

Incongruent Diffusion (Negative Main Mutual Diffusion Coefficient) for a Ternary Mixed Surfactant System

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Moments analysis of Taylor dispersion profiles is used to measure ternary mutual diffusion coefficients (D_{ik}) for dilute aqueous sodium dodecyl sulfate (SDS) + dodecylsulfobetaine (DSB) mixed surfactant solutions at 25 °C and total surfactant concentrations from 10 to 30 mmol dm⁻³. The fluxes of the SDS(1) and DSB(2) components are strongly coupled by the formation of SDS–DSB mixed micelles. At several compositions, cross-coefficient D_{12} or D_{21} is larger than main coefficients D_{11} and D_{22} . More remarkably, D_{22} is *negative* at solute fractions of SDS from 0.55 to 0.75, reaching a minimum value of $-0.056 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 13 mmol dm⁻³ SDS + 7 mmol dm⁻³ DSB. This surprising result means that DSB concentration gradients drive “incongruent” fluxes of DSB, from lower to higher DSB concentrations. A possible explanation for the incongruent diffusion of DSB is suggested on the basis of the electric field generated by gradients in the surfactant concentration. Negative D_{ii} values have been reported previously for concentrated, strongly nonideal aqueous acetic acid + chloroform solutions near a consolute point. Because the SDS + DSB solutions are dilute and far removed from phase boundaries, incongruent diffusion might be considerably more common than previously assumed.

Introduction

Diffusion in surfactant solutions is widely studied because of its role in solubilization, emulsification, digestion, and coating processes.^{1–4} Surfactant diffusion coefficients are also a valuable source of information about micelle interactions, aggregation numbers, counterion binding, extents of solubilization, etc.^{2–16} One of the most remarkable features of diffusion in these systems is the sharp drop in the binary mutual diffusion coefficient (D) as the surfactant concentration is raised through the critical micelle concentration (cmc).^{9,17–19} In the cmc region of aqueous Triton X-100 (a polyoxyethylene surfactant), for example, a mere 0.0001 mol dm⁻³ increase in the surfactant concentration reduces D by about 60%.¹⁹ The striking concentration dependence of D near a cmc is caused by the sudden onset of the aggregation of the free surfactant monomers and the resulting sharp decrease in the surfactant chemical potential gradient, the driving force for mutual diffusion.^{9,17} This behavior is analogous to diffusion in solutions at compositions approaching phase separation.²⁰ For binary solutions on the brink of phase separation at a consolute point, the chemical potential gradients and therefore D are zero.^{21–24} Micelles are not true phases, so D is reduced, but not to zero, at the cmc.

Another interesting feature of surfactant transport is the strong interaction of the diffusion fluxes in multicomponent surfactant + solubilize¹⁶ and mixed surfactant^{25–27} solutions. For these systems, it is not uncommon for a cross-diffusion coefficient describing coupled diffusion to exceed the main coefficients for the fluxes of the components driven by their own concentration gradients. A mechanism for the strongly coupled diffusion of mixed ionic surfactants has been developed on the basis of the formation of mixed micelles and the electric field generated by the simultaneous diffusion of charged micelles and mobile

counterions.²⁶ Diffusion in solutions of ionic–nonionic mixed surfactants has also been investigated.²⁵

The work reported here is a study of mutual diffusion in aqueous solutions of sodium dodecyl sulfate (SDS) + dodecylsulfobetaine (DSB), an ionic–zwitterionic mixed surfactant. Ternary mutual diffusion coefficient D_{ik} for this system gives the molar flux J_i of surfactant component i produced by the molar concentration gradient ∇c_k in surfactant component k .^{1,28}

$$J_1(\text{total SDS}) = -D_{11}\nabla c_1 - D_{12}\nabla c_2 \quad (1)$$

$$J_2(\text{total DSB}) = -D_{21}\nabla c_1 - D_{22}\nabla c_2 \quad (2)$$

The initial focus was on the interaction of the surfactant fluxes and cross-coefficients D_{12} and D_{21} , but the diffusion measurements produced a totally unexpected result: *negative* values for main diffusion coefficient D_{22} . This means that DSB concentration gradients can drive fluxes of DSB “uphill”, from regions of lower to regions of higher DSB concentration.

