative estimation of the group contribution of –CF_2– and –CH_2– to compressibility. It is to be noted that when pressure is not so high, the values of ϕ_K^0 for sodium perfluoroalkanoates are more negative than that for sodium alkanesulfonates indicating pronounced hydration around $C_nF_{2n+1}COO^-$ compared to $C_nH_{2n+1}SO_3^-$ ion. With the increase of pressure, the difference in ϕ_K^0 between them diminishes. At higher pressures (ca. 70 MPa) where the water structure is already somewhat disordered, these ϕ_K^0 values become almost the same as NaCl. This result suggests that the extent of hydration around $C_nF_{2n+1}COO^-$, $C_nH_{2n+1}SO_3^-$, and Cl^- ion becomes almost the same at 70 MPa from the view point of adiabatic compressibility.

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