Mutual Diffusion Coefficients and Resistance Coefficients for Aqueous Solutions of Sodium Alkanoate Surfactants

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Taylor dispersion is used to measure mutual diffusion coefficients (*D*) for binary aqueous solutions of sodium hexanoate, heptanoate, octanoate, decanoate, and dodecanoate salts at 25 °C. The diffusion coefficients of sodium hexanoate and heptanoate drop smoothly as the salt concentration is raised. For each of the longer-chain sodium alkanoates, *D* drops sharply in the region of the critical micelle concentration. Activity coefficient data are used to calculate resistance coefficients from the diffusion results. For aqueous sodium decanoate, micellar aggregation produces a 4-fold decrease in the friction acting on the diffusing salt. The mutual diffusion coefficient of aqueous sodium octanoate is compared with previously reported intradiffusion coefficients for sodium and octanoate ions.

Introduction

Diffusion in surfactant solutions is usually studied by NMR (Abrahmsén-Alami and Stilbs, 1994; Mittal and Lindman, 1984; Nilsson and Lindman, 1983; Stilbs, 1982) or capillary-tube (Lindman *et al.*, 1980, 1982; Stilbs, 1982) methods. These techniques provide accurate intradiffusion coefficients for the random thermal motion of labeled species in systems of uniform chemical composition. In practical applications, however, diffusion in chemical concentration gradients can be important (Shaeiwitz, 1987). This kind of diffusion (often called chemical interdiffusion or mutual diffusion) occurs, for example, when oil droplets are attacked and solubilized by aqueous detergents. Relatively little information is available for mutual diffusion in surfactant solutions (Evans *et al.*, 1983; Leaist, 1986; Weiheimer *et al.*, 1981).

In this paper mutual diffusion coefficients are reported for binary aqueous solutions of the sodium salts of hexanoic, heptanoic, octanoic, decanoic, and dodecanoic fatty acids. Aqueous sodium octanoate, decanoate, and dodecanoate have well-defined critical micelle concentrations (Mukerjee and Mysels, 1971) marking the onset of extensive ionic association. Diffusion measurements are made above and below the critical micelle concentrations of these soaps to provide information on the effects of aggregation on the diffusion behavior (Evans *et al.*, 1983; Leaist, 1986; Weiheimer *et al.*, 1981).

Experimental Procedure

Solutions were prepared with distilled, deionized water in calibrated volumetric flasks. Sodium hexanoate, octanoate, decanoate, and dodecanoate (Sigma Chemical Co., 99% purity) were dried in a vacuum oven and used without further treatment. Stock solutions of sodium heptanoate were prepared by titration of heptanoic acid (Sigma, 99% purity) with carbonate-free aqueous sodium hydroxide. The estimated accuracy of the concentrations of the solutions is (1 to 2) %.

The mutual diffusion coefficients of the solutions were measured by the Taylor dispersion (peak-broadening) method (Pratt and Wakeham, 1974). At the start of each run an injection valve was used to introduce a small volume of sodium alkanoate solution into a laminar carrier stream of slightly different composition at (25.00 ± 0.05) °C. A liquid-chromatography differential refractometer detector monitored the broadened distribution of the injected sample at the outlet of a long capillary tube. Diffusion coefficients were calculated from least-squares fits of the dispersion equation to detector voltages which were measured with a digital voltmeter at timed intervals. Details of the equipment and procedure have been reported (Leaist, 1991, 1992).

Results and Discussion

Table 1 gives the average diffusion coefficient determined from 4−8 replicate injections made into each carrier solution. The values of *D* were reproducible within (1 to 2)%. The concentrations of salt in the injected solution ($\bar{c} + \Delta c$) and the carrier solution ($\bar{c}$) differed by 0.05 mol dm^{-3} or less. In this range the measured diffusion coefficients were independent of Δc and therefore represented differential coefficients at the composition of the carrier stream.

Table 1 includes accurate mutual diffusion coefficients for infinitely dilute solutions of sodium hexanoate, octanoate, decanoate, and dodecanoate calculated independently from limiting ionic conductivities (λ_i^0, Table 2) by using Nernst's equation: $D^0 = 2RT\lambda_+^0\lambda_-^0/F^2(\lambda_+^0 + \lambda_-^0)$. *R* is the gas constant, *T* the temperature, and *F* the Faraday constant.

