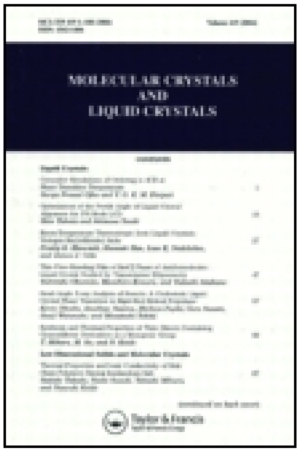

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Density and Susceptibility Measurements on a Micellar Nematic System

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Density and Susceptibility Measurements on a Micellar Nematic System

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The densities and diamagnetic susceptibilities in the nematic and isotropic ranges of two mixtures of decylammonium chloride, ammonium chloride, and water are reported. The mixtures have a lamellar smectic phase, a nematic phase, and an isotropic micellar solution. The smectic–nematic transition is second order, the nematic–isotropic transition first order. The density does not show a discontinuous change at the nematic–isotropic transition, and the expansion coefficients of the nematic and isotropic regions are the same within error limits. The diamagnetic susceptibility in the isotropic range and the susceptibility perpendicular to the optical axis in the nematic range were determined using the Gouy method. The diamagnetic anisotropy of the nematic range was derived. It varies from 2×10^{-9} near the nematic–isotropic transition to 5×10^{-9} cgs near the nematic–smectic transition.

I. INTRODUCTION

The interest on micellar liquid crystals has increased in recent years, but there are still few data available on basic physical properties. We report here density and susceptibility measurements on a micellar nematic system; the decylammonium chloride (DACl)/NH_4Cl/H_2O system. In an earlier paper[1] measurements of the bend and splay elastic constant and of the rotational viscosity were reported for this system, but only relative values for the constants could be given since data on the diamagnetic susceptibility were lacking.

The mixtures of DACl/NH_4Cl/H_2O used for this work have a nematic range of about 20 °C. The micelles formed by the DA^+-ions are disc-shaped. Upon cooling a second order transition to a lamellar smectic phase occurs. It indicates a close structural relationship between the micelles in the nematic phase and the "lamellae" in the smectic phase. We denoted this nematic correspondingly as N_L or N_d to distinguish it from another micellar nematic N_c which has cylindrical aggregates.

For technical reasons our measurements could not be extended into the smectic range. They cover only the nematic range and a range of about 10 °C into the isotropic micellar solution.

II. SAMPLE PREPARATION

Decylammonium chloride was synthesized as described earlier.[2] Measurements were made on two different mixtures with the following compositions:

A. $\mathrm{DACl/NH_4Cl/H_2O} = 43.2/4.8/52$ wt%,
B. $\mathrm{DACl/NH_4Cl/H_2O} = 45/5/50$ wt%.

The transition temperatures were 35 °C (A) and 45 °C (B) for the nematic–smectic transitions, and 55 and 65 °C for the nematic–isotropic transitions. The smectic–nematic transitions are second order; the nematic–isotropic transitions are first order with a two-phase region of about 2 °C. The temperatures listed or indicated in figures for these transitions give the beginning of the two-phase region.

For the density measurements, 30–50 g of each mixture were prepared. The components were carefully mixed with a magnetic stirrer in an air tight glass container at an elevated temperature corresponding to the middle of the nematic range. The samples were stored in an oven and checked for uniformity before measurements were made.

For the susceptibility measurements, oxygen was removed from the water by bubbling nitrogen through it for several hours. The water was added to the other components under a nitrogen atmosphere and the samples mixed as described. The samples were finally filled in quartz tubes (Wilmad Glass, i.d. (4.2 ± 0.013) mm) to a level of 3.5 inches and sealed and cut at a height of 4.5 inches. Before sealing, the air above the sample was flushed out with nitrogen.

III. DENSITY MEASUREMENTS

The densities were determined by weighing an immersed object, a hollow glass piece with a volume of 5.3285 cm^3 (including the immersed part of the suspension wire). The object was suspended by a wire from a Cahn RG electro-balance. The atmosphere above the sample was humidity controlled to prevent water loss by evaporation from the open surface, and the wire was kept at an elevated temperature using an infrared lamp to prevent condensation. The data, temperature and balance reading, were taken automatically with a controller (HP 9825). Heating and cooling rates were typically 0.2 °C/min.

