Rapid Note

Smectic A–Cholesteric liquid crystal phase transition: A density study

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Abstract. The present work is focused on density measurements near the smectic A–cholesteric liquid crystal phase transition for cholesteryl myristate (C_{14}), cholesteryl nonanoate (C_9) and binary mixtures of C_{14} and C_9 and cholesteryl caproate (C_6) and C_9. The results have evidenced that the transition crosses over from first to second order when both the mean molecular length and the reduced temperature, r (ratio between the smectic A–cholesteric and cholesteric–isotropic phase transition temperatures), decrease in the system. The occurrence of a second order phase transition is observed for a concentration very near 63.1 molar percent of C_9 in the C_6-C_9 mixture at $r \cong 0.92$.

PACS. 61.30.Eb Experimental determinations of smectic, nematic, cholesteric, and other structures – 64.70.Md Transitions in liquid crystals

1 Introduction

The nature of the either first or second order phase transition in liquid crystal systems has been the subject of extensive experimental and theoretical studies, specially when concerned to the smectic A (A)–nematic (or cholesteric, C) phase transition [1]. According to an extension of the McMillan's molecular theory proposed by Lee *et al.* [2], a second order transition was predicted for a reduced temperature, $r = T_{AN(C)}/T_{N(C)I}$, at or below 0.88, where $T_{AN(C)}$ and $T_{N(C)I}$ are referred to as smectic A–nematic (or cholesteric) and nematic (or cholesteric)–isotropic transition temperatures, respectively. Some calorimetric studies on binary mixtures [3], where the molar ratio between two different liquid crystal molecules is an important parameter, have shown that the reduced temperature can vary from 0.89 to 0.99 [4–6]. In fact, calorimetric measurements of the latent heat performed by one of us [7], through differential scanning calorimeter, on binary mixtures of cholesteryl caproate (C_6), heptanoate (C_7) and nonanoate (C_9) have indicated the possibility of second order A–C transition for r values ranging from 0.90 to 0.92. In order to better explore this possibility, we focus now on the A–C phase transition of some mixtures by means of density measurements.

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Density measurement is a powerful tool for analyzing phase transitions in liquid crystals [8]. From thermodynamic point of view, a first order transition is associated to a discontinuity in the density values at the transition, whereas a second order is related to a continuous change in the density values [9–11]. In the literature, very few investigations have been reported on the density changes associated to the A–C transition. In particular, Demus *et al.* [12] have carried out precise measurements of density as a function of temperature for the cholesteryl myristate (C_{14}) in the smectic A, cholesteric, blue and isotropic phases. The authors showed that the C–blue phase is a transition of second order, within a very narrow temperature interval. Measurements of the density obtained (with a vibrating densitometer [13]) from pure compounds of both C_{14} and C_9 as well as from binary mixtures composed of C_{14} and C_9 and C_6 and C_9 are here reported as a function of temperature in the vicinity of the A–C phase transition. The results evidence a second order phase transition at $r \cong 0.92$ for 63.1 molar percent of C_9 in C_6, in good agreement with previous calorimetric measurements [7], as discussed below.