Coupled fluxes of components are routinely driven to higher concentrations by concentration gradients in other components.^{28,29} It is exceedingly rare, however, for a component to be driven from lower to higher concentrations by its own concentration gradient (incongruent diffusion). Only one case of incongruent diffusion appears to have been reported previously: negative D_{22} values for concentrated, strongly nonideal aqueous solutions of acetic acid(1) + chloroform(2) near a consolute point.²¹ This behavior has been interpreted as a thermodynamic effect caused by the diffusion of “salted-out” chloroform down the water concentration gradient produced by the chloroform gradient under conditions of constant acetic acid concentration. The negative main diffusion coefficients reported here refer to dilute solutions ($\leq 30 \text{ mmol dm}^{-3}$ total surfactant) far removed from phase boundaries. Thus incongruent diffusion might be considerably more common than previously assumed.

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Experimental Section

Solutions were prepared by mass by dissolving SigmaUltra grade surfactants (purity > 99%) in distilled, deionized water. Volumetric concentrations were calculated using solution densities measured at 25 °C with a vibrating-tube density meter (Paar model DMA 58). The surface tensions of binary SDS and DSB solutions were measured by the drop-weight method. Breaks in the plots of surface tension against the logarithm of surfactant concentration gave 8.1 and 3.0 mmol dm⁻³ for the respective cmc's, in good agreement with literature values.^{30–34} A minimum in the surface tension (an indicator of surfactant impurities) was not observed. The cmc's for ternary SDS + DSB solutions were evaluated from plots of the molar conductivity of SDS against the square root of the SDS concentration. The conductivities were measured with an Orion model 160 conductivity meter and a type 16010 cell.

The Taylor dispersion (peak-broadening) method was used for the diffusion measurements.²⁸ Dispersion profiles were generated by injecting 20 mm³ samples of SDS(1) + DSB(2) solution of composition $\bar{c}_1 + \Delta c_1$, $\bar{c}_2 + \Delta c_2$ into laminar carrier streams of composition \bar{c}_1 , \bar{c}_2 . The broadened distribution of the dispersed samples was monitored by a differential refractometer detector (Hewlett-Packard model 1047A) at the outlet of a Teflon capillary tube (length 16.00 m, internal radius $r = 0.406_0$ mm). A computer-controlled digital voltmeter (Hewlett-Packard model 3478A) measured the detector voltage $V(t)$ at accurately timed intervals. The ratio $R_2/R_1 = (\partial n/\partial c_2)/(\partial n/\partial c_1)$ of refractive-index increments (~ 1.50) was calculated by taking the ratio of peak areas per mole of excess SDS or DSB in the injected solution samples.

Dispersion profiles generally resemble Gaussian peaks, even for systems with interacting diffusion fluxes. However, the peak shapes for the SDS + DSB solutions were highly unusual, which indicated very strong coupling of the surfactant fluxes. The dispersion profiles were therefore analyzed by a moments procedure³⁵ designed specifically for systems with large cross-diffusion coefficients. In this procedure, dispersion profiles are measured for each carrier stream for different values of $\alpha_1 = R_1\Delta c_1/(R_1\Delta c_1 + R_2\Delta c_2)$, the fraction of the refractive-index difference produced by the initial SDS gradient. The D_{ik} coefficients are evaluated from the height, area (zeroth moment), and first moment of the profiles: $V(t_R)$, $I_0 = \int V(t) dt$, and $I_1 = \int |t - t_R| V(t) dt$, respectively. Typical retention times (t_R) were about 4300 s. Slower runs were used to verify that the measured D_{ik} coefficients were independent of the flow rate.

Results

Figure 1 shows a set of five dispersion profiles for a 13.0 mmol dm⁻³ SDS + 7.00 mmol dm⁻³ DSB carrier solution. The profile produced by an initial DSB gradient ($\alpha_1 = 0.020$) has a deep central depression that drops to the baseline. An initial gradient in SDS ($\alpha_1 = 0.998$) generates a profile with leading and trailing edges that dip below the baseline. Initial concentration differences were in the range $-12 \text{ mmol dm}^{-3} \leq \Delta c_i \leq 12 \text{ mmol dm}^{-3}$. The concentration differences across the measured dispersion profiles were typically 50 to 100 times smaller as a result of dilution of the injected samples with the carrier solution. Large changes in the D_{ik} coefficients across the profiles were avoided by using carrier solutions and injected solutions at compositions above the cmc (see Figure 2).

Moments analysis of ternary dispersion profiles³⁵ indicates that the reduced peak heights, $V'(t_R)/I_0' = (\pi r^2 t_R/12)^{1/2} V(t_R)/I_0$, and reduced first moments, $I_1'/I_0' = (12\pi/(r^2 t_R))^{1/2} I_1/I_0$, are linear functions of α_1 . Despite the unusual shapes of the SDS + DSB

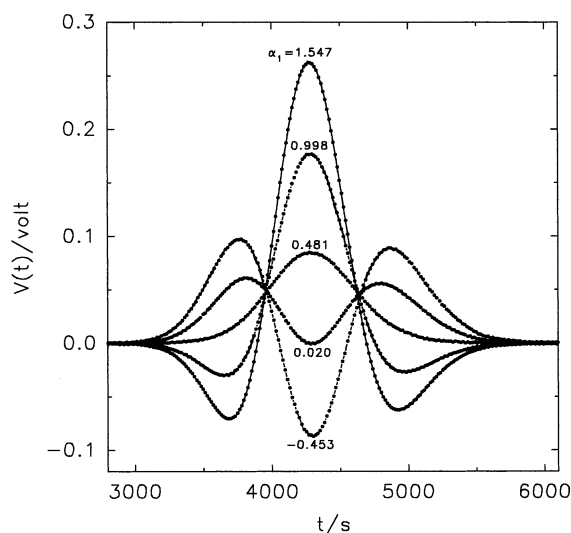


Figure 1. Dispersion profiles for a 13.0 mmol dm⁻³ SDS + 7.00 mmol dm⁻³ SB12 carrier stream for the following values of α_1 (initial SDS and DSB concentration differences in parentheses): -0.453 ($\Delta c_1 = -3.520 \text{ mmol dm}^{-3}$, $\Delta c_2 = 7.513 \text{ mmol dm}^{-3}$); 0.020 (0.153 , 5.033); 0.481 (3.461 , 2.479); 0.998 (7.088 , 0.011); 1.547 (10.573 , -2.487).

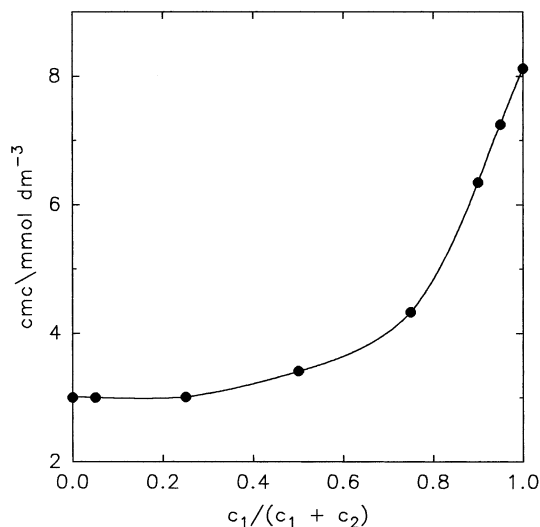


Figure 2. Critical micelle concentrations for aqueous SDS(c_1) + SB12-(c_2) solutions plotted against the solute fraction of SDS.

profiles, the reduced heights and first moments were linear in α_1 , as illustrated in Figure 3, and therefore conformed to the ternary dispersion equations. This check also indicated that the initial concentration differences were small enough to ensure that the D_{ik} coefficients were effectively constant across the profiles and therefore represented differential values at the carrier stream composition.

Ternary mutual diffusion coefficients were measured for aqueous SDS(1) + DSB(2) solutions at 25 °C and total surfactant concentrations from 10 to 30 mmol dm⁻³. Table 1 gives the average D_{ik} values for each composition from moments analysis of at least four different sets of profiles. Binary mutual diffusion coefficients measured for 20.0 mmol dm⁻³ solutions of each surfactant are also recorded in Table 1. In Figure 4, the diffusion coefficients for the solutions containing 20 mmol dm⁻³ total surfactant are plotted against $c_1/(c_1 + c_2)$, the solute fraction of SDS. This plot illustrates the composition dependence of the surfactant diffusion coefficients moving from a binary DSB solution (left intercept) through ternary SDS + DSB solutions to a binary SDS solution (right intercept).

