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Latent heat measurements of the smectic A–cholesteric transition on binary mixtures

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New differential scanning calorimetry measurements of the smectic A–cholesteric latent heat of transition for binary mixtures of cholesteryl nonanoate (C_9) and cholesteryl heptanoate (C_7), cholesteryl nonanoate and cholesteryl caproate (C_6) are reported for cooling cycles. These measurements give evidence of a tricritical point at approximately the reduced temperature $T_{S_ACh}/T_{ChI} \cong 0{\cdot}92$ for 63·1 mol per cent C_9 in the mixture of C_6 and C_9. This tricritical point occurs at reduced temperatures and concentrations different from those already obtained for heating cycles for the same mixture.

1. Introduction

In a recent paper [1], strong evidence for a smectic A (S_A)–cholesteric (Ch) tricritical point in C_6–C_9 binary mixtures of liquid crystals was reported for the heating cycles. The results were in good qualitative agreement with McMillan's molecular theory extension proposed by Lee *et al.* [2]. It was also pointed out that the latent heat decreases much more abruptly for cooling cycles than for the heating cycles. The new data we report here show a pronounced difference in the latent heat between the two cycles. Within the experimental resolution, we have found that the location of the tricritical point for the cooling cycle is different from that found for the heating cycle.

The main purpose of this paper is to present these new data on the tricritical behaviour of the mixture, focusing our attention on the measurement of the latent heat for the cooling cycles. To the best of our knowledge, data for the cooling cycles for this binary mixture are not previously reported in the literature. The marked difference between the heating and cooling cycles may be related to the fluctuations of the order parameter [3] in the neighbourhood of these tricritical points, but the whole question was not completely clarified up to now, despite more recent theoretical efforts [4]. Furthermore, we try to present some general considerations about this interesting tricritical phenomena, based on the existing molecular models for the nematic/cholesteric–smectic A transition [5].

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2. Experimental

The liquid crystals used in these experiments were obtained from the Aldrich Chemical Company Ltd. and recrystallized from ethyl acetate. The transition temperatures were determined with a polarizing microscope equipped with a Mettler FP 5 hot stage, and a Perkin–Elmer DSC-2 differential scanning calorimeter (see table). The accuracy in the measurements of the temperatures of transition was 0·2°C. An indium calibration standard was used for calculating the latent heat (and the entropy of transition) of the S_A–Ch transition. Full scale ranges of 1·0, 0·5 or 0·2 mcal s^{-1} and 2·5, 1·25, or 0·625°C min^{-1} are used during these measurements in order to facilitate more accurate estimates of the usually low latