into the bilayer matrix of triple-chain amphiphiles. Figure 6 is an example of the spectral change at 48 °C. The mixing is complete in ca. 1 h, because the $3C_{12}$-tris-$C_{11}N^+$ bilayer ($T_c$ = 41.5 °C) is fluid at this temperature. The mixing rate becomes much smaller when the bilayers are in the crystalline state.

It is evident from the DSC and spectral results that the triple-chain amphiphiles show mixing behaviors very similar to those of double-chain (dialkyl) amphiphiles.

**Amphiphile Structure and Bilayer Formation.** In all aspects examined, triple-chain amphiphiles produce typical bilayer aggregates. Table IV summarizes types of synthetic amphiphiles which form molecular membranes (monolayer and bilayer). They are classified by the number of alkyl tails as single-chain, double-chain, triple-chain, related compounds, and the polymeric analogues. Single-chain amphiphiles are capable of forming a bilayer or monolayer, depending on the number of hydrophilic heads. They contain rigid segments and flexible tails as hydrophobic moieties. The flexible tail may be either hydrocarbon or fluorocarbon. Double-chain amphiphiles are composed of a variety of hydrophilic heads and flexible tails that are either hydrocarbon or fluorocarbon. They produce bilayers. Triple-chain amphiphiles are made of a hydrophilic head and three flexible tails of hydrocarbons or fluorocarbons and form bilayers. Other membrane-forming compounds include amphiphiles which are derived by connecting one of the alkyl tails of two double-chain amphiphiles. Further variations of membrane-forming amphiphiles are possible by combinations of these structural units. Polymeric and polymerized bilayers are yet another group of molecular membrane.

It is now established that formation of stable molecular membranes (monolayer and bilayer) is a general physicochemical phenomenon observed for a wide variety of amphiphiles. There have been proposed theories to account for self-assembly of surfactant molecules into micelles and vesicles. The original formulation of Tanford[30] was extended by Israelachvilli and others,[31] and, more recently, the quantitative aspects were discussed by Nagarajan and Ruckenstein[32] and by Mitchell and Ninham.[33] In these theories, however, the hydrophobic core is assumed to be liquid like, and the types of membrane-forming amphiphiles of Table IV may not be readily accommodated. It is evident that the improved molecular orientation and packing in the hydrophobic core promote the two-dimensional molecular assembly.

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**Registry No. 2** ($n$ = 12), 29920-02-3; **2** ($n$ = 16), 88932-02-9; **3**, 88932-05-2; **4** ($n$ = 12), 88932-03-0; **4** ($n$ = 16), 88932-04-1; **5** ($m$ = 2; $n$ = 12), 88932-06-3; **5** ($m$ = 2; $n$ = 16), 88932-07-4; **5** ($m$ = 11; $n$ = 12), 88932-08-5; **6** ($m$ = 4), 88932-09-6; **6** ($m$ = 10), 88932-10-9; $CH_3(CH_2)_{15}Br$, 112-82-3; $[CH_3(CH_2)_{10}C(O)O(CH_2)_2]_3N$, 3002-20-8; $[CH_3(CH_2)_{14}C(O)O(CH_2)_2]_3N$, 88931-91-3; $[CH_3(CH_2)_{10}C(O)OCH_2]_3CNH_2$, 88931-92-4; $[CH_3(CH_2)_{14}C(O)OCH_2]_3CNH_2$, 88931-93-5; $[CH_3(CH_2)_{10}C(O)OCH_2]_3CNHC(O)CH_2Br$, 88931-94-6; $[CH_3(CH_2)_{14}C(O)OCH_2]_3CNHC(O)CH_2Br$, 88931-95-7; $HO_2C$-$p$-$C_6H_4O(CH_2)_4Br$, 88931-96-8; $HO_2C$-$p$-$C_6H_4O(CH_2)_{10}Br$, 88931-97-9; ClC(O)-$p$-$C_6H_4O(CH_2)_4Br$, 88185-43-7; ClC(O)-$p$-$C_6H_4O(CH_2)_{10}Br$, 88931-98-0; $[CH_3(CH_2)_{10}C(O)OCH_2]_3CNH_2$·TsOH, 88931-99-1; $[CH_3(CH_2)_{10}C(O)OCH_2]_3CNHC(O)$-$p$-$C_6H_4O(CH_2)_4Br$, 88932-00-7; $[CH_3(CH_2)_{10}C(O)CH_2]_3NHC(O)$-$p$-$C_6H_4O(CH_2)_{10}Br$, 88932-01-8; $2C_{16}N^+2C_2Br^-$, 70755-47-4; $C_{12}AzoC_{10}N{\cdot}Br^-$, 88932-11-0; $[CH_3(CH_2)_{10}C(O)OCH_2]_3CNHC(O)(CH_2)_{10}CH_3$, 88932-12-1; dodecylamine, 124-22-1; dodecyl bromide, 143-15-7; tridodecylamine, 102-87-4; methyl bromide, 74-83-9; hexadecylamine, 143-27-1; dioctadecyl $N,N$-dimethylglutamate hydrochloride, 88931-89-9; dioctadecyl $N,N$-dimethylglutamate, 88931-90-2; octadecyl bromide, 112-89-0; dodecanoyl chloride, 112-16-3; hexadecanoyl chloride, 112-67-4; triethanolamine, 102-71-6; tris(hydroxymethyl)aminomethane, 77-86-1; hexadecanoic acid, 57-10-3; dodecanoic acid, 143-07-7; trimethylamine, 75-50-3; 1,6-diphenyl-1,3,5-hexatriene, 1720-32-7; riboflavin, 83-88-5.

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# Simple Method for Quantifying the Distribution of Organic Substrates between the Micellar and Aqueous Phases of Sodium Dodecyl Sulfate Solution[1]

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**Abstract:** A simple technique, involving the measurement of diffusion coefficients, was used to determine partition coefficients for the distribution of a variety of organic substrates between the micellar and aqueous phases of sodium dodecyl sulfate (SDS) solution. The data additionally revealed two mechanisms for the apparent diffusion of the micelles. One involved true micellar diffusion and was monitored by the use of tracer molecules. The second involved a more rapid redistribution of micelles by a mechanism involving the diffusion of individual SDS molecules. Nonpolar molecules with more than 10 heavy atoms were essentially localized in the micellar phase of 0.1 M SDS.

There has been substantial interest in the use of micelles as devices for modifying chemical reactions.[2] In order to understand this chemistry, it is vital to known the extent to which an organic molecule is partitioned between the aqueous and micellar phases, yet there are few general methods for making such measurements since most require special spectral or other physical properties of the partitioned organic molecules.[3-6] Indeed, it is probably

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Table I. Values of Diffusion Coefficients for a Variety of Organic Molecules Measured in Methanol, Water, and SDS (0.1 M) at 25 °C

| compd[a] | $10^5D$, cm²/s | | | |
|---|---|---|---|---|
| | methanol | water | SDS | $f$ |
| I, acetone | 2.38 ± 0.18 | 1.27 ± 0.11[b] | 1.07 ± 0.07 | 0.17 ± 0.11 |
| II, iodomethane | 2.96 ± 0.08 | 1.27 ± 0.03 | 0.81 ± 0.04 | 0.39 ± 0.05 |
| III, cystine | [c] | 0.78 ± 0.08 | 0.51 ± 0.02 | 0.40 ± 0.07 |
| IV, SDS | [c] | | 0.51 ± 0.04[d] | |
| V, benzene | 2.55 ± 0.07[e] | 1.09 ± 0.04[f] | 0.46 ± 0.04 | 0.64 ± 0.02 |
| VI, tryptophan | 0.75 ± 0.05 | 0.659 ± 0.001[g] | 0.347 ± 0.006 | 0.56 ± 0.06 |
| VII, naphthalene | 1.94 ± 0.07 | 0.88 ± 0.02 | 0.189 ± 0.004 | 0.895 ± 0.09 |
| VIII, di-*tert*-butyl disulfide | 1.60 ± 0.07 | 1.19 ± 0.002 | 0.153 ± 0.004 | 0.958 ± 0.04 |
| IX, pyrene | 1.37 ± 0.05 | [c] | 0.109 ± 0.004 | 1[h] |
| X, anthracene | 1.78 ± 0.05 | [c] | 0.107 ± 0.004 | 1[h] |
| XI, 1-methylnaphthalene | 1.84 ± 0.17 | [c] | 0.106 ± 0.004 | 1[h] |

[a] Concentrations of solute (mM) at injection in methanol, water, and SDS, respectively: I (13, 13, 41); II (16, 16, 48); III (–, saturated, saturated); IV (–, 100, 230); V (11, 11, 11); VI (2.7, –, saturated); VII (0.8, saturated, <1.6); VIII (5.1, 5.1, <1); IX (saturated, –, 1.7); X (0.73, –, saturated); XI (0.70, –, 7.0). [b] Lit. value $1.23 \times 10^{-5}$ cm²/s.[26] [c] Solubility too poor for measurement. [d] This result does not represent $D_m$; see text. [e] Lit. 2.80 cm²/s; see: Caldwell, C. S., Babb, A. L. *J. Phys. Chem.* **1955**, *59*, 1113. [f] See also: Simon, S. A.; McDaniel, R. V.; McIntosh, T. J. *J. Phys. Chem.* **1982**, *86*, 1449. And ref 26. [g] From Longworth, L. G. *J. Chem. Soc.* **1953**, *75*, 5709. [h] These values are assumed; see text.

fair to say that as much is known about the partitioning of transient species such as photoexcited molecules and free radicals[7,8] as the partitoning of simple organics.

In an effort to address this problem, we have used measurements of diffusion coefficients to determine the extent to which organic molecules are partitioned between the organic and micellar phases of detergent solutions. The principle of the method is quite simple.[3,9,10] In a micellar solution containing an organic solute, the solute molecules in the water will diffuse with their normal diffusion coefficient $D_w$, while those in the micelle will diffuse at the same rate as their host, i.e., with the micellar diffusion coefficient $D_m$. Thus, the observed diffusion coefficient for the organic solute, $D$, will depend upon the fraction of organic molecules, $f$, present in the micellar phase (eq 1).[3]

$$D = f \cdot D_m + (1 - f) \cdot D_w \quad (1)$$

We have used this approach and a very simple diffusion apparatus, to determine partition coefficients for a number of organic substrates in sodium dodecyl sulfate, SDS, solution. In addition, we report diffusion coefficients for those molecules in water and methanol.

## Experimental Section

**Materials.** Acetone, water, and methanol were either HPLC or spectro grade and were used as received. Trypotophan, cystine (Sigma), and electrophoresis purity sodium dodecylsulfate (Bio*Rad) were used without further purification. Benzene was distilled from $CaH_2$, iodomethane, 1-methylnaphthalene, and di-*tert*-butyl disulfide were purified by chromatography on an alumina column. Pyrene, anthracene, and naphthalene were purified by sublimation or were zone refined.

**Apparatus.** The Taylor diffusion apparatus used in this work follows the design developed by Huggenberger, Lipscher, and Fischer.[9] Basically, solvent was pumped at a steady flow (6–12 mL/h) through 10 m of stainless steel tubing (0.03-in. i.d.) by using a Varian 8500 syringe drive pump. The tubing was immersed in a thermostated water bath at 25 ± 0.1 °C. These conditions were chosen so as to establish a laminar flow in the apparatus. Samples were introduced at the beginning of the tubing by using a Valco HPLC injector fitted with a 10-μL loop. The dispersion of the sample which occurred during its passage through the tubing was detected with a Varian Varichrome UV–vis detector or a Waters R403 refractive index detector. Signals were recorded on a Hewlett-Packard 3390a recorder/integrator. A Nupro CA relief valve was normally fitted to the exit tubing of the detectors so as to provide a small back pressure for the system.

**Samples.** Samples were prepared by dissolving 1–10 μL or mg of solute in 10 mL of solvent. The concentration of solute and injector size (10 μL) were designed to ensure that a dilute sample was introduced as a "Δ function" spike; i.e., the volume injected was very small when compared with the total volume of the capillary tubing. When the UV–vis detector was used with the diffusion apparatus, the solute was detected at a wavelength where the solution injected had an absorbance of 0.5 as measured in a 1-cm pathlength cell.

## Results and Discussion

A variety of methods are available for the measurement of diffusion coefficients. For this work we chose the Taylor method, which has a number of advantages. The theory is well understood,[11–13] analysis of the experimental data is straightforward, and the sources of error have been thoroughly explored.[12] In addition, the apparatus is simple and inexpensive to build and operate and diffusion coefficients can routinely be measured to a precision of ca. ±2%.

In the experiment a small sample of solute was introduced into a stream of solvent that was flowed slowly through a long capillary. The axial distribution of the solute at injection was essentially a "Δ function" spike.[9,12] That is, the time taken for the injection and the volume injected were very small when compared with the duration of the experiment and the volume of the capillary tube. This condition ensured that the dispersion of the sample when injected was negligible when compared with its dispersion at the detector.

The experimental conditions were such that laminar flow was established in the tube and therefore the solvent flow rate decreased as a function of the radial distance from the center of the tube. As a result the solute near the center of the tube flows faster than that near the walls causing a large axial dispersion of the solute. Axial diffusion of the solute does not contribute significantly to this effect. However, radial diffusion of the solute is quite significant when compared with the diameter of the tube and tends to counteract the effect of the solvent-induced axial dispersion. As a result, solutes that diffuse slowly adopt broad Gaussian distributions when detected a long distance from the injector, while the converse is true for solutes that diffuse rapidly.[11–13]

Diffusion coefficients, $D$, were calculated by using eq 2, where

$$D = r^2t/(24\sigma^2) \quad (2)$$

$r$ was the radius of the tube, $t$ the time elapsed between the

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injection of the sample and the appearance of the maximum of the dispersion curve of the solute, and $\sigma^2$ the variance[14] of the dispersion curve.[11-13] The radius of the tube was calibrated by measuring the diffusion of benzene in cyclohexane for which $D$ has been accurately determined ($D = 1.87 \pm 0.02) \times 10^{-5}$ $cm^2/s$).[16-19] In fact, the value found for $r$ was within 2% of the manufacturers's specification for the capillary tubing.

All of the recommended precautions[9,11-13] to avoid sources of error were followed in these experiments. In particular, determinations were made at several flow rates to test that, under the experimental conditions, eq 2 was satisfied.

Diffusion coefficients for a variety of organic molecules were measured in water, methanol, and 0.1 M SDS as solvents and are reported in Table I.

The values obtained in methanol and water do not follow the Stokes–Einstein equation,[20] which defines the diffusion coefficient for a large spherical particles of radius $a$ moving in a continuous medium of viscosity $\eta$ (eq 3). For a given compound, the equation

$$D = kT/(6\pi\eta a) \quad (3)$$

predicts that the ratio of diffusion coefficients in water and methanol should be equal to the ratio of the solvent viscosities, i.e., 1.63 at 25 °C.[21] The data in Table I show that this is clearly not the case for the compounds investigated.