A plot of *D* against $\bar{c}$ contains a number of overlapping data points, especially at low concentrations. In Figure 1, for greater clarity, the diffusion coefficients of the aqueous sodium alkanoates are plotted against the square root of $\bar{c}$. For sodium hexanoate and heptanoate, *D* decreases relatively smoothly as the concentration is raised. For the longer-chain alkanoates the drop in *D* becomes increasingly sharp and shifts to lower concentrations.

Sodium alkanoates are completely dissociated in dilute aqueous solutions, but ion association definitely occurs at higher concentrations. Sodium octanoate and the longer-chain alkanoates each have a well-defined critical micelle concentration (cmc) marking the onset of the formation of large micellar aggregates. As the length of the hydrocarbon chain increases the cmc becomes increasingly sharp and shifts to lower concentrations (Mukerjee and Mysels,

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Table 1. Binary Mutual Diffusion Coefficients, Thermodynamic Factors, and Resistance Coefficients of Aqueous Sodium Alkanoates and Sodium Dodecyl Sulfate at 25 °C

$\bar{c}$/(mol dm^{-3})	D/ (10^{-5} cm^2 s^{-1})	1 + (d ln $\gamma_\pm$)/ (d ln m)	φ_{12}/ (10^{12} N s m^{-1} mol^{-1})	$\bar{c}$/(mol dm^{-3})	D/ (10^{-5} cm^2 s^{-1})	1 + (d ln $\gamma_\pm$)/ (d ln m)	φ_{12}/ (10^{12} N s m^{-1} mol^{-1})	$\bar{c}$/(mol dm^{-3})	D/ (10^{-5} cm^2 s^{-1})	1 + (d ln $\gamma_\pm$)/ (d ln m)	φ_{12}/ (10^{12} N s m^{-1} mol^{-1})
					Sodium Hexanoate						
0.00	0.9427[a]	1.000	5.26	0.30	0.82	1.01	6.1	1.50	0.32	0.63	9.8
0.05	0.87			0.50	0.80	1.10	6.8	2.00	0.21	0.45	10.6
0.10	0.86	0.94	5.4	0.75	0.74	1.14	7.6				
0.20	0.84	0.98	5.8	1.00	0.65	1.03	7.9				
					Sodium Heptanoate						
0.01	0.86			0.30	0.79	1.01	6.3	1.00	0.23	0.27	5.8
0.05	0.84			0.50	0.77	0.99	6.4	1.50	0.23	0.28	6.0
0.10	0.83	0.94	5.6	0.60	0.56	0.93	8.2	2.00	0.22	0.38	8.6
0.20	0.80	0.98	6.0	0.75	0.24	0.52	10.7				
					Sodium Octanoate						
0.00	0.8415[a]	1.000	5.89	0.20	0.75			0.75	0.20	0.15	3.7
0.01	0.83			0.30	0.70			1.00	0.21	0.22	5.2
0.05	0.81			0.40	0.51			1.50	0.21	0.29	6.8
0.10	0.79			0.50	0.27	0.41	7.5				
					Sodium Decanoate						
0.00	0.8144[a]	1.000	6.09	0.08	0.69	0.87	6.2	0.20	0.22	0.07	1.6
0.01	0.78	0.96	6.1	0.09	0.67	0.84	6.2	0.22	0.23	0.08	1.7
0.02	0.78	0.94	6.0	0.10	0.38	0.70	9.1	0.25	0.26	0.09	1.7
0.05	0.73	0.91	6.2	0.12	0.27	0.48	8.8	0.30	0.28	0.11	1.9
					Sodium Dodecanoate						
0.000	0.7791[a]	1.000	6.36	0.025	0.75			0.075	0.26		
0.005	0.77			0.028	0.52			0.100	0.29		
0.015	0.76			0.030	0.32			0.150	0.36		
0.020	0.75			0.050	0.21						
					Sodium Dodecylsulfate						
0.0000	0.836[a]	1.000	5.93	0.0118	0.232	0.05	1.1	0.0375	0.336	0.07	1.0
0.0018	0.792	0.98	6.1	0.0140	0.208	0.05	1.2	0.0462	0.366	0.09	1.2
0.0028	0.784	0.97	6.1	0.0178	0.235	0.05	1.1	0.0640	0.418	0.11	1.3
0.0034	0.780	0.97	6.2	0.0249	0.270	0.06	1.1	0.0817	0.447	0.13	1.4
0.0046	0.780	0.96	6.1	0.0270	0.295	0.06	1.0				

[a] Calculated from limiting ionic conductivities (Campbell and Lakshminarayanan, 1965).

