Ternary Mutual Diffusion Coefficients and Critical Micelle Concentrations of Aqueous Sodium Dodecyl Sulfate + Lithium Dodecyl Sulfate Solutions at 25 °C

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Ternary mutual diffusion coefficients (D_{ik}) are reported for aqueous sodium dodecyl sulfate (NaDS) + lithium dodecyl sulfate (LiDS) solutions at 25 °C and (0.020 or 0.040) mol·dm^{-3} total surfactant. The main diffusion coefficient of each surfactant increases significantly with decreasing solute fraction, and each mole of diffusing surfactant countertransports up to 0.8 mol of the other surfactant. The results are interpreted by considering the limiting cases of diffusion in (a) solutions of NaDS micelles containing traces of LiDS with the counterion exchange equilibrium $Li^+ + (Na_qDS_n)^{q-n} \rightleftharpoons Na^+ + (LiNa_{q-1}DS_n)^{q-n}$ and (b) solutions of LiDS micelles containing traces of NaDS with $Na^+ + (Li_qDS_n)^{q-n} \rightleftharpoons Li^+ + (NaLi_{q-1}DS_n)^{q-n}$. At fixed total surfactant concentration, the measured D_{ik} coefficients are closely approximated by a simple linear interpolation of the limiting D_{ik} values against solute fraction. Binary mutual diffusion coefficients for aqueous LiDS solutions and critical micelle concentrations for ternary aqueous NaDS + LiDS solutions are also reported.

Introduction

Diffusion in solutions of surfactant micelles is widely studied[1−14] because of its important role in detergency, solubilization, digestion, emulsification, and coating processes. Diffusion data for micelle solutions also provide basic information about the effects of aggregation on transport properties. Most studies of mutual diffusion (chemical interdiffusion) in micelle solutions have focused on binary diffusion in two-component systems,[4−14] such as sodium dodecyl sulfate + water. Limited amounts of ternary mutual diffusion data are available for micelle solutions.[15−19] These results indicate that micelle diffusion is strongly coupled with the diffusion of added salts[15,16] or solubilizates.[17,18]

In this paper ternary mutual diffusion coefficients for aqueous sodium dodecyl sulfate (NaDS) + lithium dodecyl sulfate (LiDS) solutions are reported to provide information about the coupled diffusion of ionic micelles with mixed counterions. The ternary diffusion coefficients of the mixed surfactant solutions are compared with binary mutual diffusion coefficients of aqueous NaDS and aqueous LiDS solutions. Critical micelle concentrations (cmc's) for ternary aqueous NaDS + LiDS solutions are also reported.

Experimental Section

Solutions were prepared by dissolving weighed amounts of NaDS (BDH “Specially Pure”, >99% purity) and LiDS (Aldrich, >99% purity) in distilled, deionized water in calibrated volumetric flasks. To identify the solutions that contained micelles, an Orion model 160 conductivity meter was used to measure the conductivities of series of solutions prepared by diluting stock NaDS + LiDS solutions with water. Critical micelle concentrations (accuracy ±0.0002 mol·dm^{-3}) were determined for fixed NaDS/LiDS ratios from the breaks in the molar conductivities plotted against the square root of the total surfactant concentration.

Mutual diffusion coefficients were measured by the Taylor method using a Teflon dispersion tube (length 2590 cm, inner radius 0.0458$_8$ cm) and a differential refractometer detector (Hewlett-Packard model 1047A). Retention times were typically 7000 to 8000 s. Details of the equipment and procedure have been reported.[20,21]

Dispersion profiles for binary aqueous LiDS solutions were analyzed by fitting the equation

$$V(t) = V_0 + V_1 t + V_{\max}\left(\frac{t_r}{t}\right)^{1/2} \exp\left(-\frac{12D(t - t_R)^2}{r^2 t}\right) \quad (1)$$

to the measured detector voltages, $V(t)$. $V_0 + V_1 t$ is the baseline voltage, $V_{\max}$ is the peak height, and t_r is the retention time. D, the binary mutual diffusion coefficient, relates the flux of the total LiDS component to the gradient in its concentration.

The ternary mutual diffusion coefficient D_{ik} for aqueous NaDS (1) + LiDS (2) solutions gives the flux of total surfactant i produced by the gradient in the concentration of total surfactant k.

$$J_1(\text{total NaDS}) = -D_{11}\nabla C_1 - D_{12}\nabla C_2 \quad (2)$$

$$J_2(\text{total LiDS}) = -D_{21}\nabla C_1 - D_{22}\nabla C_2 \quad (3)$$

Ternary dispersion profiles were analyzed by fitting the equation

$$V(t) = V_0 + V_1 t + V_{\max}\left(\frac{t_r}{t}\right)^{1/2}\left[W_1 \exp\left(-\frac{12D_1(t - t_R)^2}{r^2 t}\right) + (1 - W_1)\exp\left(-\frac{12D_2(t - t_R)^2}{r^2 t}\right)\right] \quad (4)$$

to pairs of peaks generated by initial gradients in NaDS or LiDS. The ternary diffusion coefficients were evaluated from the relative weights W_1 and $1 - W_1$ of the pre-

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Table 1. Critical Micelle Concentrations of Aqueous NaDS (C_1) + LiDS (C_2) Solutions at 25 °C

$C_1/(C_1 + C_2)$	C_1/mol·dm^{-3}	C_2/mol·dm^{-3}	cmc/mol·dm^{-3}
0.000	0.0000	0.0089	0.0089
0.250	0.0022	0.0064	0.0086
0.500	0.0044	0.0044	0.0087
0.750	0.0062	0.0021	0.0083
1.000	0.0082	0.0000	0.0082

Table 2. Binary Mutual Diffusion Coefficients of Aqueous LiDS Solutions at 25 °C

C/mol·dm^{-3}	$D/(\times 10^{-5}$ cm^2·s^{-1})	C/mol·dm^{-3}	$D/(\times 10^{-5}$ cm^2·s^{-1})
0.0020	0.74_6	0.020	0.23_4
0.0060	0.73_2	0.030	0.29_5
0.0080	0.72_0	0.040	0.33_1
0.0150	0.20_5		

exponential factors and the eigenvalues D_1 and D_2 of the ternary diffusion coefficient matrix.[21]

In the derivation of eqs 1 and 4, the assumption is made that the diffusion coefficients are effectively constant across the dispersion profiles. Previous work has shown, however, that surfactant mutual diffusion coefficients drop abruptly as the surfactant concentration is raised through the cmc.[10,11,14] Accordingly, the carrier solution and the injected solution for each run were both above or both below the cmc.

Results and Discussion

Critical Micelle Concentrations of NaDS (C_1) + LiDS (C_2) + H_2O Solutions. Critical micelle concentrations were measured for aqueous NaDS (1) + LiDS (2) solutions at NaDS molar solute fractions of 0.25, 0.50, and 0.75. Table 1 gives the results. Critical micelle concentrations for binary solutions of the surfactants were also measured. The binary cmc's are consistent with previously reported[22] values: (0.0079 to 0.0084) mol·dm^{-3} for NaDS and (0.0087 to 0.0089) mol·dm^{-3} for LiDS.

Binary Mutual Diffusion Coefficients of Aqueous NaDS and Aqueous LiDS Solutions. Four or five dispersion profiles were measured for each LiDS carrier solution. D values from replicate profiles were reproducible within $\pm(0.01 \times 10^{-5})$ cm^2·s^{-1}. The average D value for each LiDS carrier solution is listed in Table 2 and plotted against the LiDS concentration in Figure 1. D values for aqueous NaDS solutions[10] determined previously by an accurate conductometric method are also plotted in Figure 1.

