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Comparison between densitometer and dilatometer measurements in liquid-crystal phases

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This study focuses on a comparison between densitometer and dilatometer measurements of two liquid-crystal systems: the 4-methoxybenzylidene-4′-butlylamiline (MBBA) system and a micellar system consisting of octyammonium chloride (OACl) and water. The measurements are taken near two phase transitions: the nematic-isotropic and the hexagonal-isotropic. The former refers to the MBBA and the latter to the OACl. It is observed that whereas, at the nematic-isotropic phase transition, the densitometer and dilatometer measurements exhibit a similar step density change, at the hexagonal-isotropic transition the densitometer measurements show a step density change which is about five times larger than the one detected in the dilatometer experiments. The results are discussed and compared to other liquid-crystal systems. [S1063-651X(97)00908-2]

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INTRODUCTION

The density is a relevant parameter in the investigation of liquid-crystal systems, particularly in the study of the phase transitions [1,2]. From the thermodynamics viewpoint, it can present either a discontinuity at a first order transition or change continuously [3] at a second order transition. The density has been used in the high resolution experiments determining the critical exponents of the thermotropic systems near the smectic-*A*–nematic transition [4]. On the other hand, in the micellar system, the density can be associated with changes in the structure of the micelles [5], which are basic constituents of the lyotropic liquid crystals [6]. Usually the density with high resolution is determined by either the vibration densitometer or classical dilatometer. However, the use of the vibrating densitometer in the amphiphilic liquid-crystal density measurements brings up some controversy in the literature [7,8].

The main purpose of this paper is to present new density measurements focusing on this interesting issue. We present density studies on the 4-methoxybenzylidene-4′-butlylamiline (MBBA) system and a micellar system octylammonium chloride (OACl)—55 wt %) and water (45 wt %), near the nematic-isotropic phase transition and hexagonal-isotropic phase transition, respectively. These systems were ideally chosen for this study because near the nematic(hexagonal)-isotropic phase transition they show a well-defined discontinuity in density [9,10]. The resulting data reported were obtained with both the vibrating densitometer and a classical dilatometer. The data from the two methods show a pronounced difference in density in the OACl system near the hexagonal-isotropic phase transition. A similar behavior has been observed in another micellar system [7] in the nematic to isotropic phase transition. On the other hand, for the thermotropic MBBA there was practically no difference in the observed density behavior. This difference between the measurements determined through densitometer and dilatometer in the micellar system has been associated with the occurrence of complex nonequilibrium configurations induced by the vibration of the sample container in the densitometer experiment [7]. Nevertheless, in spite of more recent experimental efforts [8,10,11] this issue has not been completely clarified so far. Therefore we try to present some general considerations about this point, having our additional experimental data as a basis.

EXPERIMENT

Experiments were carried out on the MBBA and OACl systems as a function of the temperature near the nematic-isotropic transition and hexagonal-isotropic transition, respectively. Measurements of the densities were determined from the oscillation period of a U tube using an Anton Paar instrument consisting of a microcell (DMA-602 HT) and a processing unit (DMA60). The sample temperature was controlled by means of a Haake K-20/DC-5 circulating temperature bath. The temperatures of the sample were stable at 10 mK. The constant calibration of the densitometer was determined from the water and air values, respectively [12,13]. Special care was taken during the experiments to ensure that there were no air bubbles in liquid-crystalline samples. The precision in the density measurements was 5×10^{-6} g/cm^3. In this experiment the sample is placed in a U tube with internal diameter of 2 mm. The curved part of the sample tube was electronically stimulated in an undamped harmonic fashion. The direction of oscillation was perpendicular to the plane of the U-shaped sample tube. The U tube was clamped so that the vibration amplitude was larger in the curved part of the tube. The measured period [8] is most sensitive to the density in the curved part of the tube. The same measurements were also realized in both liquid-crystal systems using a classical dilatometer with a large cylindrical tube with 8 mm of internal diameter and 10 cm in length. The dilatometer had a sensitivity larger than 5×10^{-6} g/cm^3 and a flat capillary with area of 0.9 mm^2 and 15 cm in length was attached to it. The height of the capillary column was measured by means of an optic system that made it possible to take measures with an 8 μm per division graduate scale adapted to a cathetometer, with the possibility of detecting volume changes of 7×10^{-6} cm^3. The phase transition temperatures were checked by using a polarized light microscopy, in the bulk and sealed in flat capillaries.

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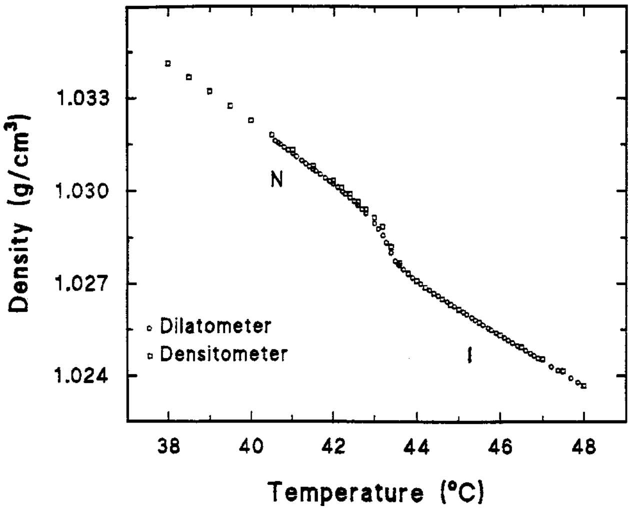

FIG. 1. Density vs temperature at nematic-to-isotropic phase transition in the MBBA system. Nematic N sample.

RESULTS AND DISCUSSION

The density results for MBBA in the vicinity of the nematic-to-isotropic transition measured by both densitometer and the dilatometer are shown in Fig. 1. No hysteresis was observed in these experiments between the cooling and heating cycles. The density readings were obtained in about 20 min after each temperature change. Note that the density change at the nematic-isotropic transition is well defined, and corresponds to a discontinuity in the density of approximately 2×10^{-3} g/cm^3. This experimental result is consistent with the thermodynamic definition of a first order transition and with other experimental data obtained with different techniques for the same thermotropic phase transition [9]. In Fig. 1, there is no noticeable difference between the behavior of the density data of the densitometer and that of the dilatometer. Therefore, despite using the vibrating-tube densitometer, this fact was not significant enough to change the equilibrium configurations of the thermotropic system, as suggested by another densitometer experiment in a micellar system [7].

On the contrary, Fig. 2 clearly shows a pronounced difference in the measured density values of the OACl system in the hexagonal phase. The trends of the experimental curves obtained with both experimental techniques are similar. In order to make the density difference explicit, we have plotted in Fig. 3 the difference ($\Delta\rho$) from the extrapolated linear density values of the isotropic phase. The densitometer measurements exhibit step density changes, at the hexagonal-isotropic transition, which is about five times larger than the one detected in the dilatometer experiments. This means that the density measured by the densitometer is being, in some way, amplified in relation to the density determined by the dilatometer. The comparison of the dilatometer data with those of the densitometer clearly shows that the observed change may have occurred due to a micellar packing in the hexagonal phase. To our knowledge, there is no independent measurements of this parameter regarding this micellar system. Boden and Jolley [7] measured the density of the CsPFO and water micellar system in lamellar, nematic, and isotropic phases. The density variation that they observed near the nematic-isotropic phase transition was similar to ours: it appears only in the densitometer experiments, but was not detected in the dilatometer experiments. The authors have suggested that the difference in the density measurements is probably related to the vibration of the U tube in the densitometer experiment. Moreover, the micelle interaction with the container boundary surface is very complex and a behavior distinct from the one presented by thermotropic systems was revealed [14]. The physical properties involved in this process have not been completely understood yet. In this sense, the combination of the nonequilibrium state of the sample, induced by the vibration of the sample container (curved part of the U tube), associated with boundary surface defects can produce a change in the density values determined by the densitometer experiments when different micellar systems are considered.

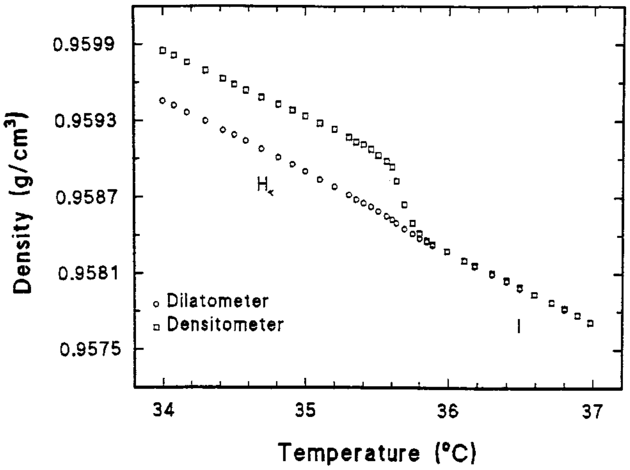

FIG. 2. Density vs temperature at hexagonal-to-isotropic phase transition in the OACl system. These values were obtained from Ref. [10]. Hexagonal H_α sample.

In conclusion, we have carried out a detailed comparison between densitometer and dilatometer measurements in two liquid-crystal systems. Our experimental data confirm that, in a micellar system, there is a difficulty in the utilization of the densitometer for the density measurements near the phase transition (see Fig. 3). However, for a thermotropic liquid

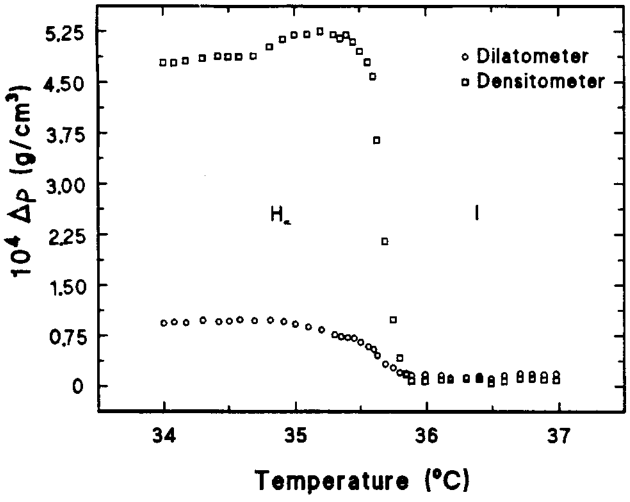

FIG. 3. Temperature dependence of the difference of the density ($\Delta\rho$) for measurements of Fig. 2, as described in the text.

crystal, the comparison between the densitometer and the dilatometer data demonstrates that the observed densities are nearly the same in the nematic thermotropic phase. Additional experiments with other thermotropic systems and a study of the critical exponent near smectic-A–cholesteric transition are in progress. In this way, we believe that the experimental fact reported here can be extended to different thermotropic liquid crystals. Finally, it is important to mention that the thermotropic liquid crystals differ strongly from the micellar systems. Having anisotropic micelles as their basic units, these systems are complex structures consisting of mixtures of amphiphilic molecules and a solvent (generally water).

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