The calibration of the experimental set-up was done by measuring the density of deionized water as a function of temperature over a range of $\approx 25\,°C$. The results were found to be in agreement with values in the literature[3] to better than 10^{-4} g/cm^3 over the entire range.

The results of the density measurements for the micellar system are given in Figure 1. The reproducibility was within the desired error limit of 10^{-4}. For neither of the two micellar concentrations measured does the density show a discontinuous change. It is estimated that any discontinuous change in density, that might exist, is less than 0.01%. The density in each phase range is a linear function of the temperature. The fitted coefficients are given in Table I.

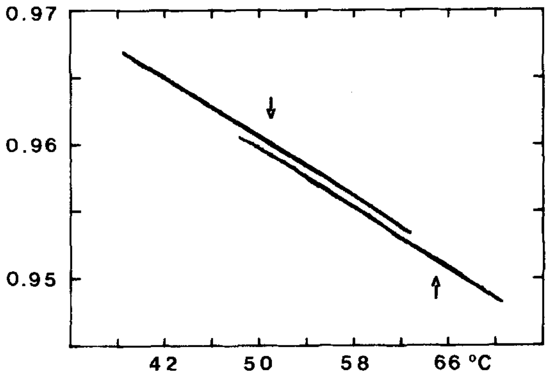

FIGURE 1 Density (g cm^3) micellar systems (Samples I and II). Arrows indicate lower end of two-phase nematic–isotropic region. Dotted curves, measurement taken in heating and cooling (10^{-7} cgs, left scale).

TABLE I

Linear Least Squares Fit for Density: $\rho = a_0 - a_1 T$
(T in °C, ρ in g/cm^3)

Sample I	a_0	a_1	rms
Nematic (35–55) °C	0.9882	5.52×10^{-4}	2.4×10^{-5}
Isotropic (> 57°C)	0.9894	5.73×10^{-4}	3.1×10^{-5}
Sample II			
Nematic (45–65) °C	0.9878	5.62×10^{-4}	6.6×10^{-5}
Isotropic (> 67 °C)	0.9881	5.66×10^{-4}	2.7×10^{-5}

The differences in the expansion coefficients, a_1 in Table I, between the nematic and isotropic regions are smaller than the error limits. It is indeed possible to fit both regions to the same linear function and within error limits.

IV. DIAMAGNETIC SUSCEPTIBILITIES

The diamagnetic susceptibilities were determined by the Gouy method. The magnetic field was produced by a 4-inch electromagnet with two-inch tapered pole caps. The maximum field strength was approximately 12.5 kG at the center of the 30 mm wide pole gap. The 4-1/2 inch long sample tube was suspended from the arm of a Cahn RG electrobalance so that its lower end was centered in a field of 12.5 kG, at maximum field setting, while the upper level of the sample was in a field of 1.5 kG. The measurements were carried out in an atmosphere of dry nitrogen. The samples were heated in an aluminum heating stage. A slow and steady stream of preheated nitrogen kept the sample chamber free from oxygen.

The experiments were run by a controller (HP 9825). Each data point for the susceptibilities given in the figures is an average of a cycle of 100 measurements during which the field at the center alternated 10 times between 12.5 kG and 1.2 kG. The resolution of the susceptibility measurements is $1 \cdot 10^{-10}$ cgs. The procedure was tested and calibrated by measuring the susceptibility of water for which very accurate data[4] are available (relative error, 10^{-6} obtained with a superconducting quantum interference device). We obtain agreement within the estimated relative error of 10^{-4} over the tested range from 35 to 65 °C.