Attempts have been made to interpret such deviations in terms of a solvation effect that enhances the effective size of the diffusion substrate molecule.[20] This explanation may be qualitatively correct for the compounds under study. However, there is abundant evidence that suggests that the Stokes–Einstein equation fails in situations for which it was not designed, i.e., when solute and solvent are of similar size.[10]

For the larger molecules investigated, i.e., naphthalene, 1-methylnaphthalene, anthracene, and pyrene in methanol, the Stokes–Einstein equation ought to have greater applicability since these molecules are structurally related and should be solvated in a similar way. Such appears to be the case since the measured diffusion coefficients were roughly proportional to the cube roots of their molecular volumes, which, to a first approximation, are proportional to $a$.[20]

When the same molecules were investigated in 0.1 M SDS, there was a dramatic reduction in their diffusion coefficients. The values for pyrene, anthracene, and 1-methylnaphthalene were the same, within experimental error, indicating that they were now localized within micelles and had effectively become "tracers" of the micellar diffusion. We therefore assigned the average value of these diffusion coefficients to $D_m$ (eq 1).

A measure of caution should be exercised when comparing our value of $D_m$ with those previously reported, since the literature on micellar diffusion has been rather confused.[22] The difficulties have arisen from the fact that different experimental techniques measure differing aspects of micellar diffusion.

The tracer approach described above follows the motion of the individual micelles in which the tracer molecules are located and therefore accurately reflects the diffusion of intact micelles. However, in an experiment where a concentration gradient in micelles is established, homogeneity is only slowly restored by micellar diffusion. A far more rapid process involves dissociation of individual SDS molecules from micelles followed by their relatively rapid diffusion through the solution and ultimate formation of new micelles.

In detail, this process almost certainly involves a "relay" mechanism in which repeated entry and exit of SDS molecules from the micelles are an essential part of the overall diffusion. Of course, there is a low probability that a SDS molecule entering a given micelle will be the one to leave.

Any experiment that involves monitoring the apparent diffusion of unlabeled micelles will reflect the latter mechanism and will give values of diffusion coefficients that are larger than those measured in tracer studies. Studies involving the use of quasielastic light-scattering techniques are experiments of the genre.[23c,d,e,g,h] We have used the Taylor method to carry out an experiment of this kind by introducing a $\Delta$ function spike of SDS into a solution of 0.1 M SDS (see Table I). This result, as well as those obtained in our labeled-micelle experiments, are in excellent agreement with recent work by Evans and collaborators,[25] which takes proper account of the fact that the different experimental approaches do not necessarily reflect the same diffusional process.

The results in Table I clearly show that the present method is a simple and reasonably accurate technique for the measurement of partition coefficients for organic molecules in micelles. The diffusion method only requires that the organic substrate be detectable by refractive index or UV instruments and hence is somewhat more general than the technique pioneered by Encinas and Lissi,[4] which requires that the substrate be a fluorescence quencher.

The present method satisfactorily defines the extent to which a molecule is localized within the micelle, $f$, to a precision of ca. $\pm 10\%$. However, the ratio $f/(1-f)$ is obviously most accurately defined when $f$ is approximately 0.5, i.e., when the substrate is fairly evenly distributed between the micellar and aqueous phases.

As expected, values of $f$ increase with the molecular weight of the substrate so long as the latter contains no ionic or polar groups. Our results show that a nonpolar substrate that contains more than 10 heavy atoms will be highly localized in the micellar phase of 0.1 M SDS.

Finally, the data support the concept of two mechanisms for micellar "diffusion". One involved the true diffusion of the micelles themselves and was monitored by the use of tracer molecules, which were effectively the most persistent components of the micelles. The second involved the redistribution of micelles by a relay mechanism involving repeated exit and reentry of individual SDS molecules from existing micelles with ultimate formation of new ones.

**Registry No.** Sodium dodecyl sulfate, 151-21-3; methanol, 67-56-1; acetone, 67-64-1; iodomethane, 74-88-4; cystine, 56-89-3; benzene, 71-43-2; tryptophan, 73-22-3; naphthalene, 91-20-3; di-*tert*-butyl disulfide, 110-06-5; pyrene, 129-00-0; anthracene, 120-12-7; 1-methylnaphthalene, 90-12-0.

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