For both surfactants D drops very sharply in the region of the cmc and then increases at higher concentrations. This unusual diffusion behavior can be understood by considering the changes in the mobility and the thermodynamic driving force caused by the association of surfactant ions and counterions to form charged micelles.[8,10,14]

$$qA^+ + nDS^- \rightleftharpoons (A_qDS_n)^{q-n} \quad (A = Na^+ \text{ or } Li^+) \qquad (5)$$

This chemical equilibrium model of micelle diffusion[8–10,14] gives

$$D = \frac{c_-c_+D_-D_+ + q^2c_-c_mD_-D_+ + n^2c_+c_mD_+D_m}{c_-D_- + c_+D_+ + (n-q)^2c_mD_m} \times \frac{c_- + c_+ + (n-q)^2c_m}{c_-c_+ + q^2c_-c_m + n^2c_+c_m} \qquad (6)$$

for the binary mutual diffusion coefficient of a univalent ionic surfactant. n and q are the numbers of surfactant ions and bound counterions per micelle. D_-, D_+, D_m and c_-, c_+, c_m are the diffusion coefficients and concentrations of the free counterions, free surfactant ions, and micelles. The concentrations of the species are calculated from the equilibrium relation

$$K = \frac{c_m}{c_-^n c_+^q} \qquad (7)$$

using the well-known approximation[10] $K \cong 1/(\text{cmc})^{n+q}$.

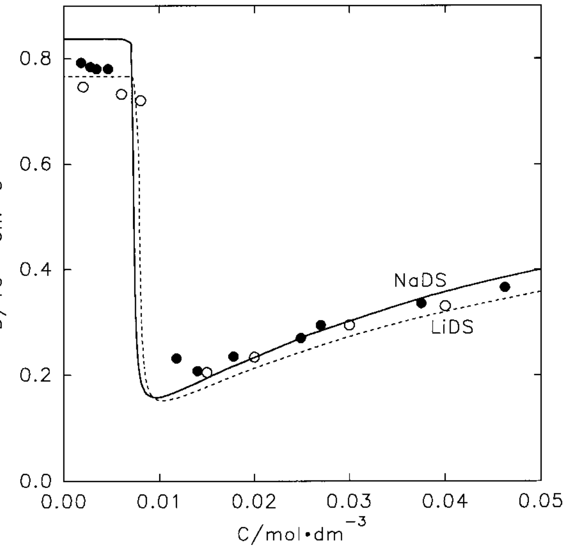

Figure 1. Binary mutual diffusion coefficients at 25 °C: aqueous NaDS solutions, ●, Leaist;[10] aqueous LiDS solutions, ○, this work.

Figure 1 gives the D values predicted by eq 6 for aqueous NaDS solutions (solid curve) using 0.0082 mol dm^{-3} for the cmc and the ionic diffusion coefficients $D_-(DS^-) = 0.61 \times 10^{-5}$ and $D_+(Na^+) = 1.33 \times 10^{-5}$ cm^2 s^{-1} calculated from accurate limiting ionic conductivities.[23,24] The recommended values[8–10] $n = 60$, $q = 50$, and $D_m = 0.10 \times 10^{-5}$ cm^2·s^{-1} were also used in the calculations.

The dashed curve in Figure 1 gives the D values for aqueous LiDS solutions predicted by eq 6 using[24] $D_+(Li^+) = 1.030 \times 10^{-5}$ cm^2·s^{-1} and 0.0089 mol·dm^{-3} for the cmc together with the same values of n, q, and D_m employed for the NaDS micelles. The measured and predicted LiDS mutual diffusion coefficients are in close agreement. This result suggests that NaDS and LiDS micelles have similar surfactant aggregation numbers (~60), numbers of bound counterions (~50), and diffusion coefficients (~0.10×10^{-5} cm^2·s^{-1}).

Ternary Mutual Diffusion in NaDS (C_1) + LiDS (C_2) + H_2O Solutions. Ternary dispersion profiles were measured for carrier solutions containing 0.020 or 0.040 mol·dm^{-3} total surfactant at NaDS molar solute fractions of 0.05, 0.25, 0.50, 0.75, and 0.95. Table 3 gives the average D_{ik} values determined from four to six dispersion profiles at each composition. Replicate D_{ik} measurements were reproducible within $\pm(0.02 \times 10^{-5})$ cm^2·s^{-1} or better. All of the ternary diffusion measurements were made at surfactant concentrations above the critical micelle values.