TABLE 1: Ternary Mutual Diffusion Coefficients of Aqueous SDS(1) + DSB(2) Solutions

c_1 (mmol dm ⁻³)	c_2 (mmol dm ⁻³)	D_{11} (10 ⁻⁹ m ² s ⁻¹) ^a	D_{12} (10 ⁻⁹ m ² s ⁻¹) ^a	D_{21} (10 ⁻⁹ m ² s ⁻¹) ^a	D_{22} (10 ⁻⁹ m ² s ⁻¹) ^a	det(D) (10 ⁻¹⁸ m ⁴ s ⁻²)
2.50	7.50	0.511(2)	0.001(2)	0.542(12)	0.330(2)	0.168
5.00	5.00	0.624(4)	-0.152(4)	0.400(4)	0.070(2)	0.104
7.50	2.50	0.63(6)	-0.68(4)	0.12(2)	-0.03(2)	0.063
0.00	20.00				0.119(3) ^b	
3.00	17.00	0.346(2)	0.029(2)	1.033(2)	0.270(2)	0.063
5.00	15.00	0.405(10)	0.057(6)	0.51(4)	0.351(12)	0.113
7.00	13.00	0.448(6)	0.062(2)	0.387(8)	0.295(6)	0.108
10.00	10.00	0.553(4)	-0.128(2)	0.334(10)	0.053(2)	0.072
11.00	9.00	0.544(24)	-0.205(10)	0.322(14)	-0.016(2)	0.057
12.00	8.00	0.53(3)	-0.31(2)	0.29(2)	-0.052(14)	0.062
13.00	7.00	0.53(2)	-0.34(5)	0.24(2)	-0.056(26)	0.053
13.00 ^c	7.00 ^c	0.50(2) ^c	-0.34(2) ^c	0.20(2) ^c	-0.032(8) ^c	0.052 ^c
14.00	6.00	0.523(14)	-0.436(10)	0.182(6)	-0.044(4)	0.056
15.00	5.00	0.486(26)	-0.45(4)	0.12(2)	-0.013(12)	0.049
19.00	1.00	0.294(4)	-0.54(4)	0.015(2)	0.084(4)	0.032
20.00	0.00	0.241(2) ^b				
20.00	10.00	0.51(2)	-0.32(2)	0.23(2)	-0.047(10)	0.048

^a Precision quoted as two standard deviations (in parentheses) applies to the last digits indicated. ^b Binary mutual diffusion coefficients. ^c For LiDS(1) + SB12(2) solutions.

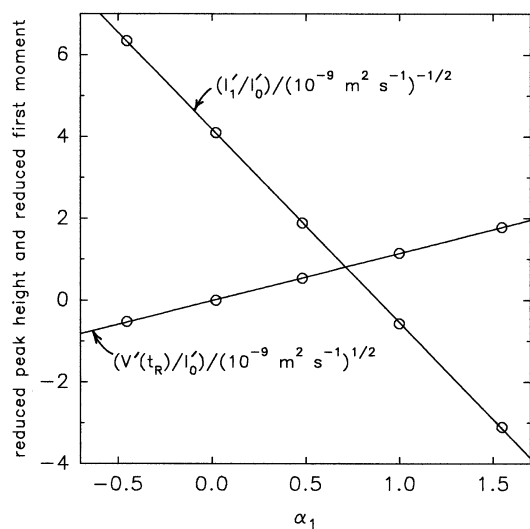


Figure 3. Reduced peak heights, $V'(t_R)/I'_0$, in units of $(10^{-9} \text{ m}^2 \text{ s}^{-1})^{1/2}$ and reduced first moments, I'_1/I'_0 , in units of $(10^{-9} \text{ m}^2 \text{ s}^{-1})^{-1/2}$ plotted against α_1 for the dispersion profiles in Figure 1.

Illustrating the strong coupling of the surfactant fluxes, cross-coefficient D_{12} or D_{21} is larger than both main coefficients at several compositions. At low solute fractions of SDS (large positive D_{21} values), SDS gradients drive very substantial coupled flows of DSB toward regions of lower SDS concentrations. Conversely, at high SDS fractions (large negative D_{12} values), significant coupled flows of SDS are driven up DSB gradients.

The composition dependence of main diffusion coefficient D_{22} shown in Figure 4 is noteworthy. In the limit $c_1/(c_1 + c_2) \rightarrow 0$, D_{22} is the binary mutual diffusion coefficient³⁶ of 20 mmol dm⁻³ aqueous DSB, $0.119 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (left intercept in Figure 4). As the solute fraction of SDS is raised, D_{22} passes through a maximum and a minimum and then rises to a limiting value of about $0.11 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for the tracer diffusion of DSB in a 20 mmol dm⁻³ SDS solution (right intercept). Moreover, D_{22} is negative at SDS solute fractions from 0.55 to 0.75 and reaches a minimum value of $-0.056 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ in this composition region. Negative D_{22} values were also measured at 10 and 30 mmol dm⁻³ total surfactant (see Table 1). At several compositions, therefore, DSB concentration gradients drive incongruent fluxes of DSB from lower to higher DSB concentrations.

