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ORIGINAL CONTRIBUTION

Volume study on the exclusion of lithium naphthylsulfonate from lithium decylsulfonate micelles

Michio Yamanaka · Yuichi Takajo · Shinji Ono · Hitoshi Matsuki · Shoji Kaneshina

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Abstract Densities of aqueous solutions of lithium 1-naphthylsulfonate (1-LiNSO)–lithium decylsulfonate (LiDeSO) and 2-LiNSO–LiDeSO mixtures were measured as a function of total molality and composition of the mixtures. The partial derivative of the solution with respect to the total molality was calculated for the monomer and micellar regions. It was found that the values of the partial derivative are larger for the 2-LiNSO–LiDeSO system than for the 1-LiNSO–LiDeSO system. This fact is attributable to the larger value of the partial molar volume of monomer of 2-LiNSO than that of 1-LiNSO. For the two systems, the micellar molar volume of the mixtures varied linearly with the composition from the partial molar volumes of 1- and 2-LiNSO in their single systems to the micellar molar volume in the single LiDeSO system. Miscibility of the solutes in the mixed micelles was examined by drawing the critical micelle concentration (CMC) vs composition diagrams. The diagrams for the 1- and 2-isomers coincided with each other and showed that molecules of 1- and 2-LiNSO are excluded from the micelles. The contribution of the micelle-unforming component to the volume of micelle formation is positive and large because of the exclusion from the micelles. On the other hand, the contribution of the micelle-forming component to the volume of micelle formation is unchanged. The dependence of the monomer molalities of LiNSO and LiDeSO on the total molality, evaluated by means of the CMC vs composition diagrams, substantiated the validity of the approximations used in the derivation of the equations in this study.

Keywords Solution density · Partial molar volume · Micelle · Miscibility · Composition diagram of micellization

M. Yamanaka (✉) · Y. Takajo · S. Ono
Department of Chemistry, Faculty of Sciences,
Kyushu University, 4-2-1 Ropponmatsu, Chuo-Ku,
810-8560 Fukuoka, Japan
e-mail: yamanaka@chem.rc.kyushu-u.ac.jp

H. Matsuki · S. Kaneshina
Division of Life System,
Institute of Technology and Science,
The University of Tokushima,
2-1 Minamijosanjima, 770-8506 Tokushima, Japan

Introduction

Surface-adsorbed films and micelles formed by surfactants are regarded as models of biomembranes. Interaction of medicine molecules with lipid membranes can be presumed from analogy with interaction between the medicine molecules and the adsorbed films and micelles of surfactants. Investigating the thermodynamic properties of the assemblies and miscibility of components in the assemblies is important in understanding the structure and properties of biomembranes. Mixed adsorbed films and mixed micelles of binary surfactant mixtures were investigated by measuring surface tension of the aqueous solutions [1–5] and densities of the solution [6–13]. The miscibility in the adsorbed films and micelles of binary surfactants is well-examined by drawing the composition diagram of adsorption (CDA) and the composition digagram of micellization (CDM) [14], respectively. CDA is composed of the curves of the total concentration vs bulk composition and the total concentration vs surface composition at constant surface tension, while CDM is composed of

the curves of the critical micelle concentration (CMC) vs monomer composition and CMC vs micellar composition curves. CDM can be drawn not only for the mixtures of micelle-forming (MF) surfactants but also for those of MF surfactant and a micelle-unforming (MU) substance such as inorganic salts and organic compounds with a short hydrocarbon chain.

Local anesthetics are amphiphilic and behave like surfactants in water. The surface activity of the anesthetics may be related to the anesthesia potency. Some local anesthetics are known to be incorporated in the adsorbed films and micelles of surfactants [15–21]. The thermodynamic behavior of the aggregates of mixtures of a local anesthetic and a surfactant is of interest [22, 23]. Generally, molecules of local anesthetics have a heterocyclic ring and/or an aromatic ring, which makes the hydrophobic part of the anesthetic molecules more rigid and bulky and less hydrophobic than alkyl chains of usual surfactants. The size and rigidity of hydrophobic and hydrophilic groups and the balance of the strength of hydrophobicity and hydrophilicity of the anesthetics may affect the surface activity of the anesthetics, which corresponds to the anesthetic potency and the miscibility of the anesthetics with the surfactant in the aggregates. Actually, weakly hydrophobic anesthetics such as hydrochloride salts of bupivacaine, lidocaine, and procaine do not partition into the hydrophobic environment of the adsorbed film and micelle of decylammonium chloride, while strongly hydrophobic ones such as hydrochloride salts of dibucaine and tetracaine partition into the aggregates. The partitioning of the anesthetics into the globular micelles is influenced by the size of the hydrophobic and polar head groups [24–27]. Furthermore, the protonation of the polar head groups of the anesthetic molecules greatly affects the balance between the hydrophobicity and the hydrophilicity of the anesthetics, so that uncharged local anesthetics transfer into hydrophobic environments more than charged ones [28, 29]. The more intricate molecular structure of the anesthetics compared to that of usual surfactants seems to complicate the subject.

It is known that naphthalene and some of its hydrophobic derivatives are incorporated into ionic micelles [30–34]. However, the excess free energy and enthalpy of mixing of aliphatic and aromatic hydrocarbons are generally positive and larger than those of aliphatic hydrocarbons. The excess volume is negative for the latter mixtures, but positive for the formar mixtures [35]. The rigidity of the aromatic molecules and the van der Waals interactions may affect the miscibility of the hydrocarbons in the liquid state. The substitution of a hydrogen atom at 1- or 2- position of the naphthalene ring by an ionic group makes the molecule amphiphilic and increases their solubility in water. These may enhance the tendency of intrinsically poor miscibility between aromatic and aliphatic hydrophobic groups in the micelles. To get information about the miscibility of the solutes in micelles, it is useful to draw and examine the shape of the CDM. Furthermore, it is effective to examine the volume behavior of the aqueous micellar solutions of the mixtures together with the shape of the CDM. Therefore, it is interesting to see how the position of the ionic group affects the shape of the CDM and the volume behavior of the aqueous micellar solutions of the mixtures of the isomer and a surfactant.

In the present study, we choose two isomers of lithium naphthylsulfonate (1-LiNSO and 2-LiNSO) as model compounds of the local anesthetics. We are concerned with the volume behavior of aqueous solutions of mixtures of the isomers and lithium decylsulfonate (LiDeSO; see Fig. 1). Since, within our knowledge, it has not been reported that 1-LiNSO and 2-LiNSO

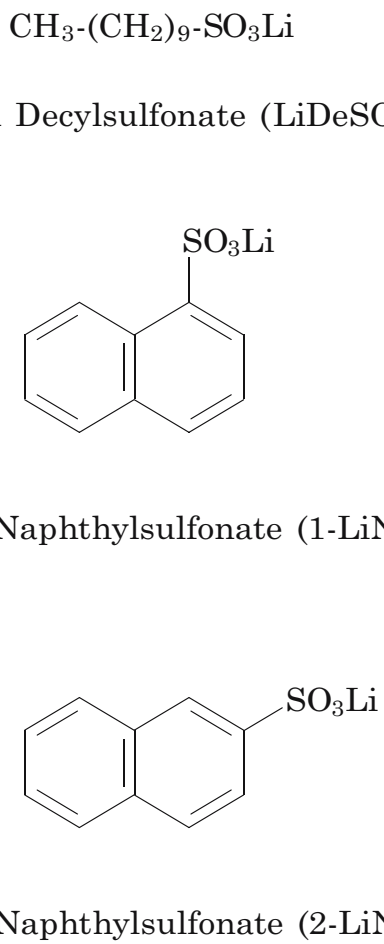

Fig. 1 Molecular structures of solutes

form micelles in water, 1-LiNSO and 2-LiNSO may be regarded as MU substances. The thermodynamic treatment to analyze the density of aqueous solutions of binary mixtures of MF substances developed in our recent papers [6, 27] is arranged to treat binary mixtures of an MU substance and an MF surfactant. The values of the partial derivative of the solution volume with respect to the total molality of the mixtures are estimated from the experimental densities measured and examined using the thermodynamic equations derived. The miscibility of the solute molecules in the micelles are examined by drawing the CDM. Furthermore, the monomer concentrations of the solutes are estimated as functions of total concentration using the CDM and a simple mass balance.

Theoretical

Consider an aqueous solution of m_1 moles of micelle-unforming (MU) solute 1 and m_2 moles of micelle-forming (MF) solute 2 dissolved in 1 kg of water. The MF solute 2 is an ionic surfactant, which forms micelles in water at concentrations above the critical micelle concentration (CMC), while the MU solute 1 is an ionic amphiphile, which forms no micelles by itself. The solutes are assumed to be strong 1:1 electrolytes and have a common counterion. Similar to the thermodynamic treatment [6, 27], we adopt temperature T, pressure p, the total solute molality of the solute mixtures m_t, and the mole fraction of solute 2 in the mixtures (solute composition) X_2 as the independent thermodynamic variables. m_t and X_2 are defined by

$$m_t = m_1 + m_2 \tag{1}$$

and

$$X_2 = m_2/m_t = 1 - X_1, \tag{2}$$

respectively.

When the solution is free from micelles, the thermodynamic equations for the aqueous mixtures of MU and MF solutes are identical with those for the aqueous mixtures of MF solutes [6, 27]. The volume of the solution V per 1 kg of water is given by

$$V = V_w/M_w + m_1 V_1^W + m_2 V_2^W, \tag{3}$$

where M_w and V_w are the molar mass and the partial molar volume of water, respectively, and V_i^W is the partial molar volume of solute i ($i = 1$ and 2) in the monomeric state. The total differential of V at constant T and p is written in the form:

$$\begin{aligned} dV &= V_1^W dm_1 + V_2^W dm_2 \\ &= (X_1 V_1^W + X_2 V_2^W) dm_t + m_t (V_2^W - V_1^W) dX_2. \end{aligned} \tag{4}$$

Thus, the partial derivative of V with respect to m_t at constant T, p, and X_2 gives the partial molar volume of solute mixtures in the monomeric state V_t^W:

$$(\partial V/\partial m_t)_{T,\,p,\,X_2} = X_1 V_1^W + X_2 V_2^W \equiv V_t^W, \quad (m_t < C_t) \tag{5}$$

where C_t is CMC.

In the concentration range above CMC, the volume of micelles should be taken into consideration. According to the thermodynamic treatment of mixed micelles [14], the micellar thermodynamic quantities are defined as the surface excesses in reference to the dividing surface around micelle particles the position of which is determined so as to make the excess moles of water molecules zero, i.e.,

$$n_w - c_w^W V^W = 0, \tag{6}$$

where n_w is the number of moles of water in the whole solution, c_w^W the number of moles of bulk water per unit volume, and V^W the volume outside of the dividing surface. The micellar molar volume V^M and the number of molecules of solute i in a micelle are given by

$$V^M = (V - V^W)/m_m \tag{7}$$

and

$$N_i^M = (m_i - m_i^W)/m_m, \tag{8}$$

respectively, where m_m is the molality of micelle and m_i^W the molality of monomeric solute i ($i = 1$ and 2). Equation (8) is used to eliminate m_m from Eq. (7). When doing this, we can choose one from the equations for N_1^M, N_2^M, and N_t^M ($= N_1^M + N_1^M$). For the mixtures of binary MF surfactants, it is reasonable to use the equation for N_t^M. However, for the mixtures of MF and MU substances, the most suitable choice is to use the equation for N_2^M because the solute 1 cannot form micelles by itself. Thus, the molality of solute 2 in the whole solution is expressed from Eq. (8) as follows:

$$m_2 = m_m N_2^M + m_2^W. \tag{9}$$

Substituting Eq. (9) into Eq. (7) yields

$$V = (m_2 - m_2^W)(V^M/N_2^M) + V^W. \tag{10}$$

Taking the total differential of Eq. (10) and substituting Eq. (4) into the resultant equation, we have

$$\mathrm{d}V = (V^{\mathrm{M}}/N_2^{\mathrm{M}})\mathrm{d}m_2 + (m_2 - m_2^{\mathrm{W}})\mathrm{d}(V^{\mathrm{M}}/N_2^{\mathrm{M}}) + V_1^{\mathrm{W}}\mathrm{d}m_1^{\mathrm{W}} - \left[(V^{\mathrm{M}}/N_2^{\mathrm{M}}) - V_2^{\mathrm{W}}\right]\mathrm{d}m_2^{\mathrm{W}}. \quad (11)$$

Dividing both sides of Eq. (11) by $\mathrm{d}m_{\mathrm{t}}$ at constant T, p, and X_2, the following equation is obtained:

$$\begin{aligned}(\partial V/\partial m_{\mathrm{t}})_{T,\,p,\,X_2} = {} & X_2(V^{\mathrm{M}}/N_2^{\mathrm{M}}) \\ & + (m_2 - m_2^{\mathrm{W}}) \\ & \times \left[\partial(V^{\mathrm{M}}/N_2^{\mathrm{M}})/\partial m_{\mathrm{t}}\right]_{T,\,p,\,X_2} \\ & + V_1^{\mathrm{W}}(\partial m_1^{W}/\partial m_{\mathrm{t}})_{T,\,p,\,X_2} \\ & - \left[(V^{\mathrm{M}}/N_2^{\mathrm{M}}) - V_2^{\mathrm{W}}\right] \\ & \times(\partial m_2^{\mathrm{W}}/\partial m_{\mathrm{t}})_{T,\,p,\,X_2}, \end{aligned} \quad (12)$$

where $(\partial m_2/\partial m_{\mathrm{t}})_{T,\,p,\,X_2} = X_2$ has been used.

Since the molar volume of micelle per a solute 2 molecule in a micelle $V^{\mathrm{M}}/N_2^{\mathrm{M}}$ is presumed to vary little with m_{t} in the sufficiently high concentration region above the CMC, the second term of the right-hand side of Eq. (12) may be neglected, i.e.,

$$\left[\partial(V^{\mathrm{M}}/N_2^{\mathrm{M}})/\partial m_{\mathrm{t}}\right]_{T,\,p,\,X_2} \simeq 0. \quad (13)$$

The value of $\left[(V^{\mathrm{M}}/N_2^{\mathrm{M}}) - V_2^{\mathrm{W}}\right]$ in the fourth term of the right-hand side of Eq. (12) is very small compared to the value of $V^{\mathrm{M}}/N_2^{\mathrm{M}}$ or V_2^{W} because the values of $V^{\mathrm{M}}/N_2^{\mathrm{M}}$ and V_2^{W} are in the similar order of magnitude. In fact, the magnitude of ratio of the value of $\left[(V^{\mathrm{M}}/N_2^{\mathrm{M}}) - V_2^{\mathrm{W}}\right]$ to that of $V^{\mathrm{M}}/N_2^{\mathrm{M}}$ is about 4% for LiDeSO (see Fig. 4). Moreover, since the monomer molality of solute 2 m_2^{W} may not vary very much with m_{t} above CMC because of the formation of micelles, the value of $(\partial m_2^{\mathrm{W}}/\partial m_{\mathrm{t}})_{T,p,X_2}$ may be very small. Thus, the fourth term of the right-hand side of Eq. (12) may be negligibly small, i.e.,

$$\left[(V^{\mathrm{M}}/N_2^{\mathrm{M}}) - V_2^{\mathrm{W}}\right](\partial m_2^{\mathrm{W}}/\partial m_{\mathrm{t}})_{T,\,p,\,X_2} \simeq 0. \quad (14)$$

Furthermore, when the solute 1 molecule has a hydrophobic group that is hard to mix with the alkyl chain of the solute 2 molecules, the solute 1 molecules may be excluded from micelles. This gives an approximation:

$$(\partial m_1^{\mathrm{W}}/\partial m_{\mathrm{t}})_{T,\,p,\,X_2} \simeq (\partial m_1/\partial m_{\mathrm{t}})_{T,\,p,\,X_2} = X_1. \quad (15)$$

Substituting Eqs. (13), (14), and (15) into Eq. (12) yields

$$(\partial V/\partial m_{\mathrm{t}})_{T,\,p,\,X_2} = X_1 V_1^{\mathrm{W}} + X_2(V^{\mathrm{M}}/N_2^{\mathrm{M}}) \equiv V_{\mathrm{t}}^{\mathrm{M}}. \quad (m_{\mathrm{t}} \gg C_{\mathrm{t}}) \quad (16)$$

Thus, the partial derivative of the solution volume with respect to the total molality at constant T, p, and X_2 provides the mean value of the micellar molar volume per a molecule of solute 2 in the micelle $V^{\mathrm{M}}/N_2^{\mathrm{M}}$ and the partial molar volume of monomeric solute 1 V_1^{W}.