2 Experimental

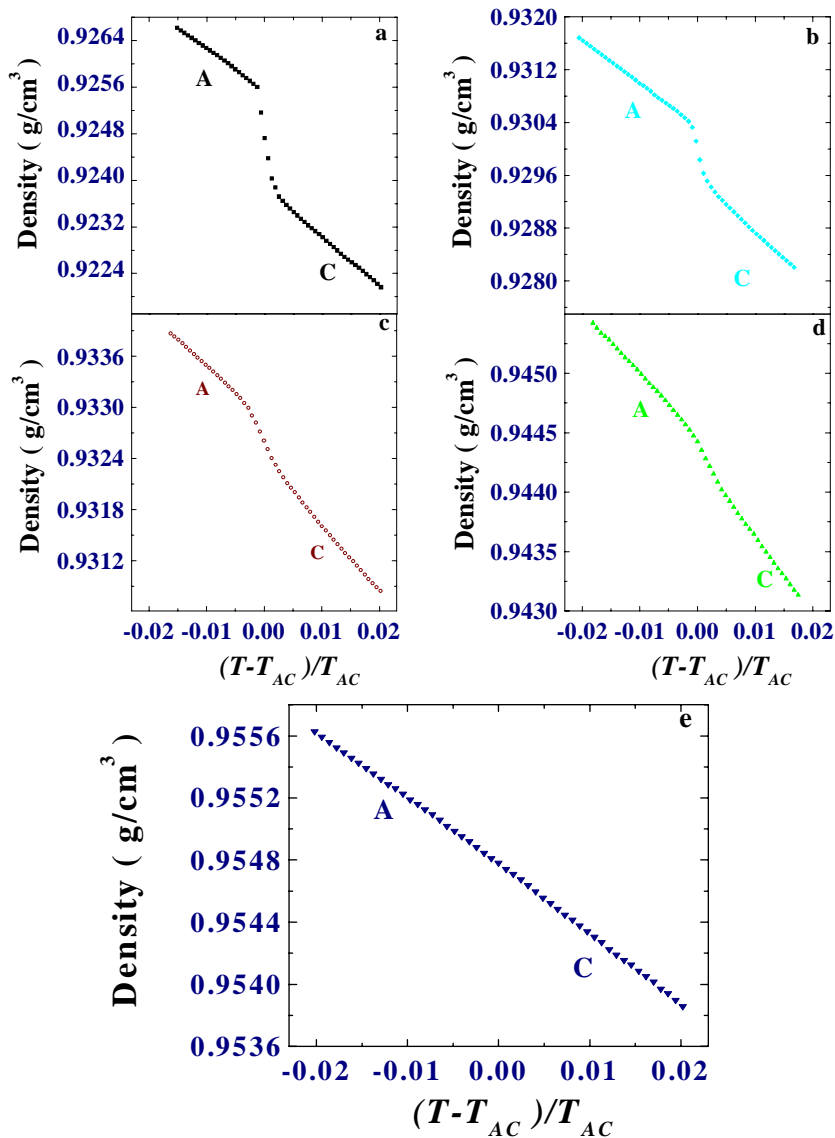All liquid crystal compounds used in the current work were purchased from the Sigma Chemical Company Ltda

Fig. 1. Density *versus* ratio $(T - T_{AC})/T_{AC}$ near the smectic A (A)–cholesteric (C) phase transition temperature (T_{AC}) for samples consisting of: (a) cholesteryl myristate (C_{14}); (b) 81.5 molar percent of C_{14} in the C_9-C_{14} mixture; (c) 63.5 molar percent of C_{14} in the C_9-C_{14} mixture; (d) cholesteryl nonanoate (C_9) and (e) 63.1 molar percent of C_9 in the C_9-C_6 mixture.

and recrystallized from ethyl acetate. The A–C and C–I transition temperatures were determined by polarized light microscope equipped with a hot stage (HS1) with an accuracy of 0.01 K. Table 1 shows such temperatures along with the respective reduced temperatures, r. Experiments were carried out on the pure C_{14}, C_9 and the binary mixtures of 81.5 molar percent of C_{14} in C_9, 63.5 molar percent of C_{14} in C_9 and 63.1 molar percent of C_9 in C_6[7] as a function of temperature near the A–C phase transition. The pure compound, cholesteryl caproate (C_6), studied in this work, exhibit only a cholesteric phase. Density measurements were determined through the oscillation period of a U tube by means of an Anton Paar instrument consisting of a microcell (DMA–602HT) and a processing unit (DMA–60). The sample temperature was controlled by a Haake K−20/DC−5 circulating temperature bath. The temperatures of the sample were stable at 0.01 K. The densimeter calibration constant was determined from the known values of the water and the air [14,15]. Special care was taken during the experiments in such a way that no air bubbles were presented in the liquid-crystalline samples. The precision of the densimeter is 5×10^{-6} g/cm^3. For these experiments, the samples were contained in a U tube with internal diameter of 2 mm. The curve part of the sample tube was electronically stimulated in an undamped harmonic fashion. The direction of oscillation was perpendicular to the place 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. Then, the phase transition temperatures were checked from the bulk of the sample tube by using a polarized light microscope.