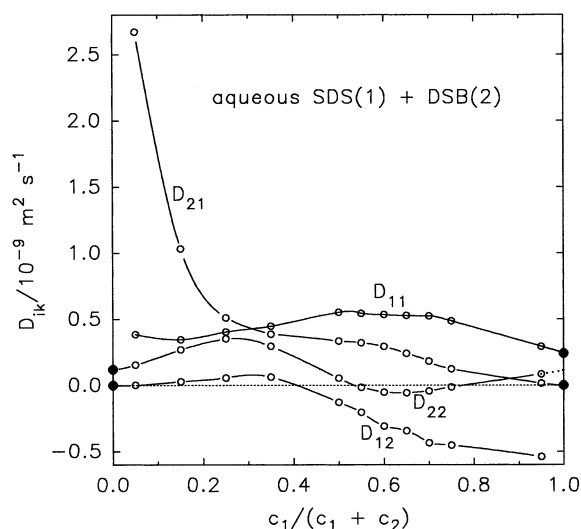


Figure 4. Ternary mutual diffusion coefficients for aqueous SDS(1) + SB12(2) solutions plotted against the solute fraction of SDS for solutions containing 20.0 mmol dm⁻³ total surfactant.

Although the results are surprising, the measured D_{ik} coefficients, including the negative D_{22} values, are consistent with accepted diffusion behavior. In particular, negative D_{ii} coefficients are not impossible. According to the second law and the Onsager reciprocal relations, however, the determinant of the matrix of D_{ik} coefficients cannot be negative: $\det(\mathbf{D}) = D_{11}D_{22} - D_{12}D_{21} \geq 0$, with the equality holding at consolute points and along spinodal curves.^{21,37} The measured D_{ik} coefficients give positive determinants and therefore obey this rule, as shown in Table 1.

In the limit $c_1/(c_1 + c_2) \rightarrow 0$, D_{12} is zero (a gradient in DSB cannot produce a coupled flow of SDS in a solution that does not contain SDS) and D_{22} is the binary mutual diffusion coefficient of aqueous DSB. Although precise extrapolations are not feasible, the measured values of D_{12} and D_{22} shown in Figure 4 appear to extrapolate to the correct limiting values (left intercepts). Similarly, as $c_1/(c_1 + c_2) \rightarrow 1$, the measured values of D_{21} and D_{11} appear to extrapolate to 0 and the binary diffusion coefficient of 20 mmol dm⁻³ aqueous SDS³⁶ (right intercepts).

Extrapolating D_{22} to $c_1/(c_1 + c_2) = 1$ gives a value of about $0.11 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for the tracer diffusion coefficient of DSB in 20.0 mmol dm⁻³ SDS solutions. Because DSB is a nonelec-

trolyte, the tracer D_{22} value is a simple average of the diffusion coefficients of free DSB monomers ($0.50 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$)³⁶ and the SDS micelles ($0.10 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$)¹⁷ weighted by the fractions of total DSB in monomer and micellar form. In view of the relatively low cmc of binary DSB solutions, most of the tracer DSB component diffuses in micellar form. These considerations suggest a tracer D_{22} value of about $0.10 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ or slightly higher, in qualitative agreement with the extrapolated D_{22} value. Thus, an extrapolation of measured D_{22} values, including the surprising negative values, leads to a physically reasonable tracer diffusion coefficient for DSB.

The evaluation of reliable ternary diffusion coefficients from refractive-index profiles is difficult if the eigenvalues of the **D** matrix are identical or nearly identical. In these cases, the equations used to analyze the profiles are ill-conditioned.³⁸ For the SDS + DSB solutions, however, the eigenvalues of **D** are well separated. At $13.0 \text{ mmol dm}^{-3}$ SDS + $7.00 \text{ mmol dm}^{-3}$ DSB, for example, the eigenvalues are 0.19×10^{-9} and $0.28 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. This check shows that the reported negative D_{22} values are not artifacts of numerical ill-conditioning.