The volume of micelle formation $\Delta_{\mathrm{W}}^{\mathrm{M}}V$ is defined by [6, 14, 27]

$$\Delta_{\mathrm{W}}^{\mathrm{M}}V = V^{\mathrm{M}}/N_{\mathrm{t}}^{\mathrm{M}} - (X_1^{\mathrm{M}}V_1^{\mathrm{W}} + X_2^{\mathrm{M}}V_2^{\mathrm{W}}), \quad (17)$$

where X_2^{M} is the micellar composition defined by

$$X_2^{\mathrm{M}} = N_2^{\mathrm{M}}/N_{\mathrm{t}}^{\mathrm{M}} = 1 - X_1^{\mathrm{M}}, \quad (18)$$

where $N_{\mathrm{t}}^{\mathrm{M}}$ $(= N_1^{\mathrm{M}} + N_2^{\mathrm{M}})$ is the total number of molecules of solutes in a micelle [14]. The value of X_2^{M} is calculated by applying

$$X_2^{\mathrm{M}} = X_2 - (2X_1X_2/C_{\mathrm{t}})(\partial C_{\mathrm{t}}/\partial X_2)_{T,\,p} \quad (19)$$

to the composition dependence of CMC [14].

The values of $\Delta_{\mathrm{W}}^{\mathrm{M}}V$ are estimated using the experimental values of the molar volumes and the micellar composition. Equation (17) can be rearranged in the form:

$$\begin{aligned}\Delta_{\mathrm{W}}^{\mathrm{M}}V &= X_2^{\mathrm{M}}(V^{\mathrm{M}}/N_2^{\mathrm{M}} - V_2^{\mathrm{W}}) - X_1^{\mathrm{M}}V_1^{\mathrm{W}} \\ &= X_2^{\mathrm{M}}\Delta_{\mathrm{W}}^{\mathrm{M}}V_2 - X_1^{\mathrm{M}}V_1^{\mathrm{W}}, \end{aligned} \quad (20)$$

where

$$\Delta_{\mathrm{W}}^{\mathrm{M}}V_2 \equiv V^{\mathrm{M}}/N_2^{\mathrm{M}} - V_2^{\mathrm{W}} \quad (21)$$

is the contribution of micelle-forming solute 2 to the volume change of micelle formation. When solute 1 does not form micelles by itself and is excluded from the micelles formed by solute 2 molecules, Eq. (20) is more useful than Eq. (17). If solute 1 is a component of a mixed solvent, $\Delta_{\mathrm{W}}^{\mathrm{M}}V_2$ can be regarded as the volume of micelle formation of solute 2 in the mixed solvent. However, in the cases like the present systems where solute 1 is treated as one of components of a binary solute mixture, Eq. (17) should be adopted as the definition of the volume of micelle formation.

Experimental

Materials

Lithium 1-naphthylsulfonate (1-LiNSO), lithium 2-naphthylsulfonate (2-LiNSO), and lithium decylsulfonate (LiDeSO) were synthesized from corresponding sodium salts purchased from Tokyo Kasei Kogyo using silver nitrate and lithium chloride, recrystallized twice

from water. An atomic absorption analysis and an elemental analysis were used to confirm that the element of the counterion was changed from sodium to lithium completely. The molecular structures of LiDeSO and 1-LiNSO and 2-LiNSO are illustrated in Fig. 1. Water distilled twice (the second distillation was carried out from an alkaline permanganate solution) was used.

Density measurement

Solution density was measured for mixtures of 1-LiNSO and LiDeSO and for mixtures of 2-LiNSO and LiDeSO as a function of the total molality m_t and the solute composition X_2 of the mixtures. The densities of aqueous solutions of the mixtures were measured at 25 °C under atmospheric pressure by means of a vibrating tube digital density meter (Anton Paar DMA 60/602), which was calibrated by using density values of water [36] and dry air [37]. Before the measurements, all the solutions were degassed by the sonication for more than 30 min. The temperature of the measuring cell tube was kept constant at 25 ± 0.001 °C by circulating thermostated water.

From the experimental data of ρ, the values of the apparent molar volume ϕ_t of the solute mixtures were calculated by means of

$$\phi_t = (1/\rho - 1/\rho_w)/m_t + (X_1 M_1 + X_2 M_2)/\rho, \qquad (22)$$

where ρ_w is the density of water and M_i the molar mass of solute i ($i = 1$ and 2).

Results and discussion

The apparent molar volumes ϕ_t of the solute mixtures are plotted against m_t at constant X_2 in Fig. 2a for the 1-LiNSO–LiDeSO system and in Fig. 2b for the 2-LiNSO–LiDeSO system. While the ϕ_t vs m_t curves for 1- and 2-LiNSO are almost horizontal within the m_t range measured, the ϕ_t vs m_t curves for LiDeSO and the mixtures of 1-LiNSO–LiDeSO and 2-LiNSO–LiDeSO have an apparent break at CMC. The ϕ_t value is almost constant against m_t in the concentration range below CMC, while it increase with increasing m_t asymptotically to a certain value of ϕ_t at a concentration far the above CMC. The vertical position and shape of the ϕ_t vs m_t curves in Fig. 2 vary regularly with X_2. The increment of the ϕ_t values with m_t above CMC increase with increasing X_2. The breaks of the ϕ_t vs m_t curves in Fig. 2 are sharp enough for the determination of the CMC values.

