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T. BEICA*, RODICA MOLDOVAN, MADALINA R. PUICA† and S. FRUNZA

National Institute of Materials Physics, Bucharest, R-76900, Romania

†Polytechnic University of Bucharest, Department of Physics,
Spl. Independentei 313, Bucharest, R-77206, Romania

Experimental results for the temperature dependence of density at normal pressure for two compositions of sodium lauryl sulphate/decanol/water solutions, exhibiting either a calamitic or a discotic lyotropic nematic phase at room temperature, are presented. Within the limits of experimental precision ($\pm 1 \times 10^{-5}$ g cm^{-3}), the systems show no jump in density at the nematic to isotropic phase transition. Over the studied temperature range, the mean thermal expansion coefficients were also evaluated.

1. Introduction

Lyotropic liquid crystals are formed by surfactant molecules in a suitable solvent, often water. Lyotropic nematic liquid crystal phases, formed by micellar aggregates with long range orientational order but no translational order, have been observed in several systems over various composition and temperature ranges [1–5]. The stability ranges of the nematic phases are narrower than those observed for other lyotropic phases. Three kinds of lyotropic nematic phases have been observed, two of which are uniaxial, a calamitic (N_c) and a discotic (N_d), and the third is biaxial (N_{bx}) [6]. The detailed shape of the micelles in the nematic phase is still a matter of discussion. It is generally assumed that oblate micelles give the nematic discotic phase while prolate micelles give the nematic calamitic phase. However, in all three nematic phases it was shown [7] that, over a large range of temperature and concentration, the micelles maintain their biaxial symmetry. The different nematic phases are then the macroscopic consequence of differing orientational fluctuations of the micellar aggregates, these orientational fluctuations being full rotations around the director in the uniaxial nematic phases, but only small amplitude oscillations in the biaxial nematic phase.

The determination of volume–temperature characteristics at constant pressure for a liquid crystal is an important part of the thermodynamic study of its properties and of phase transitions. Such measurements have been made in different lyotropic systems including, n-octylamine/water [8], decylammonium chloride/NH$_4$Cl/water [9–12], caesium perfluoro-octanoate (CsPFO)/water [9, 11, 13], and tetradecyltrimethylammonium bromide/water [14]. The CsPFO/water system has been widely studied from a thermodynamic point of view and the first results concerning the volume–temperature characteristics, indicating very special behaviour [9], led to controversial discussion in the literature [13].

In this paper we present some experimental density vs. temperature results for the sodium lauryl sulphate (SLS)/water/decanol system in concentrations corresponding to calamitic (N_c) and discotic (N_d) nematic phases at room temperature, as reported in the literature [5, 15]. In the limits of experimental precision, for both studied lyotropic systems, we obtained a variation of the density with temperature which did not include a jump at the nematic to isotropic phase transition. In the experimental section we present the materials used, sample preparation, and the experimental technique for measuring the thermal expansion; in § 3, the experimental results are presented and discussed.

2. Experimental
2.1. *Materials and sample preparation*

Sodium dodecyl sulphate (SLS) (Sigma 99% purity) used without further purification, 1-decanol (Merck) and triply distilled water were used to prepare the lyotropic solutions. Thus, SLS and water were weighed into a glass vessel, which was tightly closed with a screw cap. Solutions were mixed by slowly rotating the vessel about

*Author for correspondence; e-mail: tbeica@alpha2.infim.ro

its short axis at room temperature until the mixture appeared homogeneous. The appropriate quantity of decanol was added to the clear fluid. Finally, this mixture was again mixed for one week. Between experimental measurements the samples were maintained in a thermostated environment at $T = (23 \pm 1)^{\circ}$C in order to avoid precipitation and phase separation.

The compositions of the two samples studied (wt %), chosen in accordance with the literature phase diagram [5, 15] in order to obtain at room temperature lyotropic liquid crystal with calamitic (N_c) and discotic (N_d) behaviour, were:

25.05(SLS)/70.46(water)/4.48(decanol), giving N_c phase (solution A)
22.39(SLS)/72.71(water)/4.9(decanol), giving N_d phase (solution B).

It is known from the literature [16] that on increasing the temperature, solution A undergoes a phase transition from N_c to isotropic phase passing through a ($N_c + I$) coexistence domain. Solution B may exhibit more complex behaviour with temperature, as a system of close composition [17] undergoes a phase transition from N_d to isotropic phase passing through a ($N_d + I$) coexisting domain, followed at higher temperatures by an isotropic to lamellar (L_α) transition.

2.2. *Experimental techniques*

We investigated the expansion of the liquid crystal as a function of temperature using a dilatometer having a capillary tube (of volume $\cong 1.45$ cm^3). The volume of the liquid in the dilatometer, as a function of its level in the capillary tube measured from the top, was calibrated using mercury. The length of the liquid column in the calibrated capillary of the dilatometer (internal diameter $\cong 0.51$ mm) was measured using an Abbe comparing microscope (Zeiss) with an accuracy of ± 1 µm. The precision of the determination of the column length was high and led to small errors in the density variation determinations, of about $\pm 1 \times 10^{-5}$ g cm^{-3}. On the other hand, we note that the absolute values of the density were determined by the precision of the mass determination, which is about $\pm 1 \times 10^{-4}$ g, but this does not influence the conclusions of the study. The measurements on each sample were repeated four times.

In order to avoid the possible variation of solution composition during the measurements, we built a tightly sealed micro-chamber provided with a temperature control device and observation facilities. The temperature inside the micro-chamber was measured with a thermocouple. The temperature control was achieved using a TB-150-type device (VEB MLW Prufgerade-Werk, Medingen) circulating water within the micro-chamber walls. The stability of the temperature was $\pm 0.01^{\circ}$C.

We determined the temperature gradient in the thermostatted chamber along the dilatometer tube by observing the nematic to isotropic transition of a thermotropic liquid crystal (5CB) in a capillary tube. In the reservoir region of the dilatometer the temperature non-uniformity was evaluated to be 0.05°C. The measurements were made at a constant temperature variation with a rate of 1.5°C h^{-1}.

In order to eliminate air bubbles, the lyotropic solution was introduced into the dilatometer reservoir two days before measurements, and held in a vertical position in a tightly closed tube. The tube was firstly ultrasonicated for 1 h and then kept in a vertical position for 24 h. The next day, the dilatometer reservoir was filled up with the lyotropic solution and carefully closed with its capillary tube, placed in the sealed thermostated chamber and allowed to attain thermodynamical and mechanical equilibrium for 24 h.

During the density measurements, the dilatometer reservoir was observed between crossed polarizers to determine the transition temperatures (T_0) between anisotropic and isotropic phases. The phase transitions were observed both on heating and cooling, with results that differed by $\approx 0.5^{\circ}$C. In each case, we chose the transition temperature to be the mean value of the two determinations. For nematic to isotropic transitions we obtained $T_0 = 29.6^{\circ}$C for solution A and $T_0 = 28.6^{\circ}$C for solution B. For solution B, at about $T_b = 31^{\circ}$C, the isotropic phase underwent a transition into another anisotropic phase, exhibiting a new birefringent texture, that may be a lamellar phase L_α [17].

3. Experimental results and discussion

Figures 1 and 2 show two examples of results for the temperature dependence of the density for solutions A and B, respectively. The curves in figures 1(*a*) and 2(*a*) were obtained from the experimental determination of the liquid column length in the capillary of the dilatometer, the volume of which is calibrated and by weighing the mass of the liquid contained in it. These curves were fitted with linear regression analysis and the results are given in the figure captions.

Figures 1(*b*) and 2(*b*) show the difference between the density and the fit with the corresponding linear regression analyses for solutions A and B, respectively. This type of plot better shows the deviations of the expansion compared with linear behaviour, and makes possible the easier observation of any density jump at the phase transition. The examination of these plots shows that, within the precision of this experiment, such a jump cannot be seen either at the N–I transitions, or at the I–L_α transition of solution B.

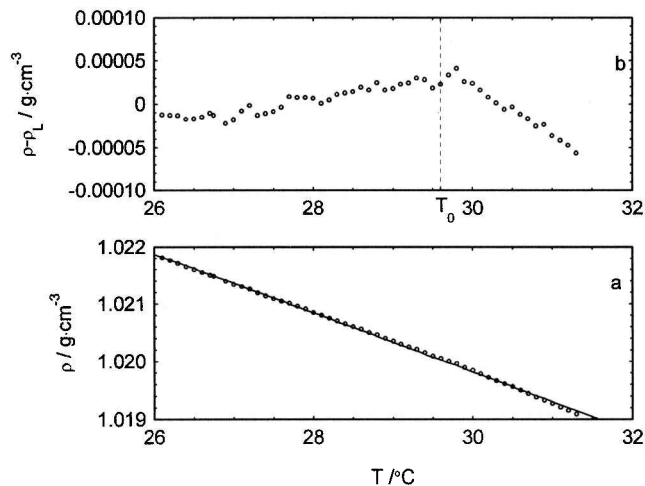The nematic to isotropic transition is first order as a result of the symmetry of the ordered phase [18]. The

Figure 1. (*a*) Temperature dependence of the density ρ for solution A; the straight line is the linear regression analysis for the data, $\rho_L = 1.0351 - 5.139 \times 10^{-4} T$. (*b*) The deviation of the density ρ from the linear variation ρ_L; T_0 is the nematic to isotropic transition temperature determined optically.
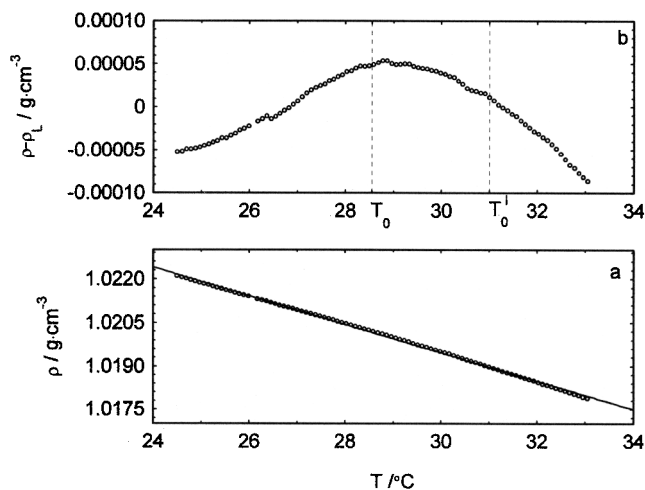

Figure 2. (*a*) Temperature dependence of the density ρ for solution B; the straight line is the linear regression analysis for the data, $\rho_L = 1.0343 - 4.9070 \times 10^{-4} T$. (*b*) The deviation of the density ρ from the linear variation ρ_L; T_0 and T_0^b are the nematic to isotropic and isotropic to lamellar transition temperatures, respectively, determined optically.

absence of density jumps in our experimental data leads to the conclusion that such a jump has to be smaller than the precision of the method. Our results are similar to those of Boden and Jolley [13] for the CsPFO/water lyotropic system and do not confirm those of Photinos and Saupe [9]. Boden and Jolley [13] studied the temperature dependence of density in CsPFO/water systems in the N^d concentration regime and obtained different behaviour depending on the experimental method

used, either the oscillating densitometer or the classical dilatometer. With the dilatometer method they could not detect any jump in density at the phase transition. They associated the changes obtained with the oscillating method to some non-equilibrium state of the sample, resulting from the method. Their theoretical estimation of the density jump at the phase transition, using previously reported pressure dependence of the isotropic to nematic transition temperature [19] and the heat absorbed at the transition [20], was 1×10^{-7} g cm^{-3}, a change smaller than the precision of the dilatometer method.

In their experiments, Photinos and Saupe [9] obtained an increase in density at the nematic to isotropic phase transition. There are thermodynamic arguments against their results. In fact, experimental measurements [19] show that $dT_{NI}/dp > 0$ for the same lyotropic system and consequently, a decrease in density has to be observed on passing from the nematic to isotropic phase. Unfortunately, for the SLS/decanol/water system studied here, such data describing the pressure dependence of the isotropic to nematic transition temperature and of the heat absorbed at the transition are not available in the literature.

The plots in figures 1(*b*) and 2(*b*) provide evidence for the existence of two regions having different slopes for the variation of volume as a function of temperature, namely in the nematic and isotropic phases. A small change in the density curve slope could also be detected at the I–L$_\alpha$ transition for solution B. In figures 1(*b*) and 2(*b*) the transition temperatures detected optically, T_0 and T_0^b, are marked.

The experimental values of the temperature dependence for the liquid crystal density were fitted with the function (1*a*) for solution A and with function (1*b*) for solution B:

$$\rho = \begin{cases} \rho_{NI} + a(T - T_{NI}), & T < T_{NI} \\ \rho_{NI} + b(T - T_{NI}), & T > T_{NI}. \end{cases} \quad (1\,a)$$

$$\rho = \begin{cases} \rho_{NI} + a(T - T_{NI}), & T < T_{NI} \\ \rho_{NI} + b(T - T_{NI}), & T_{NI} < T < T_{IL} \\ \rho_{NI} + b(T_{IL} - T_{NI}) + c(T - T_{IL}), & T > T_{IL}. \end{cases}$$

$$(1\,b)$$

The results are given in the table.

As mentioned previously, the measurements were repeated four times for each solution. The fit of the different experimental curves using equation (1) led to fitting coefficients ρ_{NI}, a, b, c, deviating from those in the table by a maximum of 10%. In the case of the T_{NI} and T_{IL} fit coefficients, a greater spread of the values obtained from the different experiments was observed.

Table.   Fitting coefficients corresponding to equation (1) for the temperature dependence of the liquid crystal solutions.

Solution	$\rho^{NI}/\mathrm{g\,cm}^{-3}$	$a \times 10^4/\mathrm{g\,cm}^{-3}\,\mathrm{K}^{-1}$	$T_{NI}/^{\circ}\mathrm{C}$	$b \times 10^4/\mathrm{g\,cm}^{-3}\,\mathrm{K}^{-1}$	$T_{IL}/^{\circ}\mathrm{C}$	$c \times 10^4/\mathrm{g\,cm}^{-3}\,\mathrm{K}^{-1}$
A	1.0199	-4.999	29.8	-5.715	—	—
B	1.0201	-4.630	28.9	-5.105	31.0	-5.353

The fit achieved using linear regression analysis of the density vs. temperature data allowed the evaluation of the mean thermal expansion coefficients at constant pressure, α_P, for each solution:

solution A $\alpha_P = 5.1 \times 10^{-4}\,\mathrm{K}^{-1}$,

solution B $\alpha_P = 4.9 \times 10^{-4}\,\mathrm{K}^{-1}$.

The thermal expansion coefficients evaluated for all the experiments, were smaller in the nematic than in the isotropic phase. However, without data for different SLS/decanol/water compositions over a similar temperature range, one cannot claim that this result is a characteristic of this lyotropic system.

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