Table 2. Limiting Ionic Conductivities[a] at 25 °C

ion	λ_i^0/(cm^2 S mol^{-1})	ion	λ_i^0/(cm^2 S mol^{-1})
Na$^+$	50.10	octanoate	23.08
hexanoate	27.37	decanoate	22.01
heptanoate		dodecanoate	20.66

1971): 0.35 mol dm^{-3} for sodium octanoate, 0.095 mol dm^{-3} for sodium decanoate, and 0.026 mol dm^{-3} for sodium dodecanoate. The cmc values (marked by vertical dashed lines in Figure 1) appear to coincide with the sharp decreases in D.

Though chemical potential gradients are recognized as the driving forces for diffusion, it is much easier in practice to use Fick's law to relate solute fluxes to concentration gradients. But as a result of this definition, the mutual diffusion coefficient is a complicated quantity: a product of a frictional factor (related to the size of the diffusing molecules and the viscosity) and an equilibrium thermodynamic factor for the change in chemical potential with concentration.

The frictional and thermodynamic factors for mutual diffusion can be separated by using the resistance coefficient (Tyrrell and Harris, 1984)

$$\varphi_{12} = \frac{-\nabla\mu_1}{v_1 - v_2} \tag{1}$$

as a measure of the friction acting on a solute (component 1) as it moves through a solvent (component 2). Physically, φ_{12} is the driving force per mole of solute ($-\nabla\mu_1$) required to maintain unit relative velocity ($v_1 - v_2$) between the diffusing solute and solvent (Tyrrell and Harris, 1984).

The Gibbs–Duhem equation can be used to show that mutual diffusion coefficients and resistance coefficients are inversely related as follows:

$$D = \frac{\mathrm{d}\mu_1/(\mathrm{d}\ln m)}{\varphi_{12}} \tag{2}$$

where m is the solute molality. In binary aqueous sodium alkanoate solutions, the sodium and alkanoate ions diffuse at identical speeds to keep the solution electrically neutral so the dissolved salt can be treated as a single neutral solute component. For these systems eq 2 can be rewritten as

$$D = \frac{2RT(1 + (\mathrm{d}\ln\gamma_\pm)/(\mathrm{d}\ln m))}{\varphi_{12}} \tag{3}$$

where $\gamma_\pm$ is the stoichiometric mean ionic activity coefficient. The numerator $2RT(1 + (\mathrm{d}\ln\gamma_\pm)/(\mathrm{d}\ln m))$ is the thermodynamic factor for mutual diffusion of a 1:1 salt.

Table 1 gives values of $1 + (\mathrm{d}\ln\gamma_\pm)/(\mathrm{d}\ln m)$ calculated from activity coefficients (De Lisi *et al.*, 1981; Robinson and Stokes, 1959; Vikingstad, 1979) available for aqueous sodium hexanoate, heptanoate, octanoate, and decanoate. The formation of micelles reduces the number of free ions diffusing in the solutions. This in turn reduces the free energy gradient driving the diffusion process and causes a sharp drop in the diffusion coefficients of sodium octanoate and the higher alkanoates.

Resistance coefficients were calculated according to eq 3 by using the measured diffusion coefficients and the

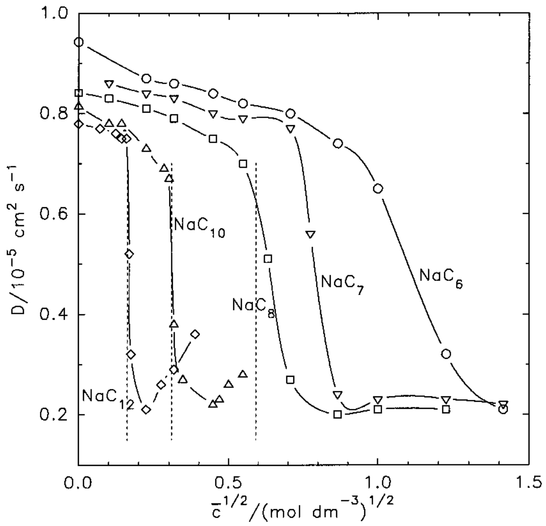

Figure 1. Binary mutual diffusion coefficients of aqueous sodium alkanoates at 25 °C. Open symbols: Taylor dispersion measurements. Solid symbols: limiting diffusion coefficients calculated from ionic conductivities (Campbell and Lakshminarayanan, 1965).

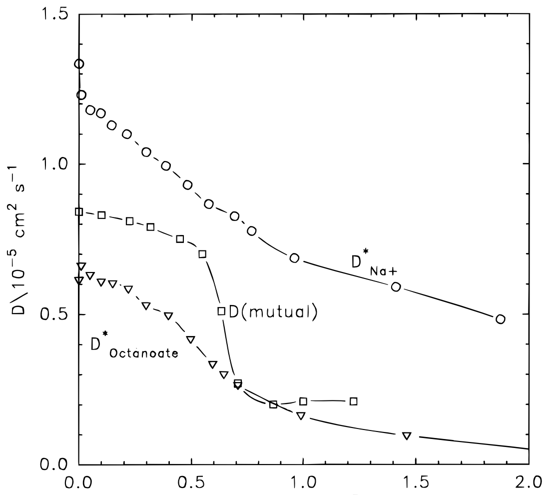

Figure 2. Mutual diffusion coefficient D (this work), sodium intradiffusion coefficient $D^{*}_{\mathrm{Na^+}}$ (Lindman and Brun, 1973), and octanoate intradiffusion coefficient $D_{\mathrm{octanoate}}$ (Lindman and Brun, 1973) for aqueous solutions of sodium octanoate at 25 °C. The solid symbols represent accurate limiting diffusion coefficients calculated from limiting ionic conductivities (Campbell and Lakshminarayanan, 1965).

values of $1 + (\mathrm{d}\ \ln\ \gamma_{\pm})/(\mathrm{d}\ \ln\ m)$. The results are summarized in Table 1. Although the activity coefficients used in the calculations are relatively precise, differentiation leads to uncertainties in $1 + (\mathrm{d}\ \ln\ \gamma_{\pm})/(\mathrm{d}\ \ln\ m)$ of about ± 0.02. For solutions with values of $1 + (\mathrm{d}\ \ln\ \gamma_{\pm})/(\mathrm{d}\ \ln\ m)$ less than 0.1, the corresponding errors in the values of φ_{12} are large: $> \pm 20\%$. Despite the lack of precision, it is clear from Table 1 that the resistance coefficient of sodium decanoate drops by a factor of 4 above the cmc. For sodium hexanoate, on the other hand, the resistance coefficient increases as the concentration is raised.

For comparison with the sodium alkanoate results, Table 1 includes resistance coefficients calculated for aqueous solutions of sodium dodecyl sulfate (Leaist, 1986; Leaist and Lü, 1989). This surfactant system, like aqueous sodium decanoate, shows a decrease in friction near its cmc (0.008 mol dm^{-3} (Mukerjee and Mysels, 1971)). The friction acting on a micellar cluster is much larger than that acting on a single surfactant monomer. On a per mole of surfactant basis, however, transport in the micellar form is actually more efficient. The Stokes law shows that the friction per mole of surfactant monomer acting on a spherical aggregate of N monomers decreases approximately as $N^{-2/3}$ (Leaist, 1986).

Lindman and Brun (1973) have used radioactive tracers and open-ended capillary tubes to measure intradiffusion in aqueous solutions of sodium octanoate. In Figure 2 the intradiffusion coefficients of sodium and octanoate ions are compared with the mutual diffusion coefficient of sodium octanoate measured in the present study. Near the cmc (0.35 mol dm^{-3}) the mutual diffusion coefficient of the salt changes more rapidly than the intradiffusion coefficients of the constituent ions. Also, the mutual diffusion coefficient for the total sodium octanoate component is significantly lower than the average intradiffusion coefficient of the sodium and octanoate ions. These results illustrate that no simple relation exists between the two kinds of diffusion coefficients.

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