Since the solution volume per 1 kg of water V is related to ϕ_t by

$$V = V_w^0/M_w + m_t\phi_t, \qquad (23)$$

where V_w^0 is the molar volume of pure water, which is a function of T and p. The partial derivative of V with respect to m_t in Eqs. (5) and (16) is estimated using

$$(\partial V/\partial m_t)_{T,\,p,\,X_2} = [\partial(m_t\phi_t)/\partial m_t]_{T,\,p,\,X_2}. \qquad (24)$$

In Fig. 3, the values of $\partial(m_t\phi_t)/\partial m_t$ obtained from the curves in Fig. 2 are shown as a function of m_t. The $\partial(m_t\phi_t)/\partial m_t$ vs m_t curves of 1- and 2-LiNSO are almost

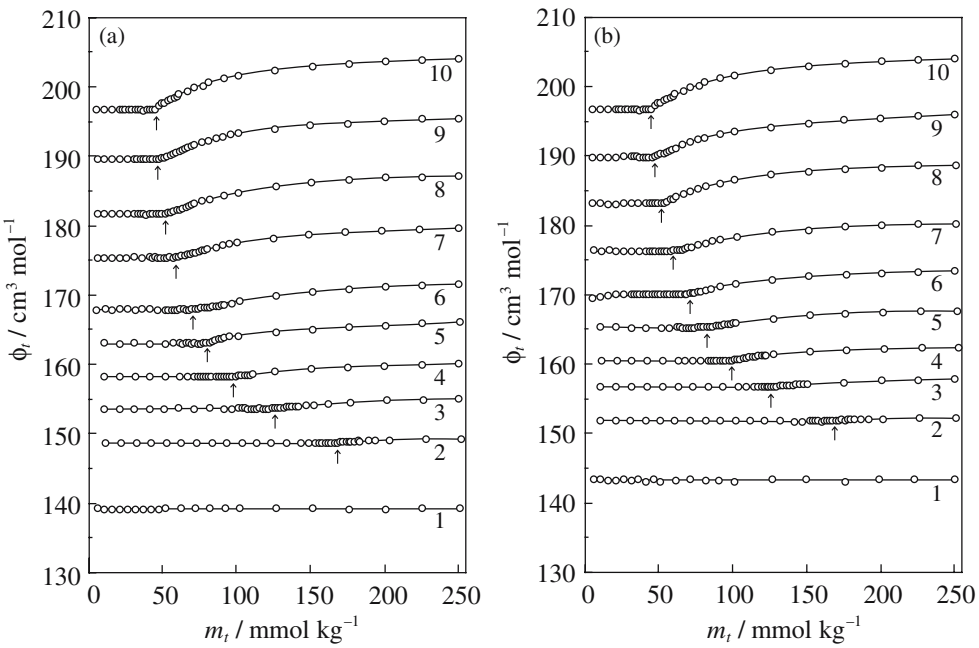

Fig. 2 Apparent molar volume vs total molality curves at constant compositions. **a** 1-LiNSO–LiDeSO mixtures at $X_2 = 0$ (1-LiNSO; *1*), 0.1635 (*2*), 0.2501 (*3*), 0.3242 (*4*), 0.4142 (*5*), 0.4943 (*6*), 0.6248 (*7*), 0.7381 (*8*), 0.8728 (*9*), 1 (LiDeSO; *10*). **b** 2-LiNSO–LiDeSO mixtures at $X_2 = 0$ (2-LiNSO; *1*), 0.1607 (*2*), 0.2465 (*3*), 0.3272 (*4*), 0.4099 (*5*), 0.4994 (*6*), 0.6184 (*7*), 0.7509 (*8*), 0.8726 (*9*), 1 (LiDeSO; *10*)

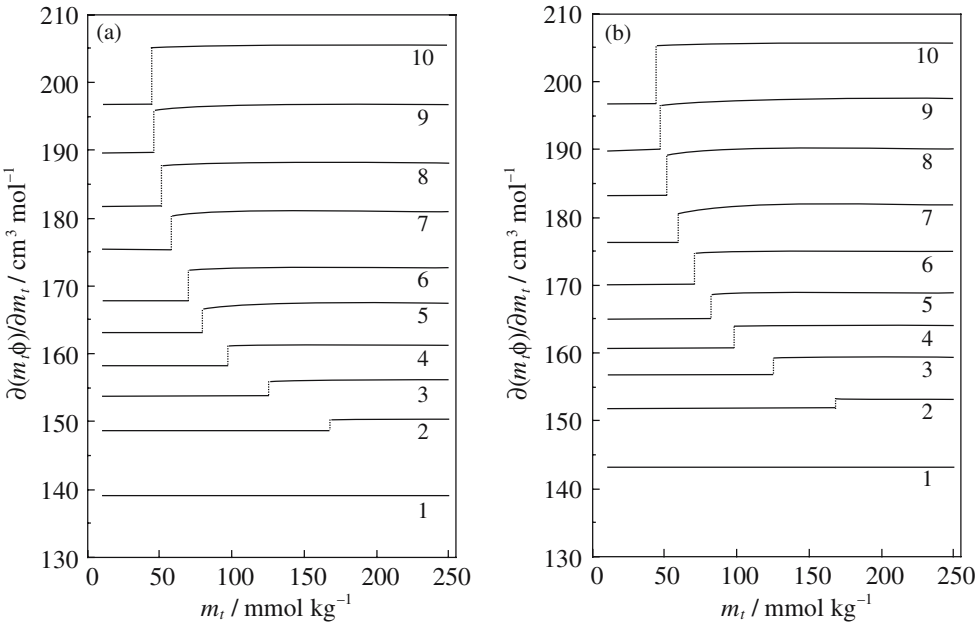

Fig. 3 Partial derivative of solution volume with respect to total molality vs total molality curves at constant compositions.
a 1-LiNSO–LiDeSO mixtures at $X_2 = 0$ (1-LiNSO; *1*), 0.1635 (*2*), 0.2501 (*3*), 0.3242 (*4*), 0.4142 (*5*), 0.4943 (*6*), 0.6248 (*7*), 0.7381 (*8*), 0.8728 (*9*), 1 (LiDeSO; *10*).
b 2-LiNSO–LiDeSO mixtures at $X_2 = 0$ (2-LiNSO; *1*), 0.1607 (*2*), 0.2465 (*3*), 0.3272 (*4*), 0.4099 (*5*), 0.4994 (*6*), 0.6184 (*7*), 0.7509 (*8*), 0.8726 (*9*), 1 (LiDeSO; *10*)

horizontal within the m_t range measured. On the other hand, the values of $\partial(m_t\phi_t)/\partial m_t$ of LiDeSO and the mixtures are almost constant below CMC, increasing discontinuously at CMC, and almost constant again in the concentration region far above CMC. For the two systems, the magnitude of the discontinuous change at CMC becomes larger with increasing X_2. In the concentration regions below and above CNC, the value of $\partial(m_t\phi_t)/\partial m_t$ increases regularly with increasing X_2 at constant m_t.

