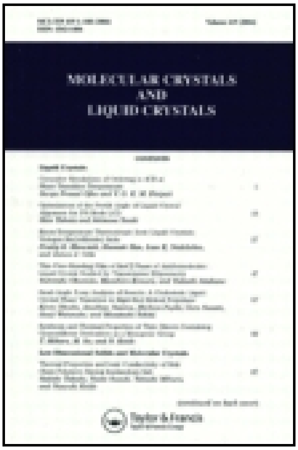

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Micellar Diffusion in the Liquid Crystalline and Concentrated Isotropic Phases of Decylammonium Chloride/NH_4Cl/H_2O Systems

John D. Gault [a] & JoÃO C. Denardin [b]

[a] Departamento de Fisica, Universidade Federal de Santa Catarina, 88049, Florianópolis, SC, Brasil

[b] Departamento de Física, UFSM, Santa Maria, RS, Brasil

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Micellar Diffusion in the Liquid Crystalline and Concentrated Isotropic Phases of Decylammonium Chloride/NH_4Cl/H_2O Systems

JOHN D. GAULT†

Departamento de Física, Universidade Federal de Santa Catarina, 88049, Florianópolis, SC, Brasil

and

JOÃO C. DENARDIN

Departamento de Física, UFSM, Santa Maria, RS, Brasil

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We have measured the diffusion coefficient of a non-water-soluable dye in aligned lamellar and nematic phases, perpendicular to the optic axis, as well as in micellar isotropic solutions of decylammonium chloride (DACl)/NH_4Cl/H_2O in the 25–90°C temperature range. The micellar diffusion in the nematic had a range of $4–15 \times 10^{-7}$ cm^2/s, in the isotropic $4–30 \times 10^{-7}$ cm^2/s and depends strongly on the sample composition. Diffusion is faster for samples containing greater amounts of DACl or NH_4Cl. Decreasing the concentration of NH_4Cl decreases the dependence of the diffusion on the water content of the sample. A simple order-disorder model is unable to account for changes in the diffusion coefficient at the nematic-isotropic transition.

INTRODUCTION

The recent revival of interest in lyotropic liquid crystals is due in large part to the special properties of the lyotropic nematic phase[1,2] however many questions remain open about this phase and also the other lyomesophases. In our opinion one of the most interesting (and

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†To whom correspondence should be addressed.

important) questions to be clarified is the way in which properties such as micellar size and the inter-micellar interaction vary from place to place in the phase diagram, *i.e.* the way in which they depend on the concentration of the various components of the system.

In order to help elucidate this problem we have undertaken a series of measurements of the diffusion of a dye in the lamellar, nematic and concentrated isotropic phases for varying water (or amphiphile) and salt concentration. The system we choose to study is decylammonium chloride (DACl)/NH_4Cl/H_2O as this is probably the system that has been investigated by the greatest number of different techniques.[1-10]

In our measurements (the complete details of the apparatus are described in References 7 and 8), the diffusion of a dye is measured perpendicular to the optic axis in aligned lamellar and nematic phases as well as in the isotropic. The dye is not water soluable and therefore is assumed to accompany the micelle, so that the diffusion measured in the nematic and isotropic phases is micellar diffusion. While micellar diffusion is not the only possible mechanism one can imagine for the diffusion of the dye in our system we believe the agreement in the order of magnitude of our measurements with those in low concentration isotropic micellar solutions[11-14] indicate that other mechanisms, if they exist, must be negligible. A discussion of other possible mechanisms can be found in References 7 and 8.

In an earlier experiment[8] diffusion in the DACl/NH_4Cl/H_2O system was measured for various samples of varying water content while the NH_4Cl/DACl weight ratio was maintained at 1:10. In the present work this ratio is maintained at 1:20. Also in reference 8 the diffusion was studied as a function of salt (NH_4Cl) content for a series of samples for which the water:DACl weight ratio was maintained at 1.16:1. Here we continue these measurements to a higher salt concentration.

RESULTS AND DISCUSSION

Samples were prepared and measurements carried out as described in Reference 8. Table I gives sample compositions and transition temperatures and Figures 1 and 2 show the measured diffusion coefficients. In Figures 3 and 4 the nematic and isotropic data are shown as a function of reduced temperature ($T_R = T - T_{N-I}$) where T_{N-I} is the nematic–isotropic transition temperature, and T the measurement temperature in degrees Celsius. The data in these last two

TABLE I

Sample compositions

Sample No.	DACl wt	NH_4CL wt	H_2O wt	L–N °C	N–I[a] °C
	(%)	(%)	(%)		
1	42.9	2.2	54.9	—	30
2	46.5	2.3	51.2	32	46
3	48.1	2.4	49.5	41	54
4	50.0	2.5	47.5	62	66
5[b]	45.5	1.8	52.7	15	30
6[b]	45.0	2.7	52.3	27	44
7[b]	44.6	3.6	51.8	33	51
8[b]	44.3	4.4	51.3	41	60
9[b]	43.8	5.3	50.9	46	65
10	43.5	6.1	50.4	55	71

[a] The temperature given is that of the beginning of the nematic–isotropic two phase region, which is typically about 2°C wide.

[b] Taken from Reference 8.

figures has also been multiplied by the viscosity of water at the temperature of the measurement. The reasons for this and its validity will be discussed below. The lines in all the figures are drawn to aid the eye, their only function being to link measurements on the same sample. In these figures the discontinuities in the lines are drawn at the phase transition temperatures as observed with the polarizing microscope.

The discontinuities in these lines at the L–N transition, as seen in Figures 1 and 2, are so small as to be within the experimental error, in contrast to our previous study[8] where this discontinuity was larger. (A discontinuity does not necessarily indicate a first order transition as the mechanism of the diffusion probably changes from that of a molecule of dye diffusing in an amphiphile bylayer to micellar diffusion, and in fact, the lamellar-nematic (L–N) transition is through to be second order).[1] The exact experimental error is difficult to define as it seems to depend to some extent on the phase (lamellar data are less reproducible than nematic and isotropic data) and perhaps also on sample history, when in the lamellar phase. There is also a possibility that some convection could be taking place at higher temperatures in the isotropic (above about 90°C). We plan to modify our experimental arrangement to improve the quality of our data.

For these reasons, the most we can say about the L–N transitions is that when our results are compared to the previous ones,[8] they seem to indicate a tendency for a decrease of the discontinuity at this

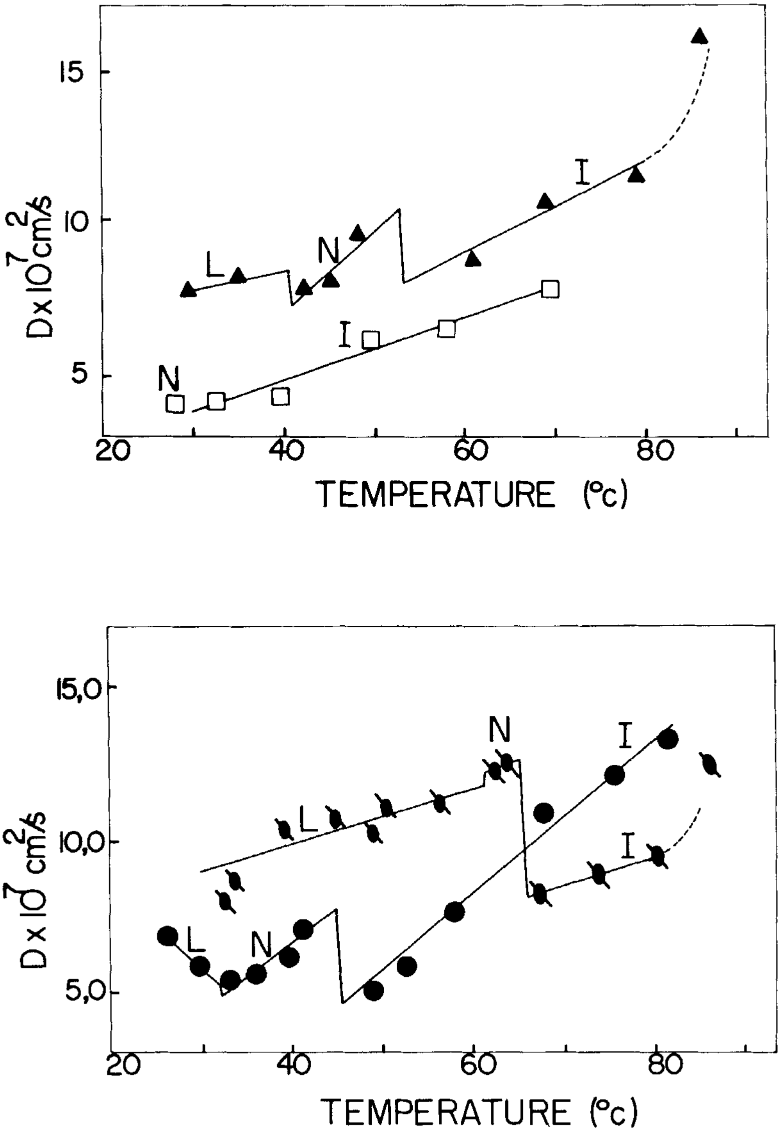

FIGURE 1 Diffusion coefficients as a function of temperature measured for samples of various water concentrations. All samples contain 1.00 g DACl and 0.05 g NH_4Cl. □ 1.28 g, ● 1.10 g, ▲ 1.03 g, ⬮ 0.95 g of H_2O, L = lamellar, N = nematic, I = isotropic.

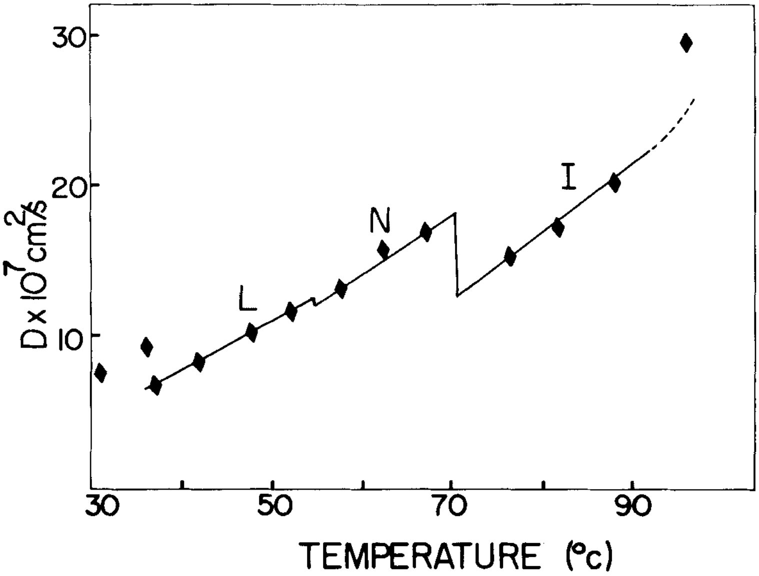

FIGURE 2 Diffusion coefficient as a function of temperature for a sample containing 1.00 g DACl, 0.14 g NH_4Cl and 1.16 g H_2O.

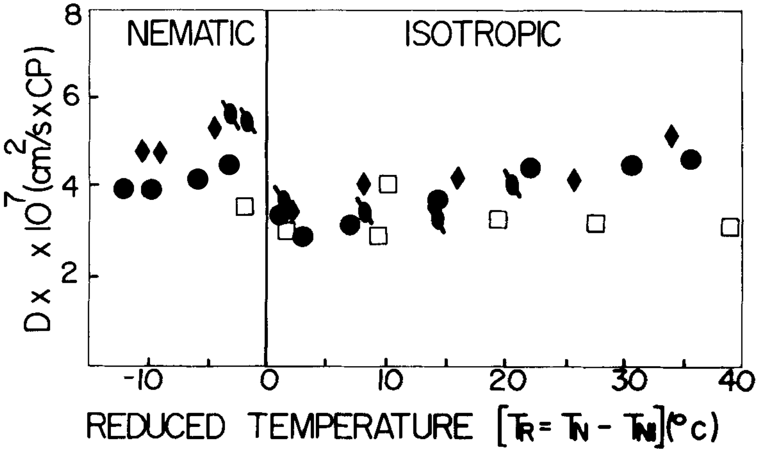

FIGURE 3 Diffusion coefficient corrected for water viscosity for samples containing different water concentrations. The diffusion in the nematic is measured perpendicular to the optic axis. (Symbols same as figure 1).