In Figures 2 and 3 the ternary diffusion coefficients for the 0.020 and 0.040 mol·dm^{-3} total surfactant solutions are plotted against the solute fraction of NaDS, $X_1 = C_1/(C_1 + C_2)$. The main diffusion coefficient of each surfactant decreases significantly as its solute fraction increases. At 0.020 mol·dm^{-3} total surfactant, for example, D_{11} for the NaDS (1) component drops from 0.74×10^{-5} cm^2·s^{-1} to 0.27

Table 3. Ternary Mutual Diffusion Coefficients of Aqueous NaDS (C_1) + LiDS (C_2) Solutions at 25 °C

C_1	C_2		D_{11}	D_{12}	D_{21}	D_{22}
mol·dm^{-3}		X_1		($\times 10^{-5}$ cm^2 s^{-1})		
0.000	0.020	0.00	(0.76)[b]	0	(−0.40)[c]	(0.23$_4$)[a]
0.001	0.019	0.05	0.74	−0.03	−0.38	0.26
0.005	0.015	0.25	0.64	−0.14	−0.32	0.35
0.010	0.010	0.50	0.50	−0.28	−0.20	0.47
0.015	0.005	0.75	0.39	−0.39	−0.10	0.58
0.019	0.001	0.95	0.27	−0.50	−0.01	0.65
0.020	0.000	1.00	(0.246)[a]	(−0.50)[c]	0	(0.67)[b]
0.000	0.040	0.00	(0.64)[b]	0	(−0.19)[c]	(0.33$_1$)[a]
0.002	0.038	0.05	0.63	−0.02	−0.18	0.35
0.010	0.030	0.25	0.57	−0.09	−0.14	0.40
0.020	0.020	0.50	0.51	−0.14	−0.09	0.44
0.030	0.010	0.75	0.44	−0.21	−0.04	0.50
0.038	0.002	0.95	0.37	−0.27	−0.02	0.53
0.040	0.000	1.00	(0.345)[a]	(−0.30)[c]	0	(0.54)[b]

[a] Binary values. [b] Extrapolated values. [c] Equation 10.

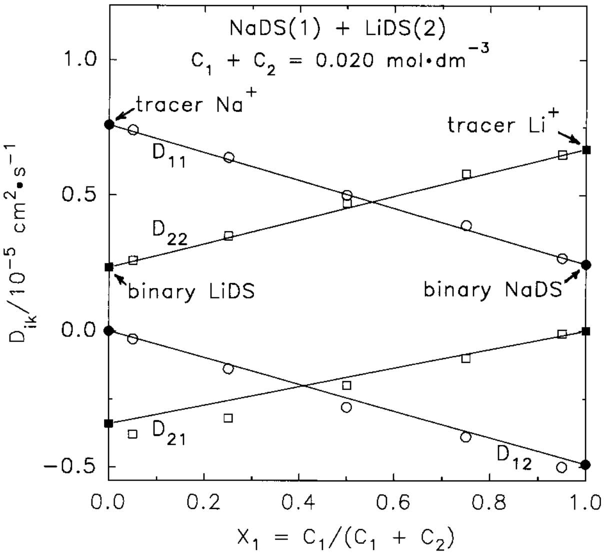

Figure 2. Ternary mutual diffusion coefficients of aqueous NaDS (C_1) + LiDS (C_2) solutions at 25 °C and 0.020 mol·dm^{-3} total surfactant: ○, □, measured values; ●, ■, limiting values for 0.020 mol·dm^{-3} LiDS solutions containing traces of NaDS (left intercepts) and for 0.020 mol·dm^{-3} NaDS solutions containing traces of LiDS (right intercepts).

$\times 10^{-5}$ cm^2·s^{-1} as the NaDS solute fraction is raised from 0.05 to 0.95.

The cross-coefficients D_{12} and D_{21} are large and negative, reaching values almost as large as those for the main coefficients D_{11} and D_{22}. Gradients in the concentration of each surfactant can therefore drive significant countercurrent coupled flows of the other surfactant. At the composition 0.019 mol dm^{-3} NaDS + 0.001 mol·dm^{-3} LiDS, the ratio $D_{12}/D_{22} = -0.77$ shows that a coupled counterflow of 0.77 mol of NaDS is generated per mole of LiDS driven by the LiDS concentration gradient.

A detailed interpretation of transport in NaDS + LiDS solutions is complicated by the large number of different $(\mathrm{Na}_q\mathrm{Li}_p\mathrm{DS}_n)^{q+p-n}$ micelle species. It is informative, however, to consider the limiting cases of diffusion in NaDS solutions containing trace amounts of LiDS ($X_1 \to 1$) and diffusion in LiDS solutions containing traces of NaDS ($X_1 \to 0$).

Aqueous NaDS (C_1) + LiDS ($C_2 \to 0$) Solutions. Aqueous solutions of NaDS containing trace amounts of LiDS will be considered first. In this case D_{11} is clearly the binary mutual diffusion coefficient of aqueous NaDS. Linear extrapolation of the measured D_{11} values to $X_1 = 1$ gives 0.24×10^{-5} and 0.35×10^{-5} cm^2·s^{-1} for the 0.020 and 0.040 mol·dm^{-3} solutions. The extrapolated D_{11} values are consistent with the binary D values 0.246×10^{-5} and 0.345×10^{-5} cm^2·s^{-1} determined conductometrically[10] for 0.020 and 0.040 mol dm^{-3} NaDS solutions.

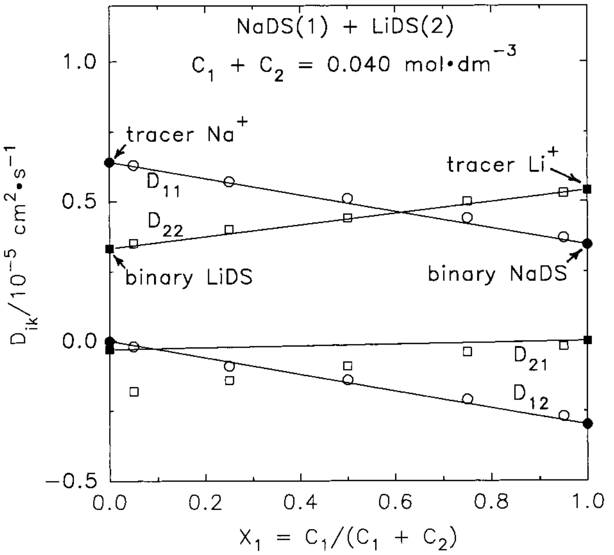

Figure 3. Ternary mutual diffusion coefficients of aqueous NaDS (C_1) + LiDS (C_2) solutions at 25 °C and 0.040 mol·dm^{-3} total surfactant: ○, □, measured values; ●, ■, limiting values for 0.040 mol·dm^{-3} LiDS solutions containing traces of NaDS (left intercepts) and for 0.040 mol·dm^{-3} NaDS solutions containing traces of LiDS (right intercepts).

A gradient in the concentration of NaDS cannot drive a coupled flow of LiDS if the solution does not contain LiDS, and hence $D_{21} \to 0$ as $X_1 \to 1$. The extrapolated D_{21} values 0.01×10^{-5} and -0.01×10^{-5} cm^2·s^{-1} for the 0.020 and 0.040 mol dm^{-3} NaDS solutions are consistent with the vanishing D_{21} values within the precision of the dispersion measurements.

In the limit $X_1 \to 1$, the main coefficient D_{22} for the LiDS component is the tracer diffusion coefficient of lithium ions in supporting solutions of NaDS.[24] The lithium ions in aqueous NaDS + LiDS solutions generally diffuse as free ions and bound counterions transported by a variety of $(\mathrm{Na}_q\mathrm{Li}_p\mathrm{D}_n)^{q+p-n}$ micelles. As the LiDS solute fraction drops to zero, however, the only remaining lithium species are free Li$^+$ ions and $(\mathrm{Na}_q\mathrm{LiD}_n)^{q+1-n}$ micelles carrying a single bound lithium ion. The tracer value of D_{22} is therefore the concentrated-weighted average

$$D_{22}(X_1 \to 1) = f_{\mathrm{Li}}D_{\mathrm{Li}} + (1 - f_{\mathrm{Li}})D_{\mathrm{Li\cdot mic}} \tag{8}$$

of the diffusion coefficients of the free Li$^+$ ions and the $(\mathrm{Na}_q\mathrm{LiD}_n)^{q+1-n}$ micelles, D_{Li} and $D_{\mathrm{Li\cdot mic}}$, respectively. f_{Li} is the fraction of the total lithium ions that diffuse as free Li$^+$ ions.

Linear extrapolation of the measured D_{22} values gives $D_{22}(X_1 \to 1) = 0.67 \times 10^{-5}$ cm^2·s^{-1} for 0.020 mol dm^{-3} NaDS solutions. Equation 8 together with $D_{\mathrm{Li}} = 1.030 \times 10^{-5}$ and $D_{\mathrm{Li\cdot mic}} = 0.10 \times 10^{-5}$ cm^2·s^{-1} gives $f_{\mathrm{Li}} = 0.61$ for the fraction of free Li$^+$ ions in 0.020 mol·dm^{-3} aqueous NaDS solutions. Similar calculations give $D_{22}(X_1 \to 1) = 0.54 \times 10^{-5}$ cm^2·s^{-1} and $f_{\mathrm{Li}} = 0.47$ for 0.040 mol·dm^{-3} NaDS solutions.

Unfortunately, a simple interpretation of the limiting $D_{12}(X_1 \to 1)$ values does not seem possible. Nernst−Planck equations can however be used to estimate the D_{12} values as the sum of the contributions to the coupled flow of NaDS from pure diffusion and migration of species in the electric field produced by LiDS concentration gradients.[25]

$$D_{12} = D_{12(\mathrm{D})} + D_{12(\mathrm{E})} \tag{9}$$

Stoichiometry dictates that the flux of the total NaDS component in aqueous NaDS + LiDS solutions equals the total sodium flux. The pure-diffusion contribution to D_{12} is therefore the sum of the diffusion coefficients of the sodium-containing species weighted by their concentration gradients produced by the LiDS concentration gradient[25]

$$D_{12(\mathrm{D})} = D_{\mathrm{Na}}\frac{\partial c_{\mathrm{Na}}}{\partial C_2} + 50D_{\mathrm{mic}}\frac{\partial c_{\mathrm{mic}}}{\partial C_2} + 49D_{\mathrm{Li\cdot mic}}\frac{\partial c_{\mathrm{Li\cdot mic}}}{\partial C_2} \tag{10}$$

The stoichiometric coefficients 50 and 49 in eq 10 give the number of sodium ions carried by the $(\mathrm{Na_{50}DS_{60}})^{-10}$ and $(\mathrm{Na_{49}LiDS_{60}})^{-10}$ species, respectively.

The electrostatic contribution to D_{12} in this case is[25]

$$D_{12(\mathrm{E})} = -\left(\frac{50t_{\mathrm{mic}}}{z_{\mathrm{mic}}} + t_{\mathrm{Na}}\right)\sum_{s=1}^{5} z_s D_s \frac{\partial c_s}{\partial C_2} \tag{11}$$

where $z_{\mathrm{mic}} = -10$, t_{Na} and t_{mic} are the transference numbers of $\mathrm{Na^+}$ and $(\mathrm{Na_{50}DS_{60}})^{-10}$

$$t_{\mathrm{Na}} = \frac{c_{\mathrm{Na}}D_{\mathrm{Na}}}{c_{\mathrm{Na}}D_{\mathrm{Na}} + c_{\mathrm{DS}}D_{\mathrm{DS}} + 100c_{\mathrm{mic}}D_{\mathrm{mic}}} \tag{12}$$

$$t_{\mathrm{mic}} = \frac{100c_{\mathrm{mic}}D_{\mathrm{mic}}}{c_{\mathrm{Na}}\mathrm{Na} + c_{\mathrm{DS}}D_{\mathrm{DS}} + 100c_{\mathrm{mic}}D_{\mathrm{mic}}} \tag{13}$$