According to Eqs. (5) and (16), $\partial(m_t\phi_t)/\partial m_t$ in Fig. 3 provides V_t^W at concentrations below CMC and V_t^M at concentrations far above CMC. The $\partial(m_t\phi_t)/\partial m_t$ values just below CMC and those at 250 mmol kg^{-1}, which are taken as the values of V_t^W and V_t^M, respectively, are plotted against X_2 in Fig. 4. It is found that, for both systems, V_t^W vs X_2 curve is a straight line connecting the value of the partial molar volume of pure 1- and 2-LiNSO at $X_2 = 0$ $(V_1^W)^0$, and that of pure LiDeSO monomer at $X_2 = 1$ $(V_2^W)^0$. This fact and Eq. (5) indicate that the partial molar volumes of the monomers of 1- and 2-LiNSO and LiDeSO, V_1^W and V_2^W, respectively, in the mixed systems are equal to those in the corresponding single systems, $(V_1^W)^0$ and $(V_2^W)^0$, respectively. Thus, it can be said that 1- and 2-LiNSO mix ideally with LiDeSO in the monomeric state from the viewpoint of volume. The value of $(V_1^W)^0$ is 139.26 cm^3 mol^{-1} for 1-LiNSO and 143.34 for 1-LiNSO and the value of $(V_2^W)^0$ is 196.87 cm^3 mol^{-1}. It is evident from these values and Fig. 4 that the difference in the V_t^W values of the monomeric mixtures at an arbitrary X_2 between the 1-LiNSO–LiDeSO and 2-LiNSO–LiDeSO systems is caused solely by the difference in the $(V_1^W)^0$ value between the single systems of 1- and 2-LiNSO. Furthermore, we can find that 2-LiNSO has a larger value of $(V_1^W)^0$ than 1-LiNSO. Since 1- and 2-LiNSO have the same molar mass, the difference in the $(V_1^W)^0$ value may be attributable to the difference in the hydration state between 1-NSO$^-$ and 2-NSO$^-$ ions. The solubility of 2-naphthalene sulfonic acid salts in water is smaller than that of 1-naphthalene sulfonic acid salts [37]. This fact indicates that 2-LiNSO is more hydrophobic than 1-LiNSO. Accordingly, water molecules around 2-NSO$^-$ ions may be slightly more structured than those around 1-NSO$^-$ ions, so that the partial molar volume of 2-LiNSO is larger than that of 1-LiNSO.

The V_t^M vs X_2 curves are also straight lines connecting $(V_1^W)^0$ and the micellar molar volume of LiDeSO in the single LiDeSO system $(V^M/N_2^M)^0$. The value of $(V^M/N_2^M)^0$ is 205.80 cm^3 mol^{-1}. Since V_1^W has the same value as $(V_1^W)^0$, this fact and Eq. (16) suggest that the value of V_t^M of the solute mixture coincides with the mean value of the $(V_1^W)^0$ and $(V^M/N_2^M)^0$ at arbitrary X_2. Therefore, V^M/N_2^M is supposed to have the same value of $(V^M/N_2^M)^0$ of the single LiDeSO system. In contrast with the aqueous systems of binary MF surfactants [6, 7], X_2^M of the present systems is not approximated to have the same value with X_2 at concentrations far above CMC. Therefore, the V_t^M vs X_2 curves in Fig. 4 cannot be regarded as the V_t^M vs X_2^M ones and provide less information about the miscibility of the solute in the micellar state. To examine the miscibility of the solutes in the micellar state, it is necessary to

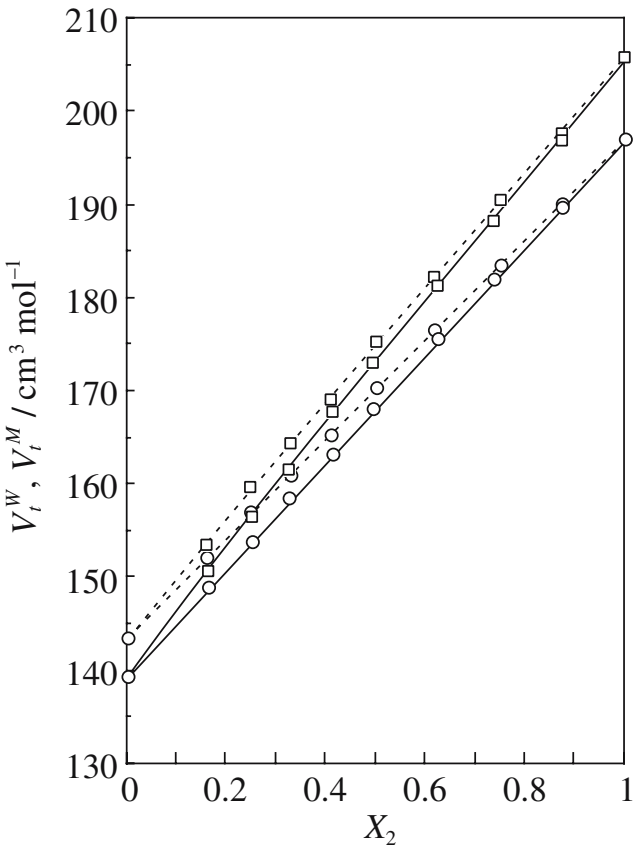

Fig. 4 Mean molar volume vs composition curves. *Open circle* Monomer molar volume (V_t^W), *open square* micellar molar volume (V_t^M), *line* 1-LiNSO–LiDeSO, *dashed line* 2-LiNSO–LiDeSO

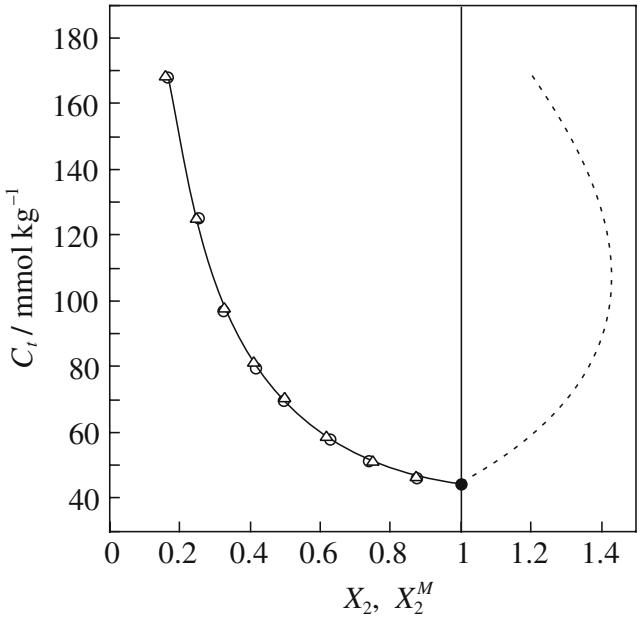

Fig. 5 Critical micelle concentration vs composition curves. *Line* C_t vs X_2, *dashed line* C_t vs X_2^M, *open circle* 1-LiNSO–LiDeSO mixtures, *open triangle* 2-LiNSO–LiDeSO mixtures, *shaded circle* LiDeSO

estimate the values of X_2^M and draw the CDM, which consists of C_t vs X_2 and C_t vs X_2^M curves [14].

In Fig. 5, the values of CMC that were obtained from Fig. 2 are plotted against X_2. The C_t values for both the systems increases with decreasing X_2. The increment becomes larger in the smaller X_2 region. Applying Eq. (19) to the C_t vs X_2 curves, the values of X_2^M were estimated. Drawing the C_t vs X_2^M curves in Fig. 5, we obtained the CDM for the present systems. It is noteworthy that the CDMs for 1-LiNSO–LiDeSO and 2-LiNSO–LiDeSO systems almost coincide with each other. This fact suggests that the effect of the position of the sulfonate ionic group on the miscibility is negligibly small. For both the systems, X_2^M is larger than one within the C_t region measured, increasing with increasing C_t in the lower C_t region, having a broad maximum, and decreasing with increasing C_t in the higher C_t region. According to Eq. (18), this feature indicates that the number of molecules of solute 1 N_1^M is negative in a micelle particle. When Eq. (8) is taken into account, the negative value of N_1^M indicates that the bulk monomer molality of solute 1 m_1^W is larger than the solution molality of solute 1 m_1. This fact indicates that 1- and 2-LiNSO molecules are excluded from the micelles of LiDeSO and expelled into the bulk phase far from the micelle surface. Similar results were obtained for the mixture of sodium chloride–dodecylammonium chloride [38] and the mixtures of hydrochloride salts of bupivacaine, lidocaine, and procaine and decylammonium chloride [25, 26].

Now, let us consider the volume of micelle formation defined by Eq. (17). As given in Eq. (7), V^M is the volume of the region surrounded by the dividing surface, which makes the excess number of water molecules zero. Although the excess number of water molecules is zero, it is true that there exists molecules of water participating in this region. Similarly, molecules of solute 1 with a negative value of N_1^M as the excess quantity in reference to the dividing surface may be contained in the region. These molecules of water and solute 1 may contribute to the value of V^M, but the magnitude of the contributions is supposed to be negligibly small compared with that of solute 2. Assuming that V^M/N_2^M, V_2^W, and V_1^W in Eqs. (20) and (21) can be replaced by $(V^M/N_2^M)^0$, $(V_2^W)^0$, and $(V_1^W)^0$, we have following equation instead of Eq. (20):

$$\Delta_W^M V = X_2^M(\Delta_W^M V_2)^0 - X_1^M(V_1^W)^0, \tag{25}$$

where $(\Delta_W^M V_2)^0 = (V^M/N_2^M)^0 - (V_2^W)^0$. Equation (25) indicates that the volume of micelle formation of the

present systems varies linearly with the micellar composition. Because of the negative value of X_1^M, $\Delta_W^M V$ increases with increasing X_2^M. Since the values of $(V_1^W)^0$ for 1- and 2-LiNSO are quite larger than the evaluated value of $(\Delta_W^M V_2)^0$ of 8.93 cm^3 mol^{-1}, the partial molar volume of monomeric solute 1 becomes a dominant contribution to the value of the volume of micelle formation.

Finally, we examine the dependence of the bulk monomer molalities, m_1^W and m_2^W, on the total solute molality m_t at constant solute compositions X_2. m_1^W and m_2^W are evaluated using CDM and a mass balance equation for the micelle formation:

$$m_t = \left[(X_2^M - X_2^W)/(X_2^M - X_2)\right] m_t^W, \tag{26}$$

which has been derived using Eq. (8) and the definitions of the solute, micellar, and monomer compositions (Eqs. (2) and (18) and $X_2^W = m_2^W/m_t^W$, respectively). Assuming that m_t^W is equal to C_t, we can obtain the values of X_2^W and X_2^M as functions of m_t from CDM in Fig. 5, and then, we can calculate the value of m_t as a function of m_t^W at constant X_2 by using Eq. (26). The values of m_1^W and m_2^W are obtained from m_t^W by applying $m_1^W = X_1^W m_t^W$ and $m_2^W = X_2^W m_t^W$, respectively.

