Diffusion in Solutions of Micelles. What Does Dynamic Light Scattering Measure?[†]

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Dynamic light scattering (DLS) is routinely used to measure the diffusion of surfactant micelles. Theory and experiment suggest, however, that the microscopic concentration fluctuations monitored by DLS obey the same mutual diffusion equations that describe the decay of macroscopic concentration gradients. According to this interpretation, DLS provides mutual diffusion coefficients for the total surfactant components, including contributions from micelles, free surfactant monomers, and counterions. An attempt is made to decide the correct interpretation of DLS measurements by comparing DLS diffusion coefficients (D_{DLS}) with mutual diffusion coefficients measured by macroscopic gradient techniques for binary aqueous solutions of ionic and zwitterionic surfactants. Possible contributions to D_{DLS} from free surfactant monomers are investigated by extending DLS measurements into the critical micelle (cmc) region where substantial portions of the surfactants diffuse as free monomers. The widely held assumption that D_{DLS} is the micelle diffusion coefficient is tested by comparing D_{DLS} with micelle diffusion coefficients measured unambiguously by NMR or Taylor dispersion techniques for solubilized trimethylsilane or decanol tracers. D_{DLS} is found to decrease sharply as the surfactant concentration is raised through the cmc, in agreement with the steep drop in the mutual diffusion coefficient caused by the association of free surfactant monomers. Above the cmc, D_{DLS} and the micelle and mutual diffusion coefficients are nearly identical for the zwitterionic surfactants. For the ionic surfactants, D_{DLS} and the mutual diffusion coefficients are several times larger than the micelle diffusion coefficients as a result of the diffusion of charged micelles with relatively mobile counterions to maintain electroneutrality. The results suggest that DLS diffusion coefficients are surfactant mutual diffusion coefficients.

Introduction

Dynamic light scattering (DLS) is frequently used to measure diffusion in solutions of surfactant micelles.[1–24] In contrast to macroscopic gradient experiments employing techniques such as optical interferometry or Taylor dispersion, DLS measurements can be made rapidly (in minutes) and conveniently on small samples of solution (< 1 cm^3). The analysis of micelle diffusion data from DLS measurements provides valuable information about micelle shapes and sizes, hydrodynamic radii, micelle−micelle interactions, and salt effects. Implicit in this work is the assumption that DLS measures the micelle diffusion coefficient (D_{mic}) which relates the flux of micelles (j_{mic}) to the micelle concentration gradient (∇c_{mic}).

$$j_{mic} = -D_{mic} \nabla c_{mic} \tag{1}$$

This interpretation of DLS measurements is sensibly based on the fact that micelles scatter light orders of magnitude more strongly than other solution species, such as free surfactant monomers or counterions.

Despite numerous reports of micelle diffusion coefficients and derived hydrodynamic radii from DLS measurements, theoretical considerations[25,26] and experimental evidence[27–34] suggest that the microscopic concentration fluctuations monitored by DLS obey the same mutual diffusion equations that describe the decay of macroscopic concentration gradients. According to this school of thought, DLS measurements on surfactant solutions provide mutual diffusion coefficients D relating the total surfactant flux J to the gradient ∇C in the total surfactant concentration.

$$J(\text{total surfactant}) = -D \nabla C(\text{total surfactant}) \tag{2}$$

Total surfactant components diffuse as micelles and relatively mobile species, such as free surfactant monomers and free counterions (for ionic surfactants). The mutual diffusion coefficients of surfactant solutions[33–35] are therefore larger than micelle diffusion coefficients.

To assess the different interpretations of DLS measurements, it is informative to compare micelle and mutual diffusion coefficients for typical surfactant solutions. The simplest case is a nonionic or zwitterionic surfactant that diffuses as free monomers (S_1) and monodisperse micelles (S_m) with aggregation number m. Combining the equations for mass balance

$$C = c_1 + mc_{mic} \tag{3}$$

$$J = j_1 + mj_{mic} = -D_1 \nabla c_1 - mD_{mic} \nabla c_{mic} \tag{4}$$

and local equilibrium of the association reaction

$$mS_1 \leftrightarrow S_m \qquad K = c_{mic}/c_1^{\,m} \tag{5}$$

shows that the mutual diffusion coefficient of the total surfactant component (D) is the average of the free-monomer diffusion coefficient (D_1) and the micelle diffusion coefficient (D_{mic}) with respective weighting factors c_1 and m^2c_{mic}.[29,30,36,37]

$$D = \frac{c_1D_1 + m^2c_{mic}D_{mic}}{c_1 + m^2c_{mic}} \tag{6}$$

Figure 1 is a plot of mutual diffusion coefficients for nonionic and zwitterionic surfactants calculated using eq 6 and the

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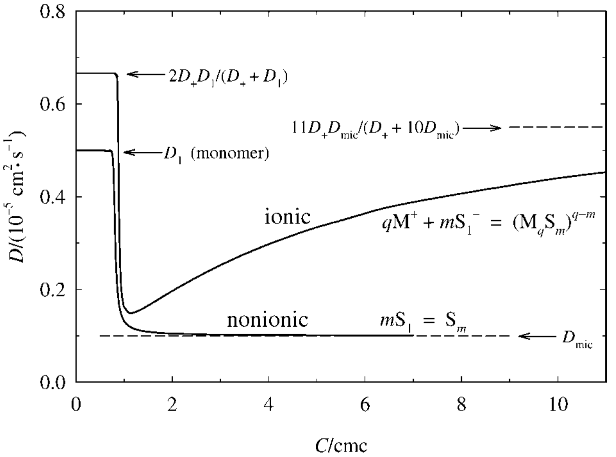