and the summation runs over all five solution species considered here: $\mathrm{Na^+}$, $\mathrm{DS^-}$, $(\mathrm{Na_{50}DS_{60}})^-$,[10] $\mathrm{Li^+}$, and $(\mathrm{Na_{49}LiDS_{60}})^-$.[10] In these calculations the concentrations of the $\mathrm{Li^+}$ and $(\mathrm{Na_{49}LiDS_{60}})^{-10}$ species are $f_{\mathrm{Li}}C_2$ and $(1 - f_{\mathrm{Li}})C_2$, respectively, and the concentrations of the remaining species are evaluated using eq 7.

The D_{12} values calculated from eq 9 for the 0.020 $\mathrm{mol \cdot dm^{-3}}$ and 0.040 $\mathrm{mol \cdot dm^{-3}}$ NaDS solutions are -0.50×10^{-5} and -0.30×10^{-5} $\mathrm{cm^2 \cdot s^{-1}}$, respectively, in reasonable agreement with the values -0.53×10^{-5} and -0.28×10^{-5} $\mathrm{cm^2 \cdot s^{-1}}$ obtained by extrapolating the measured D_{12} values to $X_1 = 1$.

The magnitude of the terms in the expressions for $D_{12(\mathrm{D})}$ and $D_{12(\mathrm{E})}$ can shed light on the mechanism of the large countercurrent coupled flow of NaDS driven by the LiDS gradient. In this case the pure-diffusion contribution $D_{21(\mathrm{D})}$ is dominant, with $D_{12(\mathrm{E})}$ contributing less than 10% of the magnitude of D_{12}. When the concentration of LiDS is increased at fixed NaDS concentration, free $\mathrm{Na^+}$ are consumed to form additional micelles. The resulting gradient in the concentration free $\mathrm{Na^+}$ ions and their diffusion up the LiDS gradient was found to be responsible for the large, negative D_{12} values, with $D_{12}(X_1 \rightarrow 1) \cong D_{\mathrm{Na}}\ \partial c_{\mathrm{Na}}/\partial C_2$.

Aqueous NaDS ($C_1 \rightarrow 0$) + LiDS (C_2) Solutions. For the other limiting case, LiDS solutions containing trace amounts of NaDS, D_{22} is the binary mutual diffusion coefficient of aqueous LiDS, D_{12} vanishes, and D_{11} is the tracer diffusion coefficient of the sodium ion.

$$D_{11}(X_1 \rightarrow 0) = f_{\mathrm{Na}}D_{\mathrm{Na}} + (1 - f_{\mathrm{Na}})D_{\mathrm{Na\cdot mic}} \tag{14}$$

Extrapolation of the measured D_{22} values to $X_1 = 1$ gives 0.76×10^{-5} and 0.64×10^{-5} $\mathrm{cm^2 \cdot s^{-1}}$ for the respective 0.020 and 0.040 $\mathrm{mol\ dm^{-3}}$ LiDS solutions, and hence 0.53 and 0.44 for the fraction of free $\mathrm{Na^+}$ ions. The $D_{21}(X_1 \rightarrow 0)$ values can be evaluated from equations 9−13 by interchanging the subscripts "Na" and "Li".

The limiting D_{ik} values for $X_1 \rightarrow 0$ and $X_1 \rightarrow 1$ discussed above are summarized in Table 3 and plotted in Figures 2 and 3. Although the $D_{12}(X_1 \rightarrow 1)$ and $D_{21}(X_1 \rightarrow 0)$ predictions are not accurate, the calculations identify the coupled diffusion of counterions as the main contribution to the large, negative cross-diffusion coefficients. Despite extensive micelle formation and counterion binding, the D_{ik} coefficients at fixed total surfactant concentration are simple linear functions of the solute fraction. Similar behavior is observed for dilute solutions of mixed strong electrolytes.[26,27] Linear variation in the diffusion coefficients at constant total solute concentrations is also a useful first approximation for concentrated and highly nonideal solutions[28−30] of mixed electrolytes.

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