Test measurements were also made in the nematic and isotropic range of methoxybenzylidene-butylaniline (MBBA; $T_{N-I} = 45\,°C$, synthesized at the Liquid Crystal Institute). The mass susceptibilities shown in Figure 2 were calculated from the directly measured volume susceptibility and density data taken from the literature.[5,6] Heating and cooling curve in Figure 2 show a separation, which is particularly obvious in the transition range, of approximately 0.8 °C. The separation is probably caused by a difference between thermistor temperature and sample temperature which was positive in heating and negative in cooling. The sweep rate for the temperature here and in the following experiments was 50 m°C/min. The diamagnetic anisotropy χ_a was calculated assuming that the mass susceptibility is temperature independent and equal to the value obtained in the isotropic region, $\chi_{\text{iso}} = -6.577 \times 10^{-7}$. The diamagnetic anisotropy of the nematic phase is positive and the material aligns with the optical axis parallel to the field. The susceptibility measured in the nematic phase $\chi_{\parallel}$ is the principal susceptibility in the direction of the optical axis. The anisotropy given in Figure 2 is calculated using

$$\chi_a = \tfrac{3}{2}(\chi_{\parallel} - \chi_{\text{iso}}) \tag{1}$$

where $\chi_{\parallel}$ are the measured values after adjusting the temperature scales by ±0.4 °C. The values reported in the literature for the anisotropy show large variations. The present results are in good

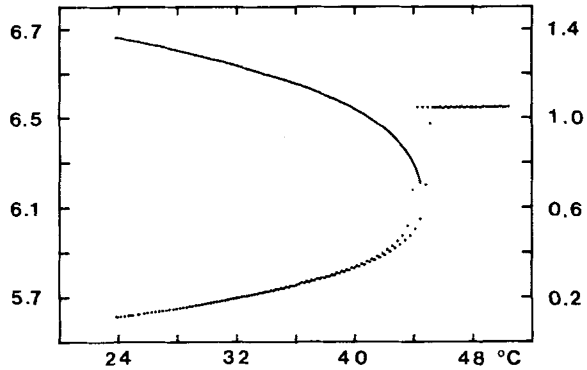

FIGURE 2 Mass diamagnetic susceptibility, dotted curves, measurements taken in heating and cooling (10^{-7} cgs, left scale) and diamagnetic anisotropy, solid line (10^{-7} cgs, right scale).

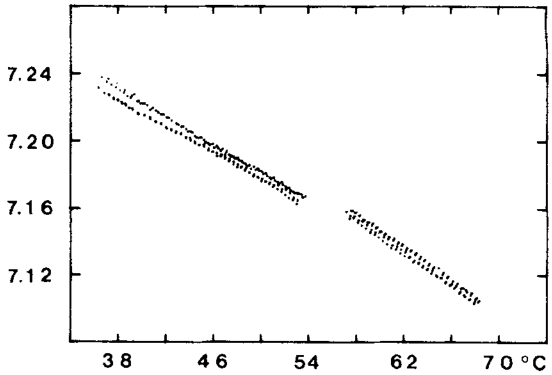

FIGURE 3 Volume diamagnetic susceptibility (10^{-7} cgs) of Sample I. Scale expanded to 10 times that of Fig. 2. Superimposed data for two consecutive heating and cooling cycles.

agreement with other data obtained with the Gouy method[8] while data obtained with the Faraday method[5,7] are lower.

The measurements with micellar mixtures reproduce, in repeated runs, within error limits except for the systematic deviations between heating and cooling (Figure 3). The experiment was programmed for these systems to jump the temperature over the two-phase range as quickly as possible, to avoid a separation of the components. The field was turned down during the jumps for the same reason. The systematic deviations between heating and cooling is again probably due to errors in the sample temperature determination.

Figure 4 shows the results for the mass susceptibilities. They represent the average of two continuous up and down runs. The sign of the diamagnetic anisotropy in these micellar nematic systems is negative. The experiment gives, therefore, the principle susceptibility perpendicular to the optical axis. In micellar systems the mean diamagnetic susceptibility has a temperature dependence which has to be taken into account when calculating the mean susceptibilities. The diamagnetic anisotropy is now given by

$$\chi_a = 3(\bar{\chi} - \chi_{\perp}). \tag{2}$$

We assumed that the mean susceptibility $\bar{\chi}$ can be obtained by linear extrapolation from the isotropic range. The results are presented in Figure 5.

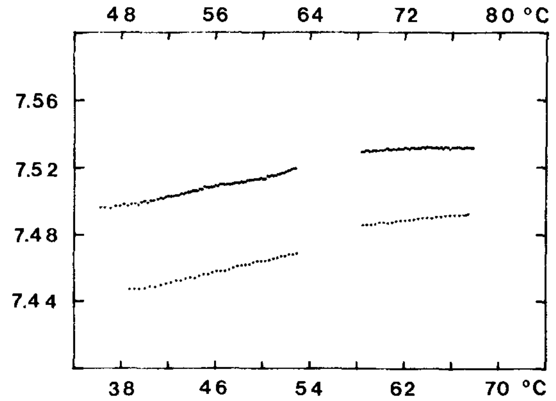

FIGURE 4 Mass diamagnetic susceptibility (10^{-7} cgs) of micellar mixtures I (lower curves and temperature scale) and II (upper curves and temperature scale).

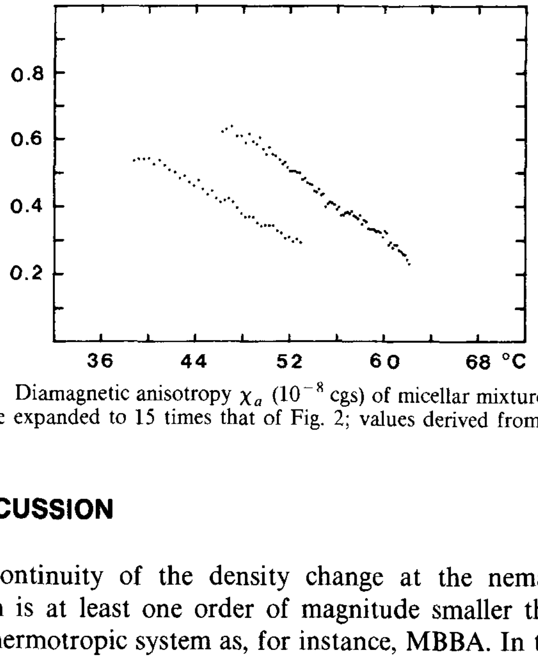

FIGURE 5 Diamagnetic anisotropy χ_a (10^{-8} cgs) of micellar mixtures I (left) and II (right). Scale expanded to 15 times that of Fig. 2; values derived from data of Fig. 4.

V. DISCUSSION

The discontinuity of the density change at the nematic–isotropic transition is at least one order of magnitude smaller than that in a typical thermotropic system as, for instance, MBBA. In thermotropics the packing density increases at the transition to the ordered state, but the density remains practically unchanged for the micellar systems. The transition to the micellar nematic state seems to consist only in an alignment of the micelles without a significant change in the micellar structure nor in the structure of water. The conclusion justifies the use of extrapolated values for $\bar{\chi}$ in Eq. (2).

The difference in the mass susceptibilities of the two micellar systems in Figure 4 is due to the difference in composition. The temperature dependence of the mean susceptibility as observed in the isotropic phase is then that of the mass susceptibility of pure water. It is due to the temperature dependence of the number of hydrogen bonds between water molecules (see for instance Ref. 9). The number of bonds depend, of course, also on the ion concentration and could be affected by a change in the micellar structure.

A recent study on a similar DACl system,[10] by light scattering and by magnetic birefringence, gives an estimated value for the diamagnetic anisotropy of -3.7×10^{-9} cgs. The order of magnitude is in agreement with the present data but it is nearly a factor two times larger than the value that our data give when extrapolated to the transition range. The deviation is larger than the experimental error of our data which we estimate to be $\pm 6 \cdot 10^{-10}$ cgs.

As mentioned in the introduction, the diamagnetic anisotropies allow the determination of the absolute values of curvature elastic constants and of the rotational viscosity coefficient. The values give some insight in the intrinsic physical properties of micellar systems and allow comparisons with thermotropic nematics.[11]

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