Table 1. Composition of the investigated samples, temperatures, T_{AC}, T_{CI} and reduced temperature, $r = T_{AC}/T_{CI}$, at the smectic A (A)–cholesteric (C) phase transition, where T_{CI} represents the C–isotropic (I) transition temperature.

	Concentration	(mol%)	$\Delta\rho \times 10^{-4} (\mathrm{g/cm^3})$	T_{AC} (K)	T_{CI} (K)	r
C_{14}	100.0	0.0	16.10	352.48	357.60	$0.986^{(a)}$
$C_{14}-C_9$	81.5	18.5	8.40	350.18	358.59	0.977
$C_{14}-C_9$	63.5	36.5	5.20	347.01	358.95	0.967
C_9	0.0	100.0	2.10	347.53	363.65	0.956
$C_6^{(b)}-C_9$	36.9	63.1	0.25	336.98	367.06	0.918

[a] In fact, a blue phase was observed between the C and I phases, in agreement with literature [12]. However, for simplicity due to its narrow domain, the blue phase was not accounted for in the reduced temperature definition.
[b] $T_{CI} = 372.73$ K

3 Results and discussion

The density results *versus* the ratio $(T - T_{AC})/T_{AC}$ of the pure compounds C_{14} and C_9, along with the binary mixtures $C_{14}-C_9$ and C_9-C_6 in the vicinity of the A–C phase transition are shown in Figure 1. The density data were recorded after 20 min each temperature was reached. The measurements were repeated and showed to be reproducible. It was previously pointed out [7] that the latent heat decreases much more abruptly in the cooling cycles than in the heating cycles. Conversely, there is not any noticeable difference between the density data during cooling and heating cycles, in this vicinity of the A–C phase transition. This can be associated to the equilibrium experimental conditions verified during the data acquisition.

As one can see from Figure 1, the density values decrease as temperature increases within a given phase. Further, there is a jump in the density values at the phase transition for the sample composed of pure C_{14} (Fig. 1a), whose amplitude decreases for the $C_{14}-C_9$ mixtures (Figs. 1b and 1c) and for pure C_9 (Fig. 1d). Unlike these results, the density values of the sample consisting of 63.1 molar percent of C_9 in C_6 (Fig. 1e) present an almost continuous change along the A–C phase transition.

With a view to stressing the difference in the density values observed at the A–C transition, Figure 2 shows the difference, from the extrapolated linear density values of the smectic A. Note that the well defined jump at the A–C transition for the C_{14} pure compound (Fig. 1a) corresponds to a discontinuity in the density value of around $1.61 \times 10^{-3} \mathrm{g/cm^3}$ at $r = 0.986$ (Tab. 1), in good agreement with Demus *et al.*'s results [12]. This experimental result is consistent with the thermodynamic definition of a first order transition. On the other hand, the steep change in the density values at the transition shown in Figure 1a, is reduced to 8.40×10^{-4} g/cm^3 and to 5.20×10^{-4} g/cm^3 for the mixture of C_{14} in C_9 while r diminishes to 0.977 and to 0.967, respectively (Tab. 1). Such decreasing can be related to the presence of two molecules of different lengths in the bilayer structure of the smectic phase, that produces changes in the molecular packing of the phase.

The tendency of a continuous change in density is evidenced in Figures 1d and 2, for the C_9 pure compound at $r = 0.956$ (Tab. 1). In addition, we have detected
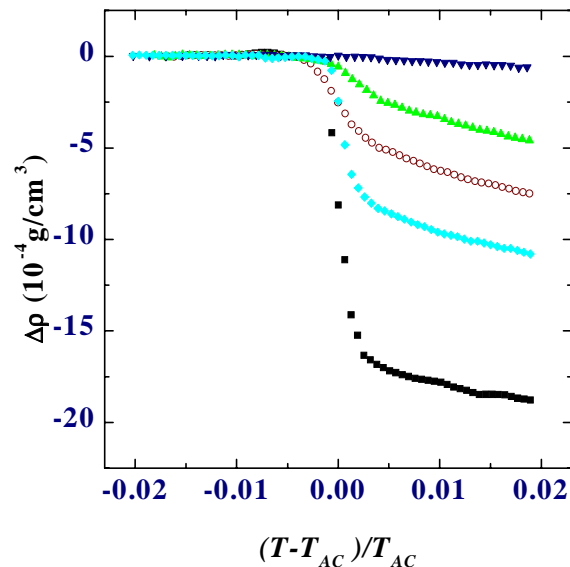