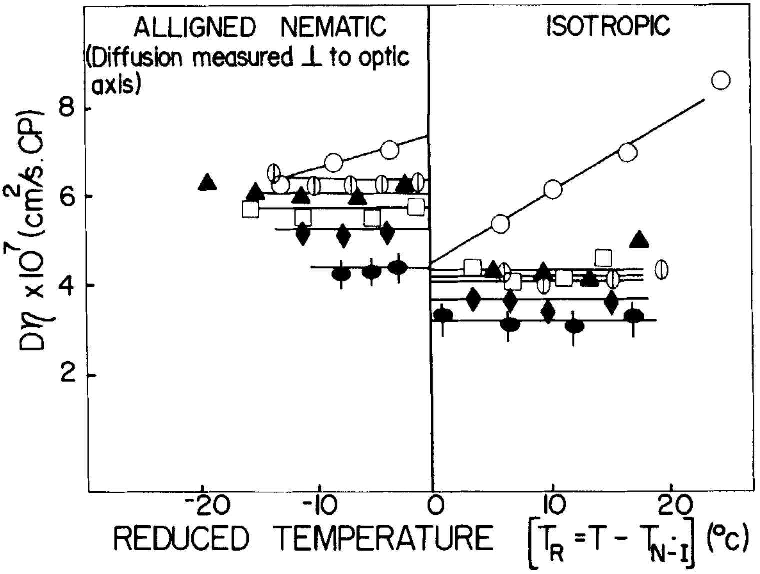

FIGURE 4 Diffusion coefficient corrected for water viscosity for samples of varying NH_4Cl concentration. ○ 0.14 g, ⏀ 0.12 g, ▲ 0.10 g, □ 0.08 g, ◆ 0.06 g, ⧫ 0.04 g, of NH_4Cl.

phase transition as the amphiphile and/or salt concentration decreases. Further studies with more precise measurements are needed to clarify the range in the behaviour of the diffusion coefficient (D) at the L–N transition.

The reason we choose to present the data in Figures 3 and 4 as a function of reduced temperature is to permit a comparison of what happens at the N–I transition for different samples. Figure 3 shows the effect of varying water concentration and Figure 4 shows the effect of varying salt concentration. In these two figures the measured D has been multiplied by the viscosity of water at that temperature. This is done to attempt to compensate for the very large variation of the viscosity of the medium through which the micelles are diffusing (a factor of 3 over the temperature range studied). We know, of course, that the medium is not pure water but contains salt and amphiphilic ions and that in a solution where 50% of the volume is occupied by the micelles, most of the water must effected in some way; however in lieu of a more realistic model, we use the viscosity of pure water. This same type of correction has been used with success for electrical conductivity measurements in this system.[9] The corrected diffusion in both Figures 3 and 4 shows much less temperature dependence than the untreated data (Figures 1–2) in fact many samples are within experimental error of a horizontal straight line, so we can say that if the temperature variation of D is not due to the variation of water viscosity, it is due to something whose temperature dependence is extremely similar.

In Figure 3, except for a tendency of D to be larger for samples containing more amphiphile, the curves of all samples essentially superimpose. When the present data is compared to that of Reference 8 (which has twice as much salt) it is readily observed that the decreased salt concentration has resulted in a system where D changes less as the water concentration is varied. It should be mentioned that the temperature range of the nematic is considerably less over most of the concentration range of the present (1:20 NH_4Cl:DACl) system than the 1:10 system used in Reference 8 and that the low temperature limit of our present apparatus is 5 degrees above room temperature so that the low temperature part of the phase diagram (where the nematic temperature range is greater) was inaccessible.

In Figure 4 we compare our high salt concentration data of the corrected diffusion constant to that of Reference 8 (note that the DACl:H_2O weight ratio is maintained constant at 1:1.16 in all measurements). At the lower salt concentrations (0.04 and 0.06 g NH_4Cl), D increases as salt is increased, both in the nematic and isotropic phases. For the intermediate salt concentrations (0.08 g–0.12 g), this dependence of D on salt concentration continues but is less especially in the isotropic. The 0.14 g NH_4Cl data is quite different and shows a temperature dependence different than that of water viscosity. This salt concentration is approaching the limit which the nematic phase will accept[6] and the behavior of the system here is obviously quite different.

To help interpret our data we have done a simple calculation of the relationship between micellar size and the diffusion coefficient (D) for disk shaped micelles. For this calculation we assume the micelle to have the shape shown in Figure 5, where a is the diameter of the flat portion of the disk and L (which corresponds to the length of the surfactant molecule) the radius of curvature of the micellar edge. The arrows labeled $D_\perp$ and $D_\parallel$ indicate diffusion perpendicular or parallel to the optic axis. We further assume that for the case when the micelle is a sphere ($a = 0$), the Stokes–Einstein equation holds, so that for a sphere of radius R diffusing in water at 20°C, we can write[7]

$$D(\mathrm{cm}^2/\mathrm{s}) = 2.15 \times 10^{-5}/R(\text{Å}) \qquad (1)$$

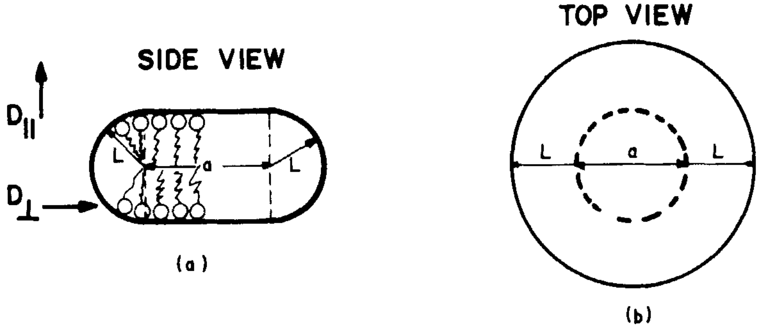

FIGURE 5 Micellar geometry used in calculation.

(we note that the only effect of this equation is to enable us to estimate the diffusion for spherical micelles, *i.e.* determines the values of the ordinate in Figure 6).

We will also assume that diffusion coefficient $D_\perp$ and $D_\parallel$ are proportional to the square root of the cross-sectional area of the micelle as seen in the direction of movement so that we obtain the Stokes–Einstein equation in the limit of spherical micelles.

In the case of thermotropic liquid crystals the diffusion in the isotropic is related to the diffusion in the nematic by the relation:[16]

$$D_{iso} = 1/3(2D_\perp + D_\parallel) \tag{2}$$

We will assume this relation is also true for micelles at the nematic–isotropic (N–I) transition, as would be expected if this phase transition was predominantly a case of order-disorder.

Based on these assumptions, we can calculate D_{iso}, $D_\perp$ and $D_\parallel$ as a function of increasing a; the results of this calculation are shown in Figure 6, for the case when L = 15 Å (a realistic value for the length of our surfactant molecule).[10] Also shown in this figure is the ratio of $D_\perp/D_{iso}$.

In Table II we give the measured values of $D_\perp$ and D_{iso} as well as the ratio $D_\perp/D_{iso}$ at the N–I transition for the different salt concentration, as determined from Figure 4.

When the data in Table II is compared to that in Figure 6, a discrepancy is readily observed. In the case of the calculation, a decreasing diffusion coefficient implies micellar growth and is always accompanied by an increase in the ratio $D_\perp/D_{iso}$. However in the experimental data, larger values of $D_\perp/D_{iso}$ correspond to a larger diffusion coefficient.

