Mutual Diffusion Coefficients for Zwitterionic and Ionic Mixed Micellar Systems: A Novel Concentration Dependence

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Mutual diffusion coefficients, D_m, have been measured for aqueous solutions containing N-tetradecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate ($C_{14}DAPS$) and sodium octadecane sulfonate ($C_{18}SO_3Na$) at 298.2 K. For a fixed concentration of $C_{14}DAPS$, D_m values increase with increasing amounts of $C_{18}SO_3Na$. For a fixed ratio of $C_{18}SO_3Na$ to $C_{14}DAPS$, D_m values do not increase with total surfactant concentration. This is in marked contrast with the results obtained for one-component ionic micellar systems.

Mutual diffusion coefficients for ionic micelles have been studied by many workers using various techniques such as dynamic light scattering,[1-11] and dynamic[12-14] and static[15,16] boundary spreading method. In all cases, mutual diffusion coefficients increase with increasing concentration of surfactant above the critical micelle concentrations (cmc).[17] The increase with increasing surfactant concentration was interpreted as being due to the repulsive interactions between charged micelles,[1] and electrostatic interactions between micelles, monomers, and counter ions.[12,13,16] In cases of mixed micellar systems, the charge of the micelles can be controlled and the ionic monomer concentration can be minimized. We report here mutual diffusion coefficients for mixed micellar systems, which display a concentration dependence that is completely different from that for conventional one-component ionic micelles.[1-16]

N-tetradecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate ($C_{14}DAPS$, Calbiochem) and sodium octadecanesulfonate $C_{18}SO_3Na$ (Tokyo Kasei, GR grade) were used as received. Pyrene (Wako Pure Chemical Ind.) was purified by sublimation. Water was distilled twice. Diffusion coefficients were measured by the Taylor dispersion method[12-14,18] with concentration profiles detected by a differential refractometer (Waters, R-401). Fluorescence decay curves were measured using a commercially available time-correlated single-photon counting apparatus (Horiba, NAES-550).

Mutual diffusion coefficients are listed in Table 1 together with standard deviations. Each value is an average of more than four determinations. These are plotted in Figure 1 together with tracer diffusion coefficients.[19] In the case of pure $C_{14}DAPS$, values for the mutual and tracer diffusion coefficients are similar. With increasing amounts of $C_{18}SO_3Na$, i.e., micellar charge, tracer diffusion coefficients decrease while mutual diffusion coefficients increase remarkably. Note that the concentration range is much higher than cmc's.[20]

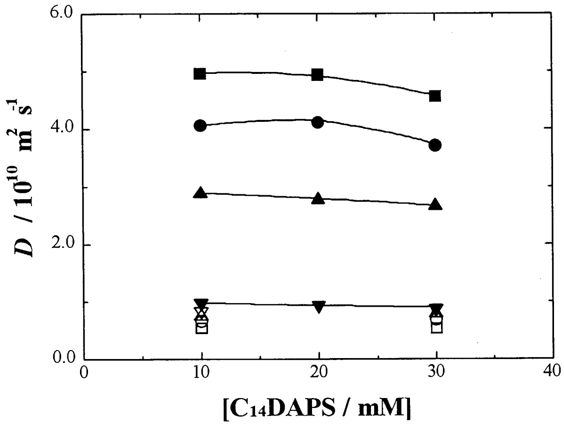

Figure 1. Mutual (closed symbols) and tracer (open symbols) diffusion coefficients for the $C_{18}SO_3Na$ + $C_{14}DAPS$ system. $C_{18}SO_3Na$:$C_{14}DAPS$ (mol:mol) = 0:1 (▽,▼),1:20 (△,▲), 1:10 (○,●), and 1:5 (□,■).

The mutual diffusion coefficient, D_m, of a polyelectrolyte comprised of a polyion with charge q and q monovalent counter ions is given by[21,22]

$$\frac{1}{D_m} = \frac{\frac{1}{D_p} + \frac{q}{D_c}}{1+q} \qquad (1)$$

where D_p and D_c are the tracer diffusion coefficients of the polyion and the counter ion, respectively. In the case of ionic micelles, there are monomer ions in addition to micelles and counter ions. Thus mutual diffusion coefficients are given by complicated functions of the aggregation number of the micelle,

Table 1. Mutual diffusion coefficients, D_m, for $C_{14}DAPS$ + $C_{18}SO_3Na$ mixed micellar systems at 298.2 K

[C_{14}DAPS] / mM[a]	D_m / $10^{-10}m^2s^{-1}$			
	$C_{18}SO_3Na$: $C_{14}DAPS$ (mol : mol)			
	0:1	1:20	1:10	1:5
10	0.977 ± 0.008	2.88 ± 0.07	4.06 ± 0.07	4.97 ± 0.03
20	0.934 ± 0.024	2.77 ± 0.03	4.12 ± 0.01	4.95 ± 0.05
30	0.881 ± 0.028	2.66 ± 0.01	3.71 ± 0.02	4.57 ± 0.04

[a] 1M = 1 mol dm^{-3}.

the number of counter ions bound to the micelle, tracer diffusion coefficients and concentrations of micelles, counter ions, and monomers as a function of the surfactant concentration.[12,13,16] In the limiting case where the monomer concentration is negligible, the mutual diffusion coefficients is given by eq. 1.

In order to estimate micellar charges, q, we determined aggregation numbers of micelles following the method developed by Atik et al.[23] and used by others.[24] The monomer fluorescence decay of pyrene following pulsed excitation is expressed by

$$\ln[I_M(t)/I_M(0)] = n[\exp(-k_E t)-1] - k_I t \qquad (2)$$

where n is the average number of the fluorophore per micelle, k_E is the rate constant for the intramicellar excimer formation, and k_I is the rate constant for the first-order decay of the pyrene monomer. Figure 2 shows the decay curves of the pyrene monomer fluorescence in 10 mM C_{14}DAPS. Aggregation numbers obtained are listed in Table 2. If we assume that all counter ions are dissociated, micellar charges are calculated to be 9.45 and 20.0 for 10 mM C_{14}DAPS + 1 mM $C_{18}SO_3Na$, and 10 mM C_{14}DAPS + 2 mM $C_{18}SO_3Na$ systems, respectively. Using the tracer diffusion coefficients and the q values, D_m values are calculated to be 4.7×10^{-10} and 6.3×10^{-10} $m^2 s^{-1}$ for 10 mM C_{14}DAPS + 1 mM $C_{18}SO_3Na$, and 10 mM C_{14}DAPS + 2 mM $C_{18}SO_3Na$ systems, respectively. The observed values are smaller than the calculated values by 14 and 21% for the former and the latter systems, respectively. This may be partly due to the effect of the presence of a small amount of $C_{18}SO_3^-$ monomers in the water phase[25] and counter ion association to the micellar surface.

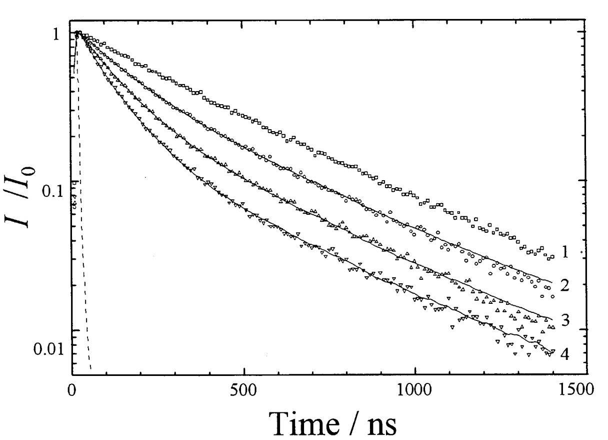

Figure 2. Fluorescence decay curves for pyrene in 10mM C_{14}DAPS at 298.2 K. [Pyrene] = 1.93 μM (1), 64.3 μM (2), 128.5 μM (3), and 192.8 μM (4). The solid lines are the best-fit curves calculated according to eq. 2. The broken line is the instrument response function.

One of the most remarkable findings is that the mutual diffusion coefficients are already high at 10 mM and do not increase with increasing surfactant concentration. This is in marked contrast with the results for pure ionic micellar systems.[1-16] Although similar results have been found for a protein solution,[26] this is the first observation for micellar systems as far as we know. The present results can be interpreted in terms of electrostatic coupling between micelles and counter ions rather than intermicellar electrostatic repulsion.

Table 2. Aggregation numbers for micelles

[C_{14}DAPS] / mM	[$C_{18}SO_3Na$] / mM	aggregation number
10	0	87
10	1	104
10	2	120

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