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Diffusion Measurements in Aligned Nematic and Smectic Amphiphilic Liquid Crystalline Decylammonium Chloride and Ammonium Chloride Water Mixtures

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Diffusion Measurements in Aligned Nematic and Smectic Amphiphilic Liquid Crystalline Decylammonium Chloride and Ammonium Chloride Water Mixtures

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The micellar diffusion constants have been measured perpendicular to the optic axis in an aligned aqueous solution of decylammonium chloride and ammonium chloride, 10:1 by weight. The diffusion constants were calculated by measuring the evolution of the dye concentration along a microslide (.2 or .3 mm thick and 10 cm long) which had initially been half filled with solution containing a dye soluble only in the micelle, the other half being pure solution. Measurements were made in the isotropic phase for solutions containing 64 wt% water; in the nematic and smectic (neat soap) phases in solutions of 54 wt% water; and in the smectic phase of a 52 wt% water solution. The measured diffusion ranges from 4×10^{-7} cm^2/sec to 7×10^{-7} cm^2/sec. Taking into account the temperature dependence of the viscosity of water, we find $D_{\mathrm{Iso}} < D^{\perp}_{\mathrm{Nm}} \approx D^{\perp}_{\mathrm{Sm}}$.

INTRODUCTION

Diffusion in thermotropic liquid crystals has been studied by a number of methods (Ref. 12 contains a recent review of this work) as has diffusion in isotropic micellar solutions.[1–5] Some work has been done

in lamellar amphiphilic mesophases[6] but to our knowledge no measurements have been made comparing diffusion in more than one mesophase of an amphiphilic system. The object of this work is to compare diffusion in the isotropic, nematic and smectic mesophases of the same amphiphilic system. To accomplish this a dye which was insoluble in water but soluble in the micelles was used and its diffusion determined by optical absorption measurements. We chose the ternary system decylammonium chloride (DACl), ammonium chloride, water, because of the information available from previous measurements.[7-10] In appropriate compositions it forms an isotropic micellar solution, a nematic micellar solution and a lamellar smectic phase. The isotropic solution is formed in the upper temperature range. When the temperature is lowered, there is a short two-phase range at the transition to the nematic phase. Further cooling produces a smectic phase (neat soap) via a second order transition from the nematic phase. The surfactant aggregates to disc-like micelles in the isotropic and nematic solution. In the smectic phase the micelles may fuse and form continuous lamellae of a very incomplete structure.[8] In this work diffusion measurements were made with concentration gradients which, in the mesophases, were parallel to the flat surfaces of the micelles (perpendicular to the optic axis).

EXPERIMENTAL PROCEDURE

The DACl used was that prepared by Radley.[10] The ammonium chloride was added maintaining a constant weight ratio of 10:1, DACl to NH_4Cl. The amount of water added to produce the isotropic micellar system (samples I1–3) was 64.58 wt% while the liquid crystal samples contained 52.15 wt% (sample LCl) or 54.15 wt% (samples LC2-3). Each sample (total wt ~2g) was stirred for several hours and then separated into two nearly equal parts to one of which dye was added. Before using, both parts were again stirred for several hours and then stored for several days at a temperature sufficient to insure they were in the nematic or isotropic phase.

After testing a number of dyes, we chose oil blue A, furnished by E. I. du Pont de Nemours and Co., Wilmington, Delaware. This dye [(1,4-di(isopropylamino) anthraquinone] had no detectable solubility in water, yet was sufficiently soluble in the DACl mixture to permit absorption measurements over a large concentration range. A spectrophotometric curve showed a strong absorption peak at 600–640μ in the DACl mixture and the logarithm of the intensity was found to

be linear for solutions from 10^{-5} molar to 7×10^{-3} molar. Sufficient dye was added to the isotropic sample to produce a 1.2×10^{-3} molar solution while the liquid crystal samples were 7×10^{-3} molar. The greater amount of dye in the liquid crystal solutions enabled a more precise determination of the concentration and produced no observable changes of the transition temperatures.

The diffusion measurements were carried out in glass microslides (Vitro-Dynamics, Rockway, N.J.) 10 cm long and of sample thickness either 0.02 cm (runs I3, LC1, LC2) or 0.03 cm (runs I1, I2, LC3) thick. After cleaning, one end of the microslide was sealed with a torch and clear sample was added until 3 to 4 cm of the microslide was filled, momentary centrifuging being necessary to bring the sample to the bottom of the tube. Approximately the same amount of sample containing dye was then added. The tube was again centrifuged, the top cleaned and sealed with a torch. As a result of water loss during the loading and sealing processes, differences of several degrees were observed in the transition temperatures of microslides loaded from the same sample. Differences of several degrees were also observed in the transition temperatures between the top and the bottom in some microslides. Therefore it was considered necessary to optically observe the texture of the sample after each temperature change to be certain that the sample was in the expected phase. For example, run LC2 was nematic at 32.7°C but LC3 was smectic, and a 4°C difference in their nematic-isotropic transitions were also observed.

Measurements were carried out with the sample in an oven which controlled the temperature to within ± 0.2°C. Care was taken that no part of the sample solidified during the loading and aligning process. When a mesophase was to be studied, the temperature of the sample was raised to the nematic range and this texture was observed with a microscope (crossed polarizers being placed on either side of the sample). The Schlieren textures typical of the nematic phase would slowly be replaced by a homeotropic texture with defects observable only along the edges of the microslide. If a smectic phase was desired, the temperature was lowered until these defects showed the texture of the neat soap phase, however, due to the second order nature of the transition, the exact transition temperatures were difficult to determine. When a series of measurements with a particular microslide was completed it was taken from the oven and examined with a polarizing microscope equipped with a Mettler hot stage. In this way a transition to a monotropic nematic phase was discovered in the isotropic sample at about 12°C.

The absorption measurements were done on an apparatus consisting of a high intensity monochromator and an optical bench which held the oven with sample, a slit, a photodiode and several lenses. Light from the monochromator was focused on the microslide containing the sample. This in turn was imaged on the slit with the photodiode measuring the transmitted intensity. The oven containing the sample could be displaced perpendicular to the light path, having a distance of travel of 2.8 cm. The microslide was positioned so that the light beam never passed close to the edges where the defects were observed. At the beginning of each set of runs, the oven was positioned so that the dye-clear interface was in the middle of the range of travel. The temperature of the sample was monitored with a thermister and is estimated to have an absolute error of $\pm$ 1°C.

To begin a run the oven was lowered to the end of its range so that the light passed through the dye end of the sample. This was then raised in steps of 0.05 cm and the intensity recorded.

EXPERIMENTAL RESULTS AND CONCLUSIONS

A typical set of data curves is shown in Figure 1. The diffusion constant was obtained by fitting the dye concentration curve as determined by the logarithm of the intensity (Lambert-Beer law) with a theoretical curve.

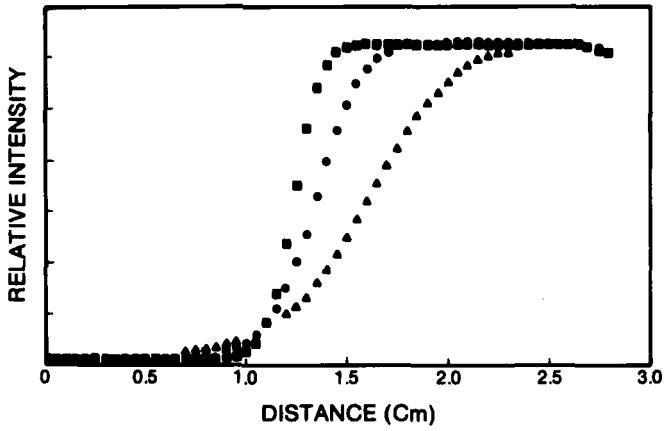

FIGURE 1 Relative intensity of light transmitted by the sample as a function of distance along the microslide. The curves shown are for sample LC2 for different elapsed times; (■) 208 min; (●) 677 min; and (▲) 2785 min.

The theoretical curve used was that for two infinite columns which come into contact at time $t = 0$. For $X < 0$ the concentration of the dye is initially C_0, and for $X > 0$ the concentration is zero. At the time t, the concentration as a function of X (distance along the column) is given by[11]

$$C(X,t) = \frac{C_0}{2}\left(\text{erfc}\left(\frac{X}{2\sqrt{Dt}}\right)\right). \quad (1)$$

Where D is the diffusion constant and erfc is the error function complement; erfc $(z) = 2/\sqrt{\pi}\int_Z^\infty e^{-y^2}\,dy$. In a least squares fit of Eq. (1) to the data, Dt (D times t) was treated as a single constant, the only other variable being the zero position of the X axis. Figure 2 shows a fit where the points are experimental data and the solid line, the theoretical calculation. The slope of a plot of Dt as a function of t gives D directly. Note that t does not correspond to the real elapsed time as the temperature varied while loading and aligning the sample and also because the plane of initial contact between the clear and dye sample was not perpendicular to the line along which the microslide was moved. The latter problem causes an error which