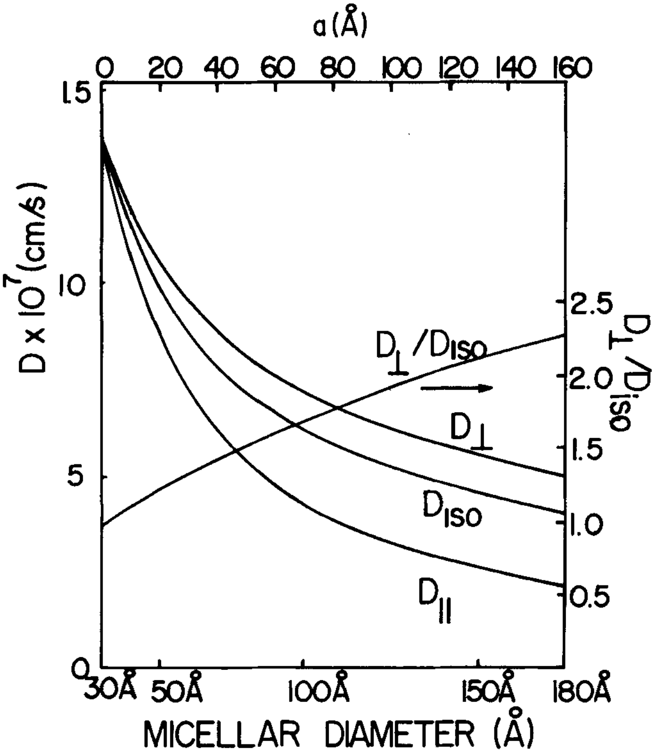

FIGURE 6 Calculation of the relationship between size and diffusion coefficient for disk-like micelles.

While the simple calculation we have done would not be expected to give the correct numerical results, the trends seem reasonable *i.e.* the fact that larger micelles diffuse slower and that larger disks have a greater anisotropy (as expressed by the ratio $D_\perp/D_{iso}$). However, the experimental data shows that one of these trends is inconsistent

TABLE II

Values of the diffusion coefficients of the N–I transition as determined from Figure 4.

Sample Number	Amount of NH$_4$Cl	$D_\perp$	D_{iso}	$D_\perp/D_{iso}$
5	0.04 g	4.3	3.2	1.34
6	0.06 g	5.2	3.7	1.40
7	0.08 g	5.7	4.1	1.39
8	0.10 g	6.1	4.2	1.45
9	0.12 g	6.4	4.3	1.48
10	0.14 g	7.4	4.3	1.72

with the observed results, either larger micelles are in fact diffusing more rapidly or some kind of a change in micellar form or interaction takes place at the N–I transition that renders equation 2 invalid.

While further experiments are necessary to resolve this question, we believe that when we consider that salt is known to cause growth in DACl micelles[14] together with the increased anisotropy in the diffusion that we observed with increasing salt concentration, that in this system, larger micelles may be diffusing more rapidly than smaller ones, especially in the direction perpendicular to the optic axis. As the model we used in our calculation is very simple-minded, other possibilities cannot be ruled out.

CONCLUSIONS

Measurements of the diffusion of a non-water soluable dye in aligned nematic and lamellar phases as well as in the concentrated isotropic show that the behavior of lyotropic systems can change rapidly as the position in the phase diagram (sample composition) changes. When the results of the present study are considered together with those of Reference 8 we observe a tendency of the diffusion to become more rapid both when water content is decreased (maintaining a constant DACl/NH_4Cl ratio) or when NH_4Cl content is increased (maintaining a constant DACl/H_2O ratio). In both of these case an increase in the diffusion coefficient is accompanied by an increase in the ratio $D_\perp/D_{iso}$. If this ratio is related to the anisotropy ($D_\perp/D_{iso}$) of the disklike micelles, as a simple calculation indicates it may be, then in certain cases we may be observing larger micelles diffusing more rapidly than smaller ones, at least in the direction perpendicular to the symetry axis of the disks.

Further measurements are necessary including those involving other experimental techniques before any definite conclusions can be drawn.

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