Negative main diffusion coefficients can be obtained by defining diffusion fluxes in unusual frames of reference.^{21,37} For example, the negative D_{22} values reported previously for concentrated aqueous acetic acid(1) + chloroform(2) solutions refer to solvent-fixed fluxes of chloroform using water, a minor solution component (volume fraction ~ 0.1), as the solvent. In contrast, the negative D_{22} values reported here for aqueous SDS-(1) + DSB(2) solutions are directly measured in the volume-fixed (laboratory) frame and not arbitrarily transformed values. Moreover, the aqueous SDS(1) + DSB(2) solutions are dilute, so the measured volume-fixed D_{ik} coefficients, including the negative D_{22} values, are identical within experimental error to the solvent-fixed values with water as the unambiguous solvent.

Ternary diffusion can produce instabilities in diffusion boundaries.^{12,21} Avoiding these instabilities can place severe constraints on the range of initial conditions that can be used in experiments employing free-diffusion columns of solution, especially in cases of strongly coupled diffusion. In Taylor dispersion experiments, however, instabilities are prevented because the solutions are confined within narrow-bore capillaries. In fact, identical results are obtained using injected solutions that are more dense or less dense than the carrier solution.³⁹ The Taylor method is therefore well suited to studies of strongly coupled diffusion in SDS + DSB solutions.

Discussion

The reported D_{ik} coefficients give a phenomenological description of incongruent DSB diffusion and the strong, asymmetric coupling of the SDS and DSB fluxes. But what causes this unusual diffusion behavior? SDS and DSB are both very soluble in water. Concentrated solutions of the mixed surfactants ($>0.5 \text{ mol dm}^{-3}$ total surfactant) can be prepared without visible phase separation. This appears to rule out a nearby consolute point as an explanation for the unusual diffusion behavior.

Recent work²⁶ has drawn attention to the strong coupling of ionic surfactant fluxes caused by the electric field generated by the simultaneous diffusion of charged micelles and relatively mobile counterions. An SDS concentration gradient, for example, generates an electric field that speeds up the micelles and slows down the Na^+ counterions, thereby preventing significant charge separation along the diffusion path. DSB zwitterions are electrically neutral, so an electric field will not drive fluxes of free DSB monomers. In the SDS + DSB

solutions, however, DSB zwitterions are incorporated in charged ($\text{Na}_q\text{DS}_n\text{DSB}_p$) ^{$q-n$} mixed micelles. Consequently, the electric field produced by SDS gradients will drag micellar DSB(2) along with the diffusing SDS(1) component. This electrostatic mechanism might account for the large positive D_{21} values reported in the present study.

The tracer diffusion coefficient of DSB mentioned above confirms that most of the DSB component exists in micellar form. By promoting the formation of micelles, an increase in the concentration of DSB will also increase the concentration of ($\text{Na}_q\text{DS}_n\text{DSB}_p$) ^{$q-n$} micelles but will reduce the concentrations of free Na^+ and DS^- ions. The resulting diffusion of Na^+ and DS^- ions toward regions of higher DSB concentrations could explain the reported negative D_{12} values. Also, the electric field generated to slow the coupled flow of Na^+ ions will drive the ($\text{Na}_q\text{DS}_n\text{DSB}_p$) ^{$q-n$} micelles up the DSB gradient. The electric field, if sufficiently strong, would produce incongruent diffusion of DSB.

The mobility of the free Na^+ ions plays a key role in the proposed electrostatic mechanism for the incongruent diffusion of DSB. Replacing the Na^+ ions with less mobile counterions should reduce the incongruent diffusion of DSB and weaken the coupling of the surfactant fluxes. Aqueous Li^+ ions are about 30% less mobile than Na^+ ions.³⁹ As a test, diffusion coefficients were measured for a $13.0 \text{ mmol dm}^{-3}$ LiDS + $7.00 \text{ mmol dm}^{-3}$ DSB carrier solution. As shown in Table 1, changing the counterion from Na^+ to Li^+ changes D_{22} in the predicted direction, from -0.056×10^{-9} to $-0.032 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Also, cross-coefficient D_{21} is reduced in magnitude. The changes in the diffusion coefficients, however, are quite small and may also be influenced by the slightly different cmc's and extents of counterion binding for SDS and LiDS.²⁷

The main conclusion of the present study is that negative main mutual diffusion coefficients are not confined to systems near consolute points. Thus incongruent diffusion might occur in a wider range of systems than previously assumed. Work is in progress to measure ternary diffusion coefficients for other mixed surfactant and mixed cluster systems. In addition, models are being developed to investigate the proposed electrostatic mechanism for incongruent diffusion.

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