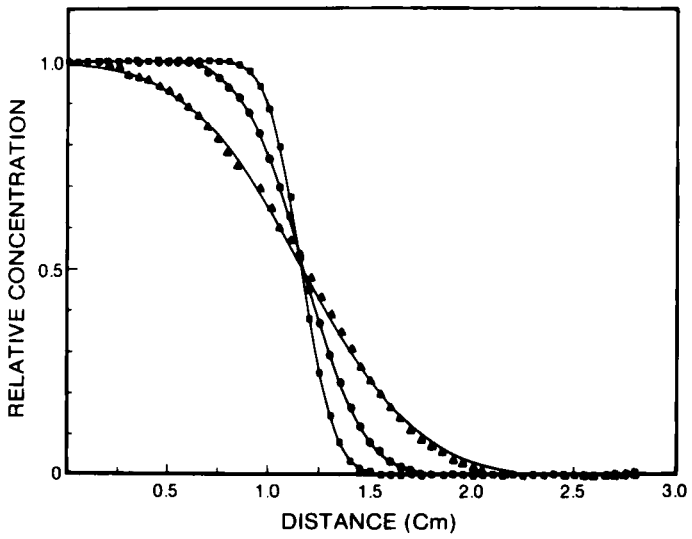

FIGURE 2 Comparison of the data and the theoretical calculation. The points are the relative concentration of dye as obtained from the data (in Figure 1) and the line is the curve as calculated by Eq. (1) where the zero point ($X = 0$) and the product Dt are obtained by a least squares fit to the data.

leads to too large diffusion coefficients. For this reason many of the early runs (less than 2 hours after filling the microslide) give points which are off the line of the *Dt vs t* curve and were therefore not included in the data for the least squares fit. After sufficient time had elapsed (several days) so that the ends of the observable regions of the microslides no longer contained regions of constant dye concentration, the method of curve fitting used no longer gave dependable results. Within these time limits the same microslide can be used to determine the diffusion constant at several temperatures (such as was done in the case of LC-3).

Figure 3 shows the *Dt vs t* curves for the isotropic samples, Figure 4 for the liquid crystalline samples and Table I gives the diffusion constants as determined by a least squares straight line fit to these curves. In Table I are also listed $D_{(20°)}$ the diffusion constants multiplied by the viscosity ratio $\eta(T)/\eta(20°)$ of water and the radius of a sphere which would have this diffusion constant as determined by Einstein's diffusion law, $D = kT/f$, using Stokes's law for a sphere of radius R in a liquid of viscosity η to determine the friction constant, $f = 6\pi\eta r$ [with $\eta = 100$ cp we have the radius in angstroms of the diffusing sphere as $R(\text{Å}) = 2.15 \times 10^{-5}/D(\text{cm}^2/\text{sec})$].

As the micelles in our DACl system are known not to be spherical and as the viscosity of water in our system may vary considerably from that of pure water, [1-5] and also because of the friction between micelles, the calculated values of R and $D_{(20°)}$ have only a comparative significance.

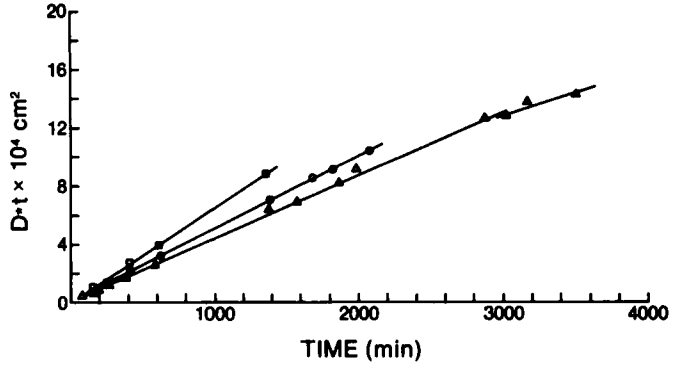

FIGURE 3 The product of the diffusion constant and time (Dt), as determined by the best fit to the data, as a function of the elapsed time, for 3 isotropic solutions (64 wt% H_2O); [(●) I1, (■) I2, (▲) I3]. The temperature of I1 and I2 was 54°C. For the first 3000 minutes of I3 the temperature was 41.8°C, it was then lowered to 32.8°C.

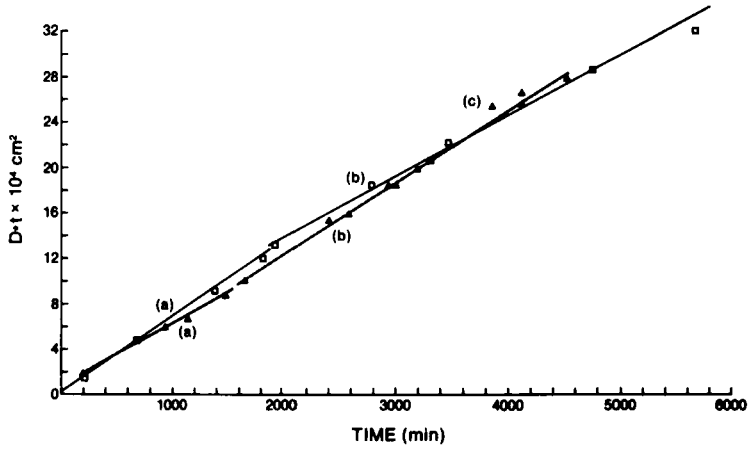

FIGURE 4 The same as Figure 3, for the liquid crystal samples; [(▲) LC2, (a) T = 32.8°C (N) to 1800 min., (b) 21.8°C (Sm) remaining time; (■) LC3, (a) T = 22.3°C (Sm) to 1483 min., (b) 32.0°C (Sm) to 2925 min., (c) 42.5°C (N) remaining time].

The values we obtained from the diffusion in the isotropic micellar systems (I1, I2 and I3) are about 1/2 of the values measured for sodium dodecylsulfate[1,2,4] $D = 6\text{–}7 \times 10^{-7}$ at 25°C. Considering that these measurements were made in less concentrated solutions that contained less salt than our systems, one would expect such a difference. In our systems the friction between the micelles is important and also the size of the micelles may be larger.[5]

Several trends can be seen from the data represented in Table I. Most surprising is that the radii of the aggregates turn out to be smaller in the nematic and smectic state than in the isotropic micellar solution. The calculated values are, of course, not reliable. The aggregates are indeed expected to be larger in the liquid crystalline states because of the higher surfactant concentration. An explanation for the relatively fast diffusion is that the effective friction between the micelles for $D_\perp$ is smaller than the friction in the isotropic state. The motion of a micelle normal to its plane involves more friction than parallel motion. For an upper estimate we write $D_{iso} = 1/3\ (D_\parallel + 2D_\perp)$, for large micelles, $D_\parallel$ is negligible and in this case $D_{iso} = 2/3\ D_\perp$.

Some consideration should also be given to the relationship between the diffusion of the dye (which we measure) and the real micellar diffusion. In the isotropic and the nematic state the micellar aggregates have a finite aggregation number. The solubility of the dye in water is negligible and the dye is practically all the time in-

TABLE I

Sample	Phase	Temp.	%H_2O (wt%)	D(cm²/sec) × 10^{-7}	$D_{(20°)}$(cm²/sec) × 10^{-7}	R(Å)
I-1	Isotropic	54	64	5.0	2.5	86
I-2	Isotropic	54	64	6.3	3.2	63
I-3a	Isotropic	41.8	64	4.5	2.8	77
LC-2a	N	32.8	54	6.4	4.8	45
LC-2b	Sm	21.8	54	5.1	4.9	45
LC-3a	Sm	22.3	54	5.2	4.9	44
LC-3b	Sm	32.0	54	6.2	4.7	46
LC-3c	N	42.5	54	6.8	4.2	51

corporated into micelles. (In the isotropic solutions there is approximately 1 molecule of dye for each 1300 molecules of surfactant, in the liquid crystal samples 1 for each 300 molecules of surfactant). The diffusion of the dye as measured by us corresponds accordingly to the diffusion of the micelles themselves provided that fusion and division of micelles are negligible.

The diffusion in the smectic phase is more difficult to analyze. There are two possible mechanisms. If the mean aggregation number remains finite then the diffusion of the dye corresponds again to the diffusion of the aggregates. If, on the other hand, the micelles fuse to continuous lamellae then the determined coefficient $D_\perp$ describes the diffusion of the dye within the lamellae. Our data do not indicate a change of the diffusion mechanism. They support the structural model that the smectic layers in this phase are formed by finite micelles and not, as usually assumed, by continuous bilayers, at least not near the phase transition.

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