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DENSITY MEASUREMENTS ON LYOTROPIC NEMATIC MIXTURES: POTASSIUM LAURATE, DECANOL, WATER AND SODIUM DECYLSULPHATE, DECANOL, WATER

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ABSTRACT:

The density as a function of temperature is measured for two nematic mixtures through a micropicnometry technique specially developped for this purpose. The samples were KL (potassium laurate) - H_2O - DeOH (decanol) and NaDs (sodium decyl sulphate) - H_2O - DeOH. The density of the former at a fixed temperature is them estimated by calculation from high resolution X-ray results obtained for a mixture of similar concentrations and found to be in good agreement with the experimental result at the same temperature. The mean aggregation number of the same phase is also estimated.

I. INTRODUCTION

Mixtures of amphiphilic molecules and water are know to exhibit three types of nematic phases, depending upon the conditions of temperature and relative concentrations. Two of these are uniaxial[1] and a third one is biaxial[2] (N_{BX}). The uniaxial phases have been further classified[3] as calamitic (N_C) and discotic (N_D), according to whether the director $\vec{n}$ orients respetively parallel or perpendicular to the magnetic field.

On the other hand, X-ray[4] and neutron[3] diffraction experiments have been meaningful in the determination of the micellar shape. Thus, on the evidence of such experiments the micelles were first thought to be prolate and oblate aggregates in the N_C and N_D phases, respectively. It was then further supposed that at the uniaxial - biaxial transition the micelles actually changed in the shape, transforming from a flat disk (N_D) or alongated cylinder (N_C) to some kind of ellipsoid.

Recently, hawever, another view was proposed, mostly on the basis of X-ray diffraction patterns obtained at different temperatures in the three nematic phases[5,6]. The different nematic phases were then analysed as being the macroscopic result of orientational fluctuations of the

micelles (full rotation around the director in the case of the uniaxial phase and small amplitude oscillations in the biaxial one). The uniaxial phases are therefore not formed, within this scheme, by cylinder or disk-like aggregates, but rather by statistically similar and biaxial shaped ones.

Adopting this model and in possession of sufficient data concerning the micellar dimensions[7] and spacing distances it is possible to make an approximate calculation of the density of the mixture in question, as well as of the mean number of amphiphilic molecules in a micelle (mean aggregation number). The latter in particular was done by Hendrikx et al.[3] for a KL - DeOH - D_2O system.

As for density measurements the available data are very few, as is also true of other basic physical properties of liquid crystals. Stefanov and Saupe[8] measured the density of the DACl (decyllammonium choloride) - NH_4Cl - H_2O of different concentrations, wich both presented the phase sequence smectic - nematic - isotropic. An electro-balance was used to measure the thrust on an immersed sphere in the sample.

In this paper we present the results obtained with a different technique to measure the density of lyotropic mixtures. The investigated systems are: KL - DeOH - H_2O and NaDs - DeOH - H_2O, with respectively the phase sequences N_D - N_{BX} - N_C and hexagonal (HEX) - N_C - isotropic (ISO).

II. EXPERIMENTAL

The device employed in the density measurements is composed essentially by a cylindric water chamber (8cm diameter) with a double wall. Inside the wall, water circulates by means of a pump which is programmable for a certain temperature and digitally controlled. The temperature within the chamber is further measured by an ordinary thermometer (accuracy of 0.05°C). Still inside the chamber is a little hollow metal cylinder, which serves the purpose of a support for a micropicnometer containing the sample to be keptin there. The shape of this picnometer is particularly important in the precision that can be attained. It consists of a capillary part which goes into a cylindric bulk filled up with almost the whole of the sample. The capillary is in turn just thin enough to allow the introduction of a needle and the placing of the material inside. At its lower end (almost at the junction with the bulk) is a tiny control mark that makes possible the definition of a fixed volume for the picnometer. Since the capillary is very thin (diameter less than 1mm) and the bulk contains practically all the fluid, even a very slight change in the density can be detected by the alteration of the level of the sample at the control mark.

The whole structure (water chamber, picnometer, connecting pipes) during the measurements is closed and protected by thick insulating layers. Once the temperature is stable, the picnometer is taken out and the mass of the sample is determined by ordinary weighing. The density is then directly calculated, provided a previous calibration is made (in our case water was used) so that we can consider the dilation of the glass due to the variation of temperature.

Finally, the samples were prepared with the following concentrations (weight percentages):

Sampe 1: KL - 28% ; DeOH - 7.26%; H_2O - 64,74%. The phase sequence is N_D 17.5°C N_{BX} ~ 20.5°C N_C

Sample 2: NaDs - 41,6%; DeOH - 6,6%; H_2O - 51,88%, with the sequence HEX (hexagonal 17.0°C N_C 38.9°C ISO.

All transition temperatures were determined by optical microscopy, except the N_{BX} —— N_C transition (sample 1), which was estimated from a phase diagram for the KL - DeOH - D_2O mixture[9].

III. RESULTS AND DISCUSSION

A. Density Measurements

The results of the density measurements for the samples 1 and 2 are shown by figure 1 and figure 2 respectively. The following aspects could be pointed out:

1. In the case of sample 1 the density d_{1C} decreases from 1.01400 ± 0.00035 (g/cm^3) to 1.00260 ± 0.00035 (g/cm^3) in the 12.5°C—— 32,8°C range. The density of sample 2 (also denoted by d_{1C} in figure 2) decreases from 1.0643 ± 0.0004 g/cm^3 to 1.0433 ± 0.0004 g/cm^3 in the 13,0°C 47.0°C range.

2. In view of the experimental error and the number of points near the transition temperatures no discontinuity in our curves can be detected. This is in accordance with the results obtained by Saupe for the DACl/NH_4Cl/H_2O system (with a better precision, as we shall soon discuss).

3. The whole behaviour of the density d_{1C} within the two total measured intervals is not linear, but the points in the intervals corresponding to the different phases (hexagonal, N_C, N_D, N_{BX} and isotropic) can be fitted by straight lines.

4. Concerning the final accuracy obtained with the method, we point out that it is proportional to the volume of the picnometer, as could be quite naturally expected (if the capillary is of the same thickness). This verification could be made comparing the previons use of a smaller picnometer (0.8 cm^3 volume, which yielded results with a 1.5×10^{-3} g/cm^3 error) and the two measurements now presented, for which the same picnometer (3.5 cm^3) was employed (the difference between the two errors 3.5×10^{-4} and 4.0×10^{-4} is explained by a higher viscosity of sample 2, which has a slight influence on the final accuracy). The control of the level of the sample becomes with a larger picnometer more troublsome, but this can be eventually coped with, which expains the proportionality.

The technique presents the advantage of being very straightforward, and much greater precision could be obtained with other picnometers, as has been shown. A 35 g amount of sample in a 35 cm^3 picnometer would make possible an error of not more than 5×10^{-5} g/cm^3 (30 - 50 g gave Saupe a 10^{-4} g/cm^3 precision with the thrust measuring electro-balance method).

Finally, we note that we couldn't make the capillary any thinner, for then the introduction of the liquid crystal would be practically impossible on account of the high viscosity involved.

B. Calculation of the density and the mean aggregation number of sample 1

From measurements on X-ray diffraction patterns obtained with high resolution at different temperatures in the three nematic phases[7] of a KL - DeOH - D_2O system the dimensions of the available micellar volume (dimension of the micelles plus water) can be obtained. In fact, the phase for which these data were obtained has similar concentration to the ones of sample 1.

If this is combined with the assumption that the water equally covers the whole of the micelle[3] thus neglecting the difference between flat and curved regions, the average dimensions of the biaxial micelles (a, b and c) can be inferred[7]. Thus the micelle is considered as a parallelepiped contained in a larger one corresponding to the available micellar volume.

The values defining the available micellar volume V_A (A, B and C) were found to be nearly constant in the measured temperature range within the experimental error limits[7]. And so the values a,b and c calculated directly by the subtraction of the spacing distance $d = 23 \pm 2$Å.

We have $A = (106.8 \pm 1.3)$ Å; $B = (82 \pm 1)$ Å; $C = (49 \pm 1)$ Å; $a = (83{,}8 \pm 2)$ Å; $b = (59 \pm 1{,}5)$ Å and $c = (26$

± 2) Å.

Furthermore, the available micellar volume is a unit whose repetition is the whole of the sample itself. This gives the possibility of a calculation of the density from this volume.