Figure 6 shows the m_1^W vs m_t curves at constant X_2. In this figure, the total molality of solute 1 $X_1 m_t$ vs m_t curves (dashed lines) are also added in the concentration range above CMC. It is clearly seen that m_1^W deviates positively from $X_1 m_t$. The magnitude of the deviation becomes larger with increasing X_2. These

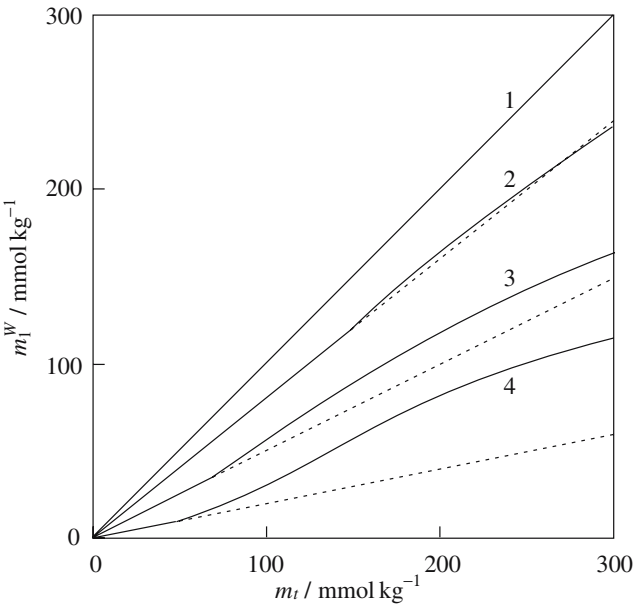

Fig. 6 Monomer molality of LiNSO vs total molality curves at constant compositions $X_2 = 0$ (*1*), 0.2 (*2*), 0.5 (*3*), 0.8 (*4*). The *dashed lines* represent $X_1 m_t$ vs m_t curves

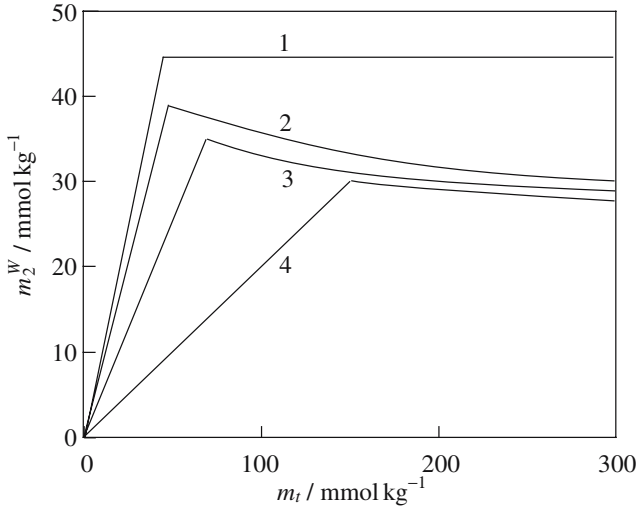

Fig. 7 Monomer molality of LiDeSO vs total molality curves at constant compositions $X_2 = 1$ (*1*), 0.8 (*2*), 0.5 (*3*), 0.2 (*4*)

facts are due to the exclusion of LiNSO from the micelles of LiDeSO and the effect of excluded volume of the micelles. The slopes of the m_1^W vs m_t curve at concentrations around 250 mmol kg^{-1} seem to be approximately equal to the slope of the corresponding dashed line. Since the slope of the dashed line gives the value of X_1, this fact means that the approximation in Eq. (15) is reasonably valid around 250 mmol kg^{-1}. The m_2^W vs m_t curves at constant X_2 are shown in Fig. 7. It is found that the values of m_2^W at constant X_2 decrease with increasing m_t in the concentration range above CMC; the negative slopes of the curves become more gentle at higher concentrations. This fact can be explained from the viewpoint of the effect of the addition of salts into the ionic micellar solution. At concentrations around 250 mmol kg^{-1}, the curves seem to be almost flat. This fact supports the validity of the approximation of Eq. (14).

Conclusions

The thermodynamic equations to treat the volume behavior of the mixtures of MU and MF substances were derived. Applying the equations to the solution densities of aqueous 1-LiNSO–LiDeSO and 2-LiNSO–LiDeSO mixtures, we obtained the values of V_t^W and V_t^M of the mixtures. We found for both the systems that V_t^W of the mixtures increases linearly with increasing X_2 from the partial molar volumes of monomeric 1- and 2-LiNSO in their single systems to the partial molar volume of monomeric LiDeSO in the single LiDeSO system. We also found that V_t^M of the mixtures

increases linearly with increasing X_2 from the partial molar volumes of monomeric 1- and 2-LiNSO to the micellar molar volume in the single LiDeSO system. The composition diagrams of micellization for 1- and 2-LiNSO coincided with each other and showed that $X_2^{\mathrm{M}} > 1$ ($X_1^{\mathrm{M}} < 0$). From the negative value of X_1^{M} and the linear dependence of $V_{\mathrm{t}}^{\mathrm{M}}$ on X_2, we concluded that the molecules of 1- and 2-LiNSO are excluded from the micelles. The contribution of the partial molar volume of monomeric MU component to the volume of micelle formation is positive and large because of the exclusion of molecules of the MU component from the micelles. The validity of the approximations used in the derivation of the equations was confirmed using the dependence of the monomer molalities of LiNSO and LiDeSO on the total molality.

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