Fig. 2. Difference of the density values, $\Delta\rho$, *versus* the ratio $(T - T_{AC})/T_{AC}$ of measurements obtained in the Figure 1 (see text for details): (■) cholesteryl myristate (C_{14}); (♦) 81.5 molar percent of C_{14} in the C_9-C_{14} mixture; (○) 63.5 molar percent of C_{14} in the C_9-C_{14} mixture; (▲) cholesteryl nonanoate (C_9); (▼) 63.1 molar percent of C_9 in the C_9-C_6 mixture.

a variation in the density value of around 2.10×10^{-4} g/cm^3. This A–C phase transition has been considered as being weakly of first order by McMillan [16]. His X-ray scattering intensity measurements indicated a kind of smectic A domain formed in the cholesteric phase before the transition. Such effect has been attributed to the so called order parameter fluctuations in the neighborhood of the smectic A phase.

From Figure 1e, one can note a slight variation in the slope of density linear behavior near the A–C phase transition ($\Delta\rho \cong 2.50 \times 10^{-5}$ g/cm^3, Fig. 2) for the sample consisting of 63.1 molar percent of C_9 in C_6 at $r = 0.918$ (Tab. 1). Note that, the value of ρ changes by 0.16 percent across the A–C phase transition for the C_{14} but only by 0.0025 percent (64 times less) across the same transition for the 63.1 molar percent of C_9 in C_6. Based on such fact,
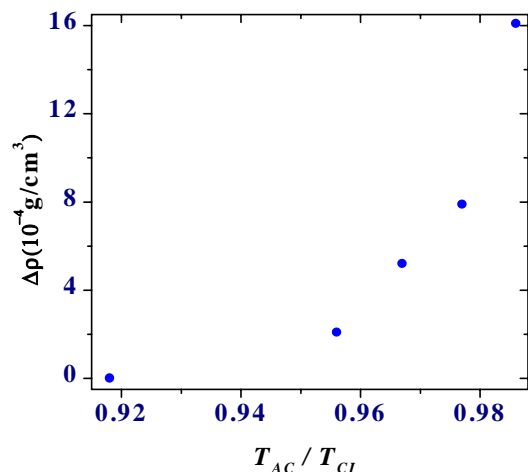
Fig. 3. Difference of the density values, $\Delta\rho$, as a function of the reduced temperature $r = T_{AC}/T_{CI}$ for all studied samples.

we infer that the A–C phase transition has a second order nature for this studied sample.

According to McMillan's molecular theory proposed by Lee *et al.* [2], the energy associated to the smectic ordering is directly described as a function of the reduced temperature and indirectly related to the chain length of the alkyl tails. Then, the nature of the phase transition is strongly dependent on both parameters. The theoretical results show that the energy increases as both chain length and reduced temperature increase in the system. As a consequence, first order phase transitions are observed when these values are large, while second order transitions can occur for smaller values. Thus, our experimental results are in qualitative agreement with McMillan's theory, once we have observed that the transition crosses over from first to second order as the mean molecular length diminishes in the system at the same time that the reduced temperature, r, decreases (Tab. 1). In order to highlight this behavior, Figure 3 shows $\Delta\rho$ as a function of r, that emphasizes the second order nature of the A–C transition ($\Delta\rho \cong 0$, $r \cong 0.92$) for 63.1 molar percent of C_9 in C_6. To our knowledge, there is not any density measurement regarding these cholesteric mixtures in the literature.

To sum up, we have carried out a detailed density study near the A–C phase transition for binary mixtures of some aliphatic cholesteryl esthers. The results are consistent with the McMillan's molecular theory proposed by Lee *et al.* [2] and confirm a second order phase transition for the sample composed of 63.1 molar percent of C_9 in the C_9-C_6 mixture. The study of the heat capacity in the vicinity of this A–C phase transition would be of considerable interest. X-ray scattering measurements are in progress with a view to better understanding and evaluating structural changes along the phase transitions.

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