The density d_{lc} will be given by:

$$d_{\ell c} = \frac{(V_A - V_M)\, d_w + M_{KL} + M_{DeOH}}{V_A}$$

where V_M is the volume of the micelle (obtained from a, b and c; V_M = a b c) d_w the density of water, M_{KL} and M_{DeOH} the masses of KL and DeOH contained in V_A (= A B C) . d_w is found in the literature[10], while M_{KL} and M_{DeOH} can be calculated since the mass of water ($(V_A - V_M) . d_w$) is known, as well as the relative concentration of KL and DeOH. On the other hand, the number of molecules of KL and DeOH in a micelle n_{KL} and n_{DeOH} are immediately obtained from the division of M_{KL} and M_{DeOH} by the mass of a molecule of KL or DeOH.

The values are: d_w (15.3°C) = 0.999129 g/cm^3, M_{KL} = 3.7591 X10^{-22} g; M_{DeOH} = 2.6285 x10^{-22} g. We therefore obtain:

d_{lc}(15.3°C) = 1.07 ± 0.10 g/cm^3

This final error results from the measurements

associated with the micellar dimensions, since the other values are known with much greater accuracy.

The measured d_{lc} at 15.3°C (Fig.1) is 1.01230 (± 3.5 x 10^{-4}) g/cm^3.

Finally, n_{KL} = 320 ± 50 and n_{DeOH} = 125 ± 20.

CONCLUSIONS AND REMARKS

The density of water does not vary significantly in the measured range as regards the estimation of d_{lc}, Since d_w (15.3°C) is the only element that specifies this calculation at 15,3°C we should expect that the error of the estimated d_{lc} includes the entire variation of the measured density.

Indeed, d_{lc} varies from 1.01400 (12.5°C) to 1.00260 g/cm^3 (32.8°C), a variation emtirely embraced by that error.

In addition, considering that the maximum value for the calculated d_{lc} is 1.17 g/cm^3, we can conclude that the error resulting from approximating the micellar shape by a parallelepiped must not be greater than 15%. This fact provides some confirmation of our original hyotesis.

On the other hand, the difference between sample 1 and the mixture whose micellar dimensions were deduced[7] is not significant, for the relative concentration of the amphiphilic components differ by less than 2%, and the

density of the micelle is quite similar to that of the water. Such a slight change in the relative concentration of any of the three components of the mixture can therefore produce only a neglectable alteration in the density.

To conclude, our result for n_{KL} can be said to be reasonably in accordance with the one obtained by Hendrikx et al[3].

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS:

1 - Variation of the density d_{1c} of sample 1 with temperature. All points are within the nematic range (N_D, N_{BX} and N_C).

2 - Variation of the density of sample 2 with temperature. All points are within the nematic phase (N_C) or the hexagonal phase (HEX) or still in the isotropic range.

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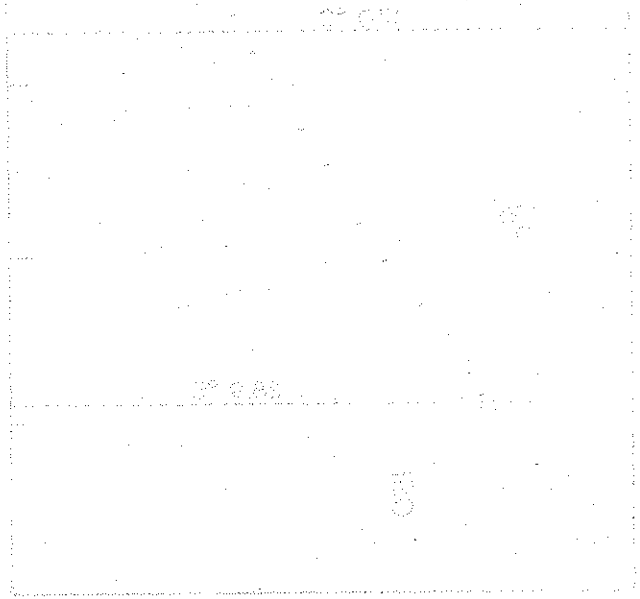

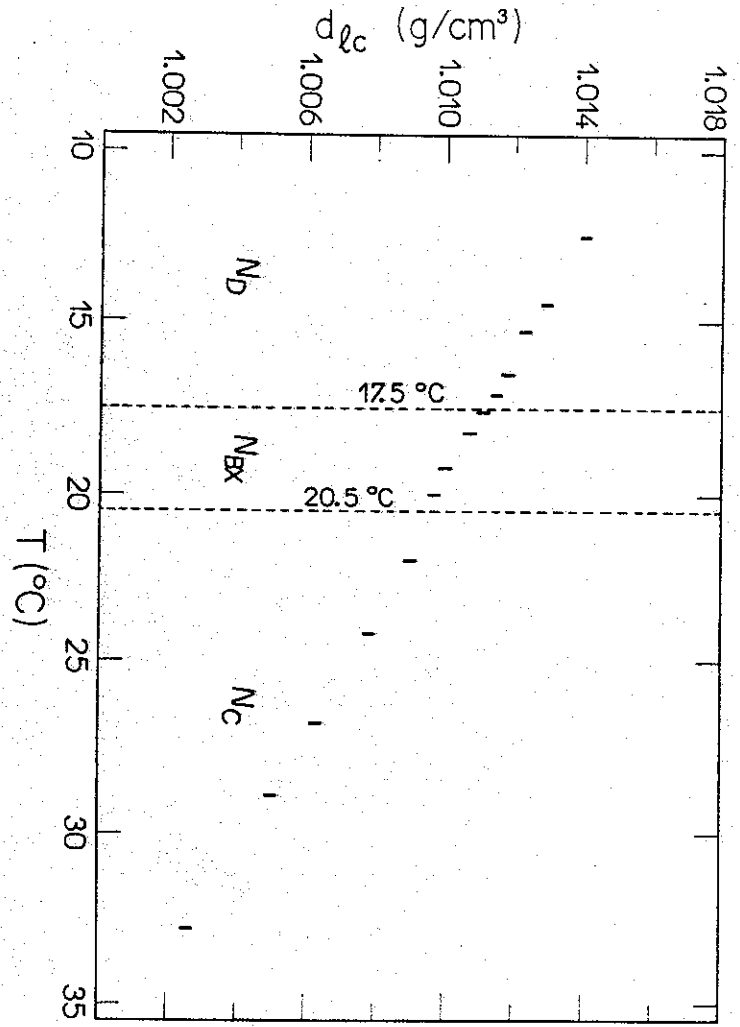

FIGURE 1

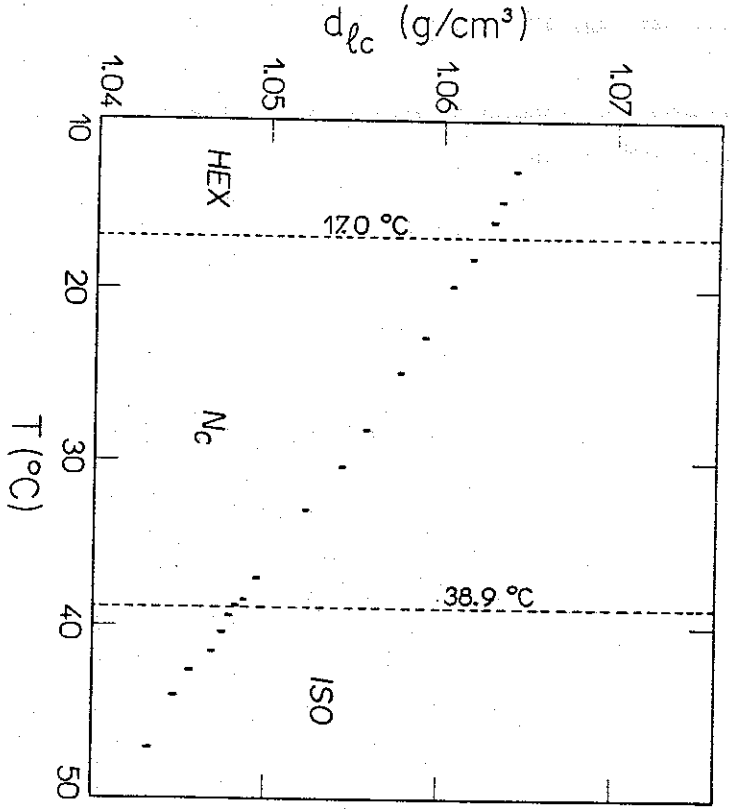

FIGURE 2