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Mutual and Intradiffusion Coefficients for the Binary System *n*-Decyl Dimethyl Phosphine Oxide + Water at 25 °C

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Diffusion coefficients for the binary system *n*-decyl dimethyl phosphine oxide + water have been studied at 25 °C, with the aim to quantitatively describe the surfactant micellization process in aqueous medium. Accurate mutual diffusion coefficients have been measured by the Taylor dispersion technique. Intradiffusion coefficients of both components have been measured by the pulsed gradient spin echo (PGSE)−FT NMR technique. The data have been compared and interpreted in the framework of the equilibrium model of surfactant self-aggregation. Interpolation of the mutual diffusion coefficients has allowed us to estimate reliable values of the average number of surfactant molecules involved in the formation of a micellar aggregate and the constant of the equilibrium between these aggregates and surfactant unimers. Interpolation of water intradiffusion coefficients has allowed us to estimate the number of water molecules involved in the hydration of surfactants in unimeric and micellized form.

Introduction

Surfactants are the main components of aqueous formulations used for solubilization and delivery of actives (e.g., in pharmaceutics) or, alternatively, for solubilization and removal of contaminants (e.g., in detergency). In both cases, diffusion of surfactant aggregates in the mixtures is fundamental in determining the treatment effectiveness. Furthermore, from a basic viewpoint, the study of the transport properties of surfactant aqueous solutions is extremely informative on the system microstructure as determined by the molecular self-aggregation.

In the literature, diffusion data are available only for a limited number of surfactants.[1] Particularly, some of us studied the aqueous solutions of various nonionic alkyl ethoxylated,[2–4] anionic sodium alkyl sulfonate,[5,6] and cationic alkyl trimethyl ammonium bromide surfactants.[7] In all cases, we considered surfactants with a relatively short hydrophobic tail (i.e., an alkyl chain formed by less than 12 carbon atoms) that, aggregating at quite high surfactant concentration, allow us to investigate in detail the self-aggregation mechanism.

In the present work, we report mutual and intradiffusion coefficients of the binary aqueous solutions of the nonionic surfactant *n*-decyl dimethyl phosphine oxide [$CH_3(CH_2)_9$-$P(CH_3)_2O$, C_{10}DMPO]. *n*-Alkyl dimethyl phosphine oxide surfactants are quite interesting for practical applications, since they are chemically very stable against oxidative or reductive conditions, in wide pH and temperature ranges.[8]

The mutual diffusion coefficient has been measured using the Taylor dispersion technique, and the intradiffusion coefficients of both components have been measured by the pulsed gradient spin echo (PGSE)−FT NMR technique. In the Discussion section, the data are analyzed to extract quantitative information on the surfactant self-aggregation process in aqueous solution.

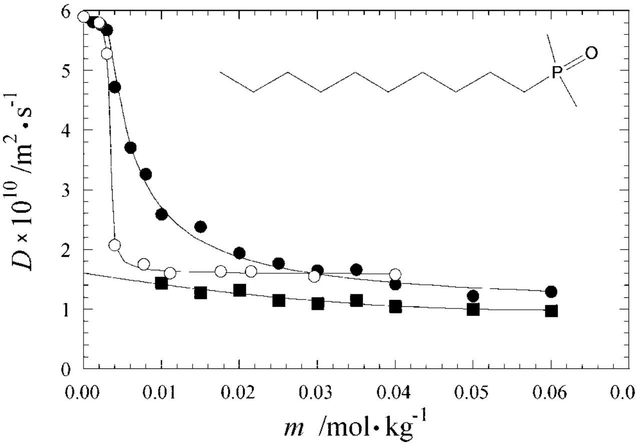

Figure 1. Mutual and intradiffusion coefficients of C_{10}DMPO + water solutions at 25 °C: ○, D; ●, $D_{C_{10}DMPO}$; ■, $D^M_{C_{10}DMPO}$. The lines are an interpolation of the experimental data by eqs 1, 2, and 3, respectively. In the inset, the C_{10}DMPO molecular structure is shown.

Experimental Section

Materials. *n*-Decyl dimethyl phosphine oxide [$CH_3(CH_2)_9$-$P(CH_3)_2O$, C_{10}DMPO, see the inset of Figure 1 for the molecular structure], purchased from Organometallics Inc. (purity > 99 %), was used without further purification. For mutual diffusion measurements, all solutions were prepared by mass using double-distilled water. For intradiffusion measurements, heavy water (Sigma Chemical Co., purity > 99.9 %) was used as solvent, both for lock purposes and for enhancing the signal intensity of the solute, allowing us to analyze very dilute solutions. As will be discussed later, solubilized tetramethylsilane (TMS, Sigma, purity 99.9 %) was used in the micellar composition range to measure the micelle intradiffusion coefficient.

Mutual Diffusion Measurements. The mutual diffusion coefficients, D, were determined by the Taylor dispersion method, which is widely described in the literature.[9] Details of the equipment, procedure, and mathematical treatment of

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Table 1. Mutual Diffusion Coefficients, D, as a Function of the Surfactant Molality, m, for the System C_{10}DMPO + Water at 25 °C

m / $\mathrm{mol \cdot kg^{-1}}$	$10^{10}D$ / $\mathrm{m^2 \cdot s^{-1}}$
0.0000	5.90
0.0020	5.80
0.0030	5.28
0.0040	2.07
0.0077	1.75
0.0111	1.56
0.0176	1.69
0.0215	1.63
0.0296	1.55
0.0400	1.58

Table 2. Intradiffusion Coefficients of the Surfactant, $D_{C_{10}DMPO}$, Micellar Aggregates, $D^M_{C_{10}DMPO}$, and Water, D_W, as a Function of the Surfactant Molality, m, for the System C_{10}DMPO + H_2O at 25 °C

m / $\mathrm{mol \cdot kg^{-1}}$	$10^{10}D_{C_{10}DMPO}$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^{10}D^M_{C_{10}DMPO}$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^{10}D_W$ / $\mathrm{m^2 \cdot s^{-1}}$
0.0000			22.99[a]
0.0012	5.81		22.95
0.0022	5.76		22.90
0.0030	5.68		22.90
0.0040	4.72		22.90
0.0060	3.71		22.85
0.0080	3.26		22.85
0.0100	2.59	1.44	22.85
0.0150	2.38	1.28	22.85
0.0200	1.94	1.32	22.80
0.0250	1.77	1.15	22.80
0.0300	1.65	1.10	22.75
0.0350	1.66	1.15	22.75
0.0400	1.42	1.05	22.70
0.0500	1.22	1.00	22.65
0.0600	1.29	0.98	22.60

[a] Datum from ref 20.

experimental results have been reported.[10] The combined effect of convection and diffusion generated the nearly-Gaussian concentration profile of the pulse at the tube outlet, as monitored by a differential refractometer detector.

To experimentally determine the mutual diffusion coefficient extrapolated to infinite surfactant dilution, samples of three aqueous solutions with decreasing surfactant molality, m, were injected into a water stream flowing in a long capillary tube. The limiting value was obtained as the limit for $m \rightarrow 0$ of the experimental data. Each D value at finite surfactant concentration was evaluated as an average of the values obtained by performing an equal number of injections of a pulse of surfactant solution at a molality $m + \Delta m$ and $m - \Delta m$ into the laminar flow of a surfactant solution at molality m.

The mutual diffusion coefficients are collected in Table 1. The experimental uncertainty is within (1 to 2) %.

Intradiffusion Measurements. Intradiffusion coefficients of both water, D_w, and surfactant, $D_{C_{10}DMPO}$, were measured using the pulsed gradient spin echo (PGSE) FT−NMR method.[11] Experiments were carried out on a Varian FT 80 NMR spectrometer operating in the ^{1}H mode, equipped with a pulsed magnetic field gradient unit, specially made by Stelar (Mede, Italy). Details of the equipment, procedure, and mathematical treatment of experimental results have been reported.[12]

$D_{C_{10}DMPO}$ was determined by following the NMR signal of the methyl groups of the surfactant headgroup (a doublet at $\delta = 1.5$); D_w was determined by following the NMR signal of OH protons ($\delta = 4.7$); the experimental data are collected in Table 2. To correct the intradiffusion coefficients obtained in deuterated solutions back to those in light water, it is necessary to multiply them by the factor 1.23,[13] which is the ratio of intradiffusion coefficients of light and heavy water. The intradiffusion coefficient of micellar aggregates was measured experimentally by the addition of TMS in trace to the system. In fact, for a compound which is entirely confined to the micelles and has a negligible solubility in the intermicellar solution, the observed intradiffusion coefficient is the same as the intradiffusion coefficient of the micelles.[6,7]

The intradiffusion coefficients are collected in Table 2. The experimental uncertainty is within (2 to 3) %.

Results and Discussion

Mutual diffusion coefficients, D, measured in this study for the system C_{10}DMPO + water are shown in Figure 1. With increasing surfactant concentration, D shows a sigmoidal trend, typical of surfactants that cooperatively self-aggregate in aqueous solution, leading to the formation of micelles.[2] Particularly, a steep decrease is detectable in the concentration range in which micelle formation begins to be appreciable. From inspection of Figure 1, the C_{10}DMPO critical micelle concentration, cmc, could be roughly evaluated as the concentration at which the D trend presents an inflection (cmc $\approx 0.003\ \mathrm{mol \cdot kg^{-1}}$). This value is in fair agreement with the literature.[14–16] In the case of surfactants with a relatively short hydrophobic tail, the self-aggregation process is well described due to the equilibrium between free surfactants, named unimers, and micelles.[17] In the hypothesis that the micelles are composed by a unique number of surfactant molecules, the self-aggregation process is described by the two parameters equilibrium constant, K, and aggregation number, n. Actually, both parameters can change with increasing surfactant concentration; however, the concentration range considered in the present work is narrow enough to make the assumption of their constancy reasonable. D is an n^2 concentration-weighted average value between the contributions of C_{10}DMPO molecules in unimeric and micellized form, indicated as D^U and D^M [18]

$$D = D^U \frac{1}{1 + n^2K(m^U)^{n-1}} + D^M \frac{n^2K(m^U)^{n-1}}{1 + n^2K(m^U)^{n-1}} \qquad (1)$$

where m^U is the molality of the surfactant in unimeric form. By assuming D^U to be constant and equal to the limiting dilution value ($D^U = 5.9 \cdot 10^{-10}\ \mathrm{m^2 \cdot s^{-1}}$), eq 1 can be fitted to the experimental data obtaining ln $K = 200 \pm 20$, $n = 37 \pm 4$, and $D^M = (1.58 \pm 0.05) \cdot 10^{-10}\ \mathrm{m^2 \cdot s^{-1}}$.

The surfactant intradiffusion coefficients, $D_{C_{10}DMPO}$, are also shown in Figure 1. As predicted by theoretical considerations,[19] $D_{C_{10}DMPO}$ tends to D in the limit of $m \rightarrow 0$. With increasing surfactant concentration, $D_{C_{10}DMPO}$ shows a trend qualitatively similar to the D one, with a clear slope change in correspondence to the cmc;[3,6,7] however, the decrease due to the micelle formation is much less steep. This is due to the fact that $D_{C_{10}DMPO}$ is an n concentration-weighted average value between the unimer and micelle contribution

$$D_{C_{10}DMPO} = D^U_{C_{10}DMPO} \frac{1}{1 + nK(m^U)^{n-1}} + D^M_{C_{10}DMPO} \frac{nK(m^U)^{n-1}}{1 + nK(m^U)^{n-1}} \qquad (2)$$

Comparison of eqs 1 and 2 shows that $D_{C_{10}DMPO}$ is much less effectively affected by the micellization process than D. For this reason, joined to the lower accuracy of the intradiffusion

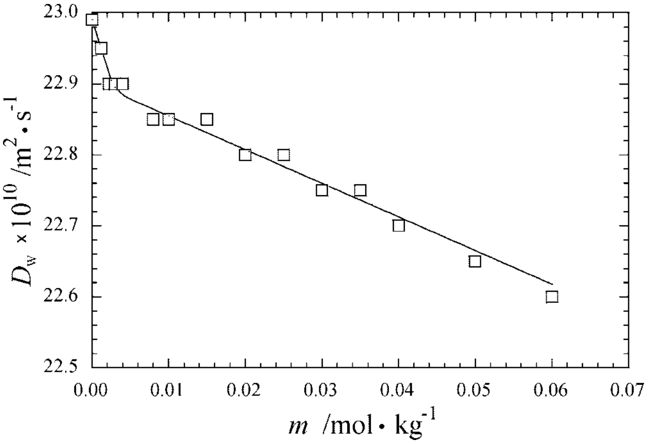

Figure 2. Water intradiffusion coefficients of C_{10}DMPO + water solutions at 25 °C. The line is an interpolation of the experimental data by eqs 4 and 5.

measurements, obtaining the K and n values from the fitting of eq 2 to the experimental data is a difficult task; i.e., a wide variation of the adjustable parameters could result in very similar fitting curves. Consequently, we prefer just to check that the values obtained from the mutual diffusion data, inserted in eq 2, lead to a $D_{C_{10}DMPO}$ trend reproducing the experimental one. The unimers' diffusivity is assumed to be constant and equal to the limiting dilution value ($D^{U}_{C_{10}DMPO} = D^{U} = 5.9 \cdot 10^{-10}$ m^2•s^{-1}). The micelles' diffusion coefficient can be determined experimentally as described in the previous section. The experimental values, also shown in Figure 1, decrease with the C_{10}DMPO concentration, according to the relation

$$D^{M}_{C_{10}DMPO} \cdot 10^{10}/\mathrm{m^2 \cdot s^{-1}} = (1.60 \pm 0.07) - (20 \pm 5)\ m/\mathrm{mol \cdot kg^{-1}} + (170 \pm 70)\ (m/\mathrm{mol \cdot kg^{-1}})^2 \quad (3)$$

The decrease of $D^{M}_{C_{10}DMPO}$ with increasing surfactant concentration is very weak, thus indicating that the obstruction effect due to the presence of an increasing number of micellar aggregates[6] is very weak.