Figure 1. Mutual diffusion coefficients D for nonionic surfactants (eq 6) and ionic surfactants (eq 7) plotted against the total surfactant concentration for surfactants with: micelle diffusion coefficient $D_{\mathrm{mic}} = 0.10 \cdot 10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$, free-monomer diffusion coefficient $D_1 = 0.50 \cdot 10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$, free-counterion diffusion coefficient $D_+ = 1.0 \cdot 10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$, aggregation number $m = 60$, and extent of counterion binding $q/m = 0.83$.

representative values $D_{\mathrm{mic}} = 0.10 \cdot 10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$, $D_1/D_{\mathrm{mic}} = 5$, aggregation number $m = 60$, and the well-known approximation $K = (\mathrm{cmc})^{1-m}$ for the equilibrium constant for micelle formation. Below the cmc, where the concentration of micelles is negligible, the surfactant mutual diffusion coefficient D equals the free-monomer diffusion coefficient D_1. As the surfactant concentration is raised through the cmc, the sudden onset of monomer association produces a steep drop in the mutual diffusion coefficient. This unusual behavior is a thermodynamic effect[35,36] caused by the sudden decrease in the number of free monomers per mole of added surfactant at the cmc, which in turn sharply reduces the gradient in surfactant chemical potential, the driving force for mutual diffusion.[38] As the surfactant concentration is raised above the cmc, the mutual diffusion coefficient is soon dominated by the micelle diffusion coefficient because of its heavy m^2c_{mic}-weighting factor. At compositions C/cmc > 5, the mutual and micelle diffusion coefficients differ by less than 5 %. Data in the cmc region would therefore appear to be most useful in helping to distinguish between the micelle and mutual diffusion interpretations of DLS measurements for nonionic and zwitterionic surfactants.

The diffusion behavior of ionic surfactants is qualitatively different.[29,30,35] In this case, the diffusion of charged micelles with relatively mobile free counterions generates an electric field which speeds up the micelles and slows down the counterions to maintain electroneutrality along the diffusion path. For an ionic surfactant that forms $(\mathrm{M}_q\mathrm{S}_m)^{q-m}$ micelles consisting of m surfactant ions (S_1^-) and q bound counterions (M^+), the equations for mass balance, local equilibrium, and electroneutrality lead to the rather cumbersome expression for the mutual diffusion coefficient[29,30,35]

$$D = \frac{c_1c_+D_1D_+ + q^2c_1c_{\mathrm{mic}}D_1D_{\mathrm{mic}} + m^2c_+c_{\mathrm{mic}}D_+D_{\mathrm{mic}}}{c_1D_1 + c_+D_+ + (m-q)^2c_{\mathrm{mic}}D_{\mathrm{mic}}} \times \frac{c_1 + c_+ + (m-q)^2c_{\mathrm{mic}}}{c_1c_+ + q^2c_1c_+ + m^2c_+c_{\mathrm{mic}}} \tag{7}$$

in terms of the diffusion coefficients of the micelles (D_{mic}), free surfactant monomers (D_1), and free counterions (D_+). The concentrations of these species are denoted by c_{mic}, c_1, and c_+, respectively.

Figure 1 shows mutual diffusion coefficients for ionic surfactants calculated from eq 7 using $m = 60$, $q = 50$, $D_1/D_{\mathrm{mic}} = 5$, and $D_+/D_{\mathrm{mic}} = 10$. Once again, there is a sharp drop in D at the cmc, but in this case D increases as the surfactant concentration is raised further. This surprising behavior is a result of ionic diffusion. At high surfactant concentrations, where the concentration of free surfactant monomers is relatively small, the expression for the mutual diffusion coefficient simplifies to the Nernst equation for the mutual diffusion coefficient of a q:($m - q$) strong electrolyte.[35,38]

$$D \approx \frac{(1 + m - q)D_+D_{\mathrm{mic}}}{D_+ + (m-q)D_{\mathrm{mic}}} \quad (C \gg \mathrm{cmc}) \tag{8}$$

In this limit, as shown in Figure 1, the mutual diffusion coefficients calculated for ionic surfactants are about five times larger than the micelle diffusion coefficient. These calculations, though qualitative, suggest that data for ionic surfactants would be particularly useful to decide between the micelle and mutual diffusion interpretations of DLS measurements.

If micelles are the only species in surfactant solutions that scatter light appreciably, then it is not immediately obvious that DLS measurements can provide mutual diffusion coefficients which include contributions from free surfactant monomers and free counterions. A similar situation is encountered when ionic conductivity techniques are used to measure diffusion in solutions of a weak electrolyte,[38–40] such as aqueous acetic acid. Conductivity detectors "see" only the ionized form of the total acid component. In solution, however, the rapidly interconverting ionized ($\mathrm{H}^+ + \mathrm{A}^-$) and molecular (HA) forms of the acid diffuse in local equilibrium. Consequently, conductivity techniques measure the mutual diffusion coefficient of the total acid component, a weighted average of the diffusion coefficients of the ionized and molecular acid. The mutual diffusion interpretation of DLS measurements for surfactant solutions, by analogy, hinges on the equilibration of surfactant monomers, micelles, and counterions on timescales that are rapid compared to the time scale of DLS measurements (about 10^{-5} s).

Other interpretations of DLS measurements for surfactant solutions can be justified. If the monomer–micelle exchange kinetics are too slow to maintain local equilibrium, then DLS diffusion coefficients could be intermediate between the micelle and mutual diffusion coefficients. Similar considerations apply to very dilute solutions of ionic surfactants for which the Debye length κ^{-1} is comparable to the wavelength of the incident light.[41] The mutual diffusion interpretation of DLS measurements would be invalid in this case because fluctuations in the concentration of charged micelles are no longer coupled by electroneutrality to the fluctuations in the concentrations of free monomers and free counterions. For nonelectrolyte surfactants, the additional suggestion has been made that DLS yields the concentration-weighted average diffusion coefficient[48]

$$D^* = \frac{c_1D_1 + mc_{\mathrm{mic}}D_{\mathrm{mic}}}{c_1 + mc_{\mathrm{mic}}} \tag{9}$$

with contributions from the micelle and free-monomer diffusion coefficients weighted in proportion to the fraction of the total surfactant diffusing in micellar and monomeric form, mc_{mic}/C and c_1/C, respectively. Whereas D^* is the ic_i-weighted average of the diffusion coefficients of the i-mers, eq 6 illustrates that the mutual diffusion coefficient is the corresponding i^2c_i-weighted average.[36,37]

The purpose of the work reported in this paper is to use diffusion data to investigate the correct interpretation of DLS measurements for surfactant solutions. With this goal in mind, DLS diffusion coefficients measured for binary aqueous solutions of eight different surfactants (zwitterionic and ionic) are compared with well-defined mutual diffusion coefficients measured previously[34,35,42–45] by accurate macroscopic gradient techniques. To search for possible contributions to the DLS diffusion coefficients from free surfactant monomers, the DLS measurements are extended into the interesting cmc region where substantial portions of the total surfactant components diffuse as free monomers. The widely held assumption that DLS measures micelle diffusion coefficients is tested by comparing the DLS diffusion coefficients with micelle diffusion coefficients measured unambiguously for micelle-solubilized trimethylsilane (TMS) or decanol tracers using pulsed-gradient spin−echo NMR spectroscopy (Paduano et al.)[46] or Taylor dispersion (this work).

Experimental Section

Materials. Decyl sulfobetaine, dodecyl sulfobetaine, decanol, and the sodium alkyl sulfonates were Sigma products (purity > 99 %). Sodium dodecyl sulfate (purity > 99 %) was supplied by EMD Chemicals. Solutions were prepared by dissolving weighed amounts of solutes in distilled, deionized water in calibrated volumetric flasks.

DLS Diffusion Measurements. DLS diffusion coefficients were measured with a 35 mW laser (wavelength $\lambda = 832.0$ nm), a 90°-scattering cell (Hellma no. 176.050), a photodiode detector, and a correlator with 250 ns channels (Wyatt Technologies). The intensity autocorrelation functions were single-exponential decays with baselines that were unity within the precision of the measurements. DLS diffusion coefficients were evaluated by fitting the equation

$$G(\tau) = A\exp(-2q^2 D_{\mathrm{DLS}}\tau) \qquad (10)$$

to the baseline-subtracted correlation functions $G(\tau)$, treating D_{DLS} and the pre-exponential factor A as adjustable parameters. τ is the delay time. The magnitude of the scattering vector

$$q = \frac{4\pi n}{\lambda}\sin(\theta/2) = 1.418 \cdot 10^5\ \mathrm{cm}^{-1} \qquad (11)$$

was evaluated using the refractive index n of pure water. Check calculations using measured refractive increments[42,43] $\mathrm{d}n/\mathrm{d}C$ showed that this approximation led to negligible errors (< 0.2 %) in the calculated DLS diffusion coefficients, even for the most concentrated solutions used in the present study. Dust was removed from the solutions by a 0.2 μm Teflon filter followed by a 0.02 μm Anotop membrane. The filters and the scattering cell were flushed with solution to ensure that surfactant adsorption was negligible. Inserting additional filters in the line leading to the scattering cell produced no detectable changes in the correlation functions or the calculated diffusion coefficients.

Micelle Diffusion Coefficients. Micelle diffusion coefficients were measured by Taylor dispersion for trace amounts of solubilized decanol. Small samples of solution (0.020 cm^3) containing surfactant at concentration C and n-decanol at concentration ΔC^* were injected into binary carrier solutions containing surfactant at concentration C. A differential refractometer detector (Agilent model 1100) monitored the broadened distribution of the injected samples at the outlet of a Teflon dispersion tube (length 3000 cm, internal radius $r = 0.0385_5$ cm). Retention times (t_{R}) were typically $(1.5 \pm 0.1) \cdot 10^4$ s.

The tracer dispersion profiles were analyzed by fitting the equation[47]

$$V(t) = V_0 + V_1 t + \sqrt{\frac{t_{\mathrm{R}}}{t}}\left[\Delta V \exp\left(-\frac{12D(t-t_{\mathrm{R}})^2}{r^2 t}\right) + \Delta V_{\mathrm{mic}} \exp\left(-\frac{12D_{\mathrm{mic}}(t-t_{\mathrm{R}})^2}{r^2 t}\right)\right] \qquad (12)$$

to the measured refractometer voltages, treating the micelle diffusion coefficient D_{mic} and the surfactant mutual diffusion coefficient D as adjustable least-squares parameters together with the baseline voltage V_0, baseline slope V_1, retention time t_{R}, and the peak heights ΔV_{mic}, ΔV for tracer and mutual diffusion. The injected solutions contained decanol at low concentrations ($\Delta C^* \leq 0.003$ mol·dm^{-3}). By the time the injected solution samples reached the detector, dilution with the carrier stream produced n-decanol concentrations that were about 100 times lower, with negligible effect on micelle size or structure.

The equation fitted to the decanol tracer profiles includes a decay in the mutual diffusion coefficient (D) of the surfactant solution. This term is required because it is impossible in practice to prepare surfactant carrier solutions and surfactant + decanol injection solutions containing surfactant at precisely the same concentration. The tracer diffusion of solubilized decanol with the micelle diffusion coefficient D_{mic} is therefore accompanied by the diffusion of a small amount of surfactant with mutual diffusion coefficient D.

Mutual diffusion in aqueous surfactant (1) + alcohol (2) solutions is generally complicated by coupled fluxes of alcohol produced by surfactant concentration gradients.[49,50] For the solutions used in the present study, however, the concentration of decanol is effectively zero. Cross-diffusion coefficient D_{21} for the coupled diffusion of decanol vanishes in this limit because it is impossible for a surfactant concentration gradient to drive a coupled flow of decanol in a solution that does not contain decanol. Consequently, the tracer diffusion of decanol is described by a single diffusion coefficient, D_{mic}. Taylor measurements of tracer diffusion are described in more detail in a previous study.[47]

Results

DLS Diffusion Coefficients. DLS diffusion coefficients were measured for binary aqueous solutions of NaDS and the sodium alkylsulfonates. At least 50 correlations were measured at each composition. The average D_{DLS} values and their uncertainties are listed in Table 1. These results and the DLS diffusion coefficients for aqueous SB10 and SB12 solutions measured previously in this laboratory[32] are plotted against the total surfactant concentration in Figures 2 to 9. The reproducibility of the D_{DLS} values was generally within ± 2 %, though poorer near the cmc where the concentration of micelles and therefore the intensity of the scattered light were relatively low.

Micelle Diffusion Coefficients. Taylor dispersion was used to measure the tracer diffusion of solubilized decanol in solutions of SB10, SB12, and NaDS. The average micelle diffusion coefficients from four to six replicate measurements at each composition are summarized in Table 2.

Discussion

In this section, DLS diffusion coefficients for solutions of the zwitterionic and ionic surfactant are compared with mutual and micelle diffusion coefficients measured in this study and in previous studies.[34,35,42–46] The sources of the D_{DLS}, D, and D_{mic} data are summarized in Table 3.

Zwitterionic Surfactants. DLS, mutual, and micelle diffusion coefficients for aqueous solutions of SB10 and SB12 are plotted

Table 1. DLS Diffusion Coefficients[a] for Binary Aqueous Surfactant Solutions at 25 °C

C (mol·dm^{-3})	D (10^{-5} cm^2·s^{-1})	C (mol·dm^{-3})	D (10^{-5} cm^2·s^{-1})
Sodium Dodecyl Sulfate (NaDS)			
0.0150	0.188(4)	0.0400	0.347(7)
0.0200	0.224(5)	0.0450	0.366(7)
0.0250	0.261(5)	0.0500	0.382(8)
0.0300	0.297(6)	0.0600	0.407(8)
0.0350	0.318(6)	0.0695	0.423(8)
Sodium Hexyl Sulfonate (NaC_6SO_3)			
0.513	0.77(6)	0.803	0.34(3)
0.556	0.71(6)	0.871	0.31(3)
0.556	0.72(1)	0.951	0.28(2)
0.598	0.62(3)	1.022	0.27(4)
0.638	0.53(2)	1.166	0.26(1)
0.678	0.47(1)	1.301	0.26(1)
0.724	0.398(8)		
Sodium Heptyl Sulfonate (NaC_7SO_3)			
0.286	0.79(7)	0.484	0.269(4)
0.309	0.70(3)	0.506	0.264(3)
0.331	0.53(1)	0.548	0.258(2)
0.353	0.41(1)	0.590	0.255(1)
0.376	0.354(2)	0.631	0.255(1)
0.398	0.318(4)	0.710	0.258(2)
0.421	0.296(2)	0.786	0.263(4)
0.442	0.284(4)	0.852	0.264(2)
0.463	0.275(3)		
Sodium Octyl Sulfonate (NaC_8SO_3)			
0.174	0.43(2)	0.329	0.258(2)
0.193	0.297(5)	0.374	0.265(3)
0.231	0.248(2)	0.414	0.272(2)
0.258	0.242(2)	0.458	0.282(3)
0.285	0.247(2)	0.525	0.292(4)
Sodium Nonyl Sulfonate (NaC_9SO_3)			
0.0882	0.38(4)	0.193	0.256(8)
0.0978	0.245(12)	0.239	0.281(4)
0.109	0.221(6)	0.284	0.302(4)
0.122	0.215(4)	0.326	0.320(4)
0.146	0.223(2)	0.369	0.333(4)
Sodium Undecyl Sulfonate ($NaC_{11}SO_3$)			
0.0229	0.140(9)	0.0486	0.214(3)
0.0248	0.143(6)	0.0585	0.243(1)
0.0269	0.144(4)	0.0681	0.269(4)
0.0293	0.150(1)	0.0772	0.291(4)
0.0293	0.153(4)	0.0873	0.311(2)
0.0390	0.187(2)	0.0997	0.332(3)

[a] Uncertainties in the last digits of the D_{DLS} values are given as two standard errors (in parentheses).

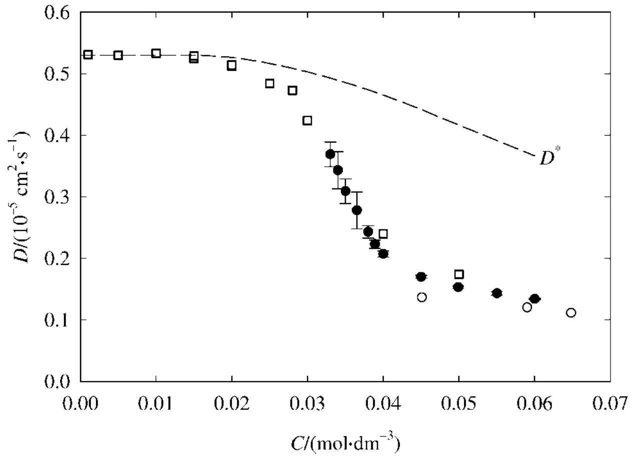

Figure 2. ●, DLS;[34] □, mutual;[36] ○, micelle; and D^*, intradiffusion coefficients for aqueous solutions of decyl sulfobetaine (SB10) at 25 °C.

against the total surfactant concentration in Figures 2 and 3. The sharp drop in the mutual diffusion coefficients caused by micelle formation at the cmc (0.032 mol·dm^{-3} for SB10 and 0.0028 mol·dm^{-3} for SB12)[34] is clearly evident. Reliable DLS diffusion coefficients could not be determined below the cmc due to the low intensity of light scattered by the free surfactant monomers. Nevertheless, the D_{DLS} coefficients measured just above the cmc region closely follow the sharply dropping mutual diffusion coefficients. The results obtained in the cmc region suggest that DLS is measuring the mutual diffusion coefficients of the SB10 and SB12 solutions, with the diffusing micelles in

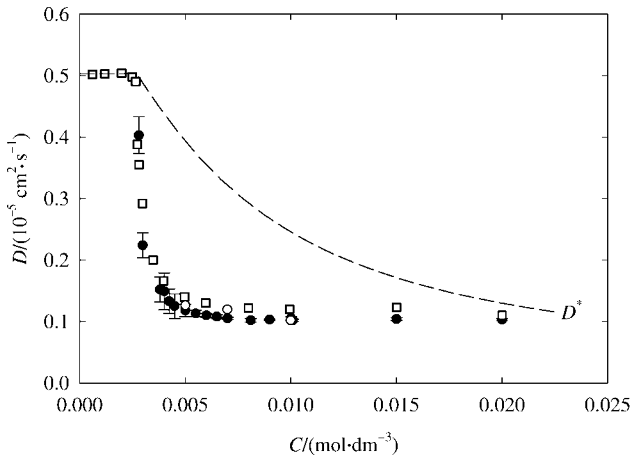

Figure 3. ●, DLS;[34] □, mutual;[45] ○, micelle; and D^*, intradiffusion coefficients for aqueous solutions of dodecyl sulfobetaine (SB12) at 25 °C.

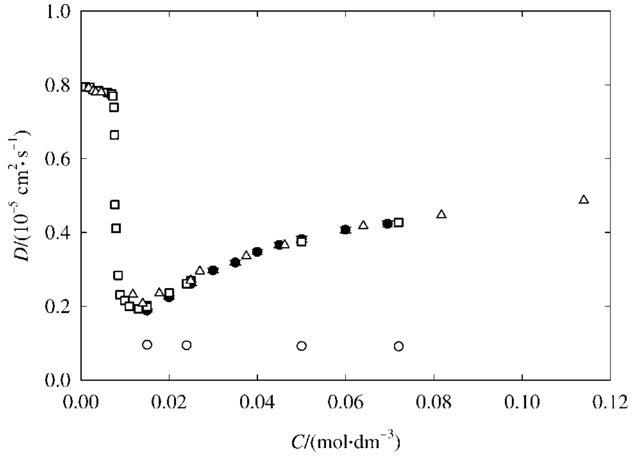

Figure 4. ●, DLS; □, mutual;[35,45] and ○, micelle diffusion coefficients for aqueous solutions of sodium dodecyl sulfate (NaDS) at 25 °C.

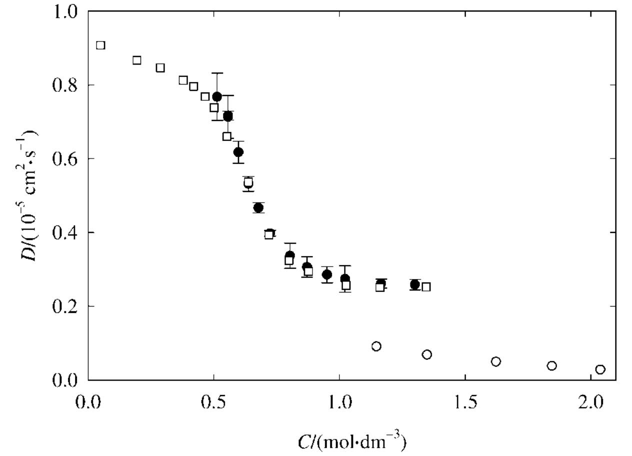

Figure 5. ●, DLS; □, mutual (Paduano et al.[42]); and ○, micelle (Annunziata et al.[46]) diffusion coefficients for aqueous solutions of sodium hexyl sulfonate (NaC_6SO_3) at 25 °C.

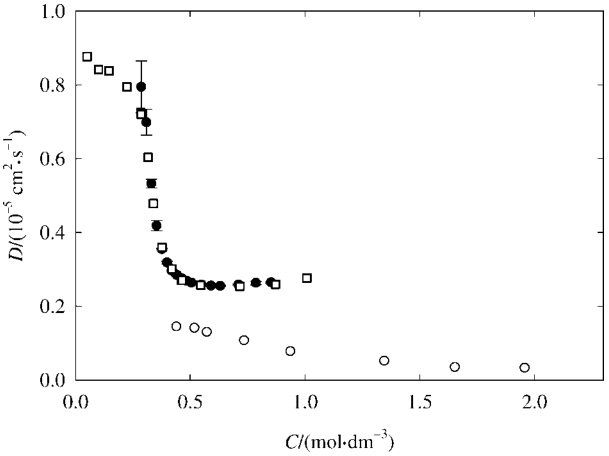

Figure 6. ●, DLS; □, mutual (Annunziata et al.[43]); and ○, micelle (Annunziata et al.[46]) diffusion coefficients for aqueous solutions of sodium heptyl sulfonate (NaC_7SO_3) at 25 °C.

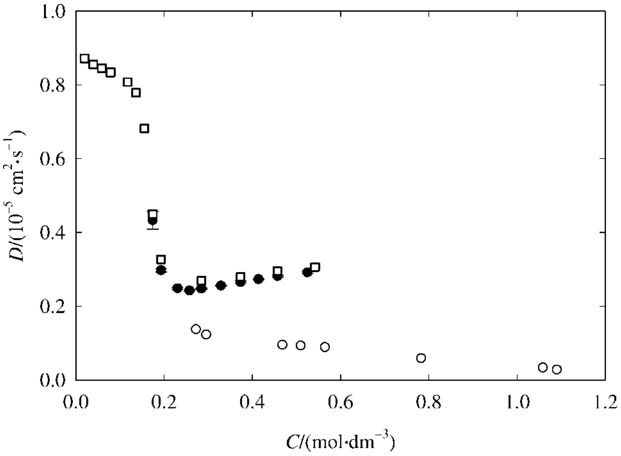

Figure 7. ●, DLS; □, mutual (Ortona et al.[44]); and ○, micelle (Annunziata et al.[46]) diffusion coefficients for aqueous solutions of sodium octyl sulfonate (NaC_8SO_3) at 25 °C.

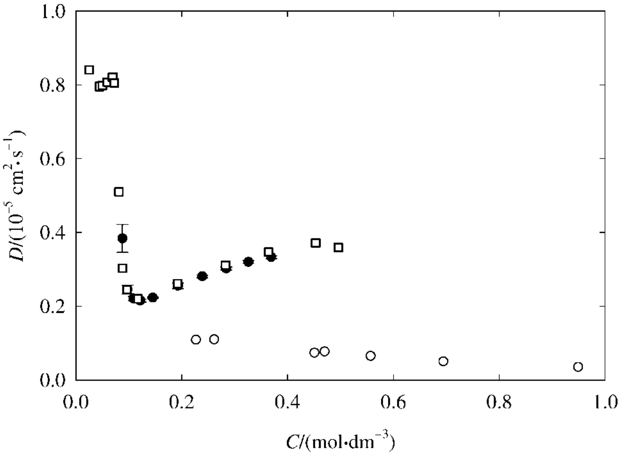

Figure 8. ●, DLS; □, mutual (Annunziata et al.[43]); and ○, micelle (Annunziata et al.[46]) diffusion coefficients for aqueous solutions of sodium nonyl sulfonate (NaC_9SO_3) at 25 °C.

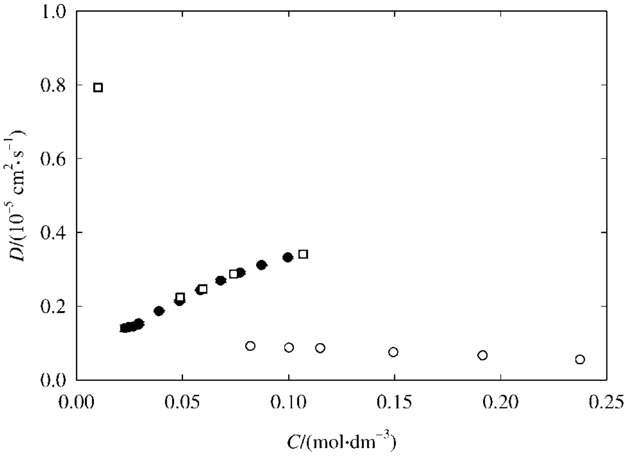

Figure 9. ●, DLS; □, mutual (Annunziata et al.[43]); and ○, micelle (Annunziata et al.[46]) diffusion coefficients for aqueous solutions of sodium undecyl sulfonate ($NaC_{11}SO_3$) at 25 °C.

Table 2. Micelle Diffusion Coefficients and Mutual Diffusion Coefficients[a] at 25 °C Measured by Taylor Dispersion for Trace Amounts of Decanol Solubilized in Aqueous Surfactant Solutions

C	D_{mic}	D
$(mol \cdot dm^{-3})$	$(10^{-5}\ cm^2 \cdot s^{-1})$	$(10^{-5}\ cm^2 \cdot s^{-1})$
Decyl Sulfobetaine (SB10)		
0.0451	0.136(3)	0.181
0.0590	0.120(3)	0.149
0.0648	0.111(2)	0.140
Dodecyl Sulfobetaine (SB12)		
0.00502	0.126(2)	0.121
0.00699	0.119(3)	0.113
0.01001	0.102(2)	0.113
Sodium Dodecyl Sulfate (NaDS)		
0.0150	0.095(2)	0.198
0.0242	0.094(2)	0.261
0.0501	0.092(2)	0.375
0.0721	0.091(2)	0.427

[a] Uncertainties in the last digits of the values of D_{mic} and D are given as two standard errors (in parentheses).

Table 3. Sources of DLS Diffusion Coefficients (D_{DLS}), Mutual Diffusion Coefficients (D), and Micelle Diffusion Coefficients (D_{mic})

surfactant	D_{DLS}	D	D_{mic}
SB10	ref 34	Taylor dispersion[34]	Taylor dispersion, decanol (this work)
SB12	ref 34	Taylor dispersion[45]	Taylor dispersion, decanol (this work)
NaDS	this work	conductometric[35] Taylor dispersion[45]	Taylor dispersion, decanol (this work)
NaC_6SO_3	this work	Gouy interferometry[42]	NMR, trimethylsilane[46]
NaC_7SO_3	this work	Gouy interferometry[43]	NMR, trimethylsilane[46]
NaC_8SO_3	this work	Taylor dispersion[44]	NMR, trimethylsilane[46]
NaC_9SO_3	this work	Gouy interferometry[43]	NMR, trimethylsilane[46]
$NaC_{11}SO_3$	this work	Gouy interferometry[43]	NMR, trimethylsilane[46]

local equilibrium with the relatively mobile free surfactant monomers. As the surfactant concentration is raised farther above the cmc, and the contribution to the mutual diffusion coefficient from the free surfactant monomers becomes unimportant, the DLS diffusion coefficients continue to follow the concentration dependence of the mutual diffusion coefficient, although the D_{DLS} values are a few percent smaller than D. In this composition region, the differences between the D_{DLS}, D, and D_{mic} coefficients are too small to distinguish between the micelle and mutual diffusion interpretations of DLS measurements.

In addition to the micelle and mutual diffusion interpretations of DLS measurements, it has been suggested that D_{DLS} for nonelectrolyte surfactant solutions represents the average of the micelle and free-monomer diffusion coefficients[48] weighted in proportion to the fractions of the total surfactant diffusing in micellar and monomeric form (eq 9). This simple average of D_1 and D_{mic} is the surfactant intradiffusion[36,37] coefficient D^* that describes surfactant diffusion in solutions of uniform chemical composition, as measured by techniques such as NMR spectroscopy. For dilute solutions of associating nonelectrolyte solutes, including nonionic and zwitterionic surfactants, the solute intradiffusion coefficient is the integral mutual diffusion coefficient[36,37]

$$D^*(C) = \frac{1}{C}\int_0^C D(C')\,\mathrm{d}C' \tag{13}$$

To investigate the possibility that D_{DLS} is the surfactant intradiffusion coefficient, values of D^* for aqueous SB10 and SB12 calculated by numerical integration of the measured mutual diffusion coefficients according to eq 13 are plotted in Figures 2 and 3. The contribution to the intradiffusion coefficient from the micelle diffusion coefficient is weighted as mc_m, whereas the micelle contribution to the mutual diffusion coefficient is much more heavily weighted, in proportion to m^2c_m. Consequently, the intradiffusion coefficients of SB10 and SB12 are substantially larger than both the DLS and mutual diffusion coefficients at compositions above the cmc. This comparison does not support the suggestion that DLS measures surfactant intradiffusion coefficients.

Ionic Surfactants. The diffusion coefficients of the ionic surfactant solutions are plotted in Figures 4 to 9. The DLS data for the hexyl, heptyl, and octyl sulfonates extend well into the cmc region. For these surfactants, the sharp drop in the DLS coefficients with increasing surfactant concentration, in good agreement with the mutual diffusion coefficients, indicates once again that D_{DLS} is the mutual diffusion coefficient. This result is supported by the close agreement between D_{DLS} and D at higher surfactant concentrations. For the NaDS solutions and the solutions of octyl, nonyl, and undecyl sulfonates, moreover, the DLS diffusion measurements agree with the mutual diffusion measurements in the composition region where the mutual diffusion coefficients increases substantially with surfactant concentration as a result of the counterion-accelerated diffusion of the charged micelles.

The good agreement between the DLS and mutual diffusion coefficients implies that the rates of the association/dissociation reactions are sufficiently rapid to maintain local equilibrium on the time scale of the DLS measurements. The DLS diffusion coefficients range from about $0.10 \cdot 10^{-5}$ cm$^2 \cdot$s^{-1} to $0.80 \cdot 10^{-5}$ cm$^2 \cdot$s^{-1} for the surfactant solutions used in the present study. The corresponding decay times in the autocorrelation functions, defined as $(2q^2D_{\mathrm{DLS}})^{-1}$, range from about (50 to 5) μs. Monomer−micelle and counterion−micelle exchange kinetics are considerably more rapid. For example, the relaxation times for the $\mathrm{S_1^-} + (\mathrm{M}_q\mathrm{S}_m)^{q-m} = (\mathrm{M}_q\mathrm{S}_{m+1})^{q-m-1}$ and $\mathrm{M^+} + (\mathrm{M}_q\mathrm{S}_m)^{q-m} = (\mathrm{M}_{q+1}\mathrm{S}_m)^{q+1-m}$ exchange reactions are typically < 0.1 μs.[51−53] The DLS measurement of surfactant mutual diffusion micelles in local equilibrium with free surfactant monomers and free counterions would appear to be feasible.

Paduano and co-workers[46] have used pulsed-gradient spin−echo NMR spectroscopy to measure accurate intradiffusion coefficients for trace amounts of trimethylsilane (TMS) in aqueous solutions of sodium alkyl sulfonates. The TMS intradiffusion coefficients and the TMS mutual diffusion coefficients are identical at these compositions. Moreover, all of the detectable TMS was solubilized in the micelles, so the TMS diffusion coefficients are identical to the micelle diffusion coefficients. The TMS diffusion coefficients can therefore be compared with the DLS diffusion coefficients to test the widely held assumption that DLS measures micelle diffusion coefficients. As shown in Figures 5 to 9, the DLS diffusion coefficients are two to five times larger than the micelle diffusion coefficients for the sodium *n*-alkyl sulfonates. The DLS diffusion coefficients for aqueous NaDS are also several times larger than the micelle diffusion determined by Taylor dispersion for solubilized decanol (Figure 4). These results demonstrate that DLS does not measure micelle diffusion coefficients for the ionic surfactants.

The DLS and mutual diffusion coefficients for the ionic surfactants are significantly larger than the micelle diffusion coefficients as the result of the diffusion of charged micelles with relatively mobile free counterions. The micelles are "pulled along" by the electric field (diffusion potential gradient) generated internally by the surfactant concentration gradient. In principle, DLS could be used to measure micelle diffusion coefficients by adding a sufficiently large excess of an inert supporting electrolyte to screen the diffusion potential gradient. In practice, however, supporting electrolytes are not inert spectators. They change the micelle size, the micelle shape, and the extent of counterion binding.[54,55] Also, diffusion in solutions of an ionic surfactant with added electrolyte (e.g., aqueous NaDS + NaCl solutions) is a strongly coupled, multicomponent diffusion process.[29] Experiment and theory indicate that DLS diffusion measurements for these solutions yield the lower eigenvalue of the matrix of multicomponent mutual diffusion coefficients[31−34] and not the micelle diffusion coefficient.

Conclusions

Diffusion coefficients for aqueous solutions of zwitterionic and ionic surfactants measured by DLS have been compared with mutual diffusion coefficients measured by macroscopic gradient techniques and with micelle diffusion coefficients measured for tracer amounts of solubilizates. Raising the surfactant concentration through the cmc produces a sharp drop in the DLS diffusion coefficients, closely following the concentration dependence of the mutual diffusion coefficients. At surfactant concentrations well above the cmc, where free surfactant monomers are less important, the DLS diffusion coefficients for the zwitterionic surfactant solutions are nearly identical to the micelle and mutual diffusion coefficients. For the ionic surfactants, the DLS and mutual diffusion coefficients are identical within the precision of the measurements but considerably larger than the micelle diffusion coefficient as a result of the mutual diffusion of the charged micelles together with relatively mobile counterions to maintain electroneutrality. The results obtained support the suggestion that DLS measures surfactant mutual diffusion coefficients, including contributions from the micelles and the relatively mobile free surfactant monomers. Caution is recommended in regarding DLS diffusion coefficients for surfactant solutions as micelle diffusion coefficients, especially for measurements made in the cmc region and for ionic surfactants at all compositions.

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