Inspection of Figure 1 shows that the same K and n values lead to a good interpolation of both D and $D_{C_{10}DMPO}$ experimental trends.

The water intradiffusion coefficient, D_w, is shown in Figure 2. It decreases with an increase of the C_{10}DMPO concentration, showing a clear slope change in the concentration range where aggregation occurs. In the dilute region, the decreasing trend can be attributed to the fact that some water molecules enter the unimer hydration shell, thus becoming slower with respect to the free ones. The smaller reduction of D_w with increasing surfactant concentration indicated that the number of water molecules hydrating the micellized surfactant is lower than that of molecules hydrating unimers. Indeed, in the case of unimeric surfactants, a high number of water molecules are involved in the hydrophobic interaction with the surfactant apolar chain. These molecules are released in the micellization process. Quantitatively, the water intradiffusion coefficient, D_w, is an average value between the contributions of free water molecules and molecules hydrating the surfactant unimers and micelles

$$D_w = D^{F}_{w}\frac{n^{F}_{w}}{n_w} + D^{U}_{w}\frac{n^{U}_{w}}{n_w} + D^{M}_{w}\frac{n^{M}_{w}}{n_w} \quad (4)$$

The diffusivity of free water molecules is considered constant and equal to the self-diffusion coefficient of neat water (D^{F}_{w} = 2.299•10^{-9} m^2•s^{-1}, ref 20), and the diffusivity of water molecules hydrating unimers or micelles is assumed to be equal to that of the hydrated object ($D^{U}_{w} = D^{U}_{C_{10}DMPO}$ and $D^{M}_{w} = D^{M}_{C_{10}DMPO}$).

n^{U}_{w} and n^{M}_{w} are the moles of water hydrating unimeric and micellized C_{10}DMPO, respectively. On the basis of 55.51 total moles of water (n_w), n^{U}_{w} and n^{M}_{w} can be computed as the number of water molecules hydrating a C_{10}DMPO molecule in unimeric and micellized form multiplied by the molality of the hydrated object

$$n^{U}_{w} = h^{U}_{w} m^{U} \qquad n^{M}_{w} = h^{M}_{w} m^{M} \quad (5)$$

Fitting of eqs 4 and 5 to the experimental D_w data, by using the K and n values determined above, allows us to obtain h^{U}_{w} = 110 ± 12 and h^{M}_{w} = 12 ± 3. These values are of the same order of those obtained for other nonionic surfactants.[4] Intradiffusion coefficients allow us to estimate the total number of water molecules whose motion is slowed down by the interaction with a solute. Particularly, in the case of amphiphilic molecules, such as unimeric surfactants, this approach includes water molecules forming the cage around the hydrophobic moieties of the solute.[4]

It is possible to relate the micellar intradiffusion coefficient estrapolated at the cmc, considered to be the infinite dilution for micelles, $(D^{M}_{C_{10}DMPO})_{cmc}$, to the hydrodynamic size of the micellar aggregates using the Stokes−Einstein equation to calculate the apparent radius[7]

$$R_{app} = \frac{k_B T}{6\pi\eta \left(D^{M}_{C_{10}DMPO}\right)_{cmc}} \quad (6)$$

where k_B is the Boltzmann constant, T the absolute temperature, and η the viscosity of the medium that, given the high dilution of the mixtures under consideration, can be taken equal to that of neat water. In turn, R_{app} can be used to compute the aggregation number of the micelles. In fact, assuming a spherical shape, n can be computed by the ratio between the experimental and calculated hydrodynamic volumes

$$n = \frac{(4/3)\pi R^{3}_{app}}{V^{M}_{C_{10}DMPO} + h^{M}_{w} V_w} \quad (7)$$

where $V^{M}_{C_{10}DMPO}$ = 239.6•10^{-6} m^3•mol^{-1} is the partial molar volume of the surfactant[21] in micellized form and V_w = 18.07•10^{-6} m^3•mol^{-1} is the water molar volume. By applying eq 7, the value n = 40 ± 8 is obtained, which confirms the reliability of the fitting procedure of mutual diffusion data.

Conclusions

Diffusion data of surfactants in aqueous mixtures, besides being of evident technological interest, give substantial information on the molecule self-aggregation process. Particularly, mutual diffusion coefficients allow a reliable determination of parameters such as aggregation number and equilibrium constant. Surfactant intradiffusion coefficients are affected by a higher experimental uncertainty but present the advantage that the micelle diffusivity can be directly determined by using an apolar probe such as TMS. Water intradiffusion coefficients are particularly interesting because they show the reduction in the number of hydrating molecules when a surfactant molecule passes from the unimeric to the micellized form, which is the fundamental driving force of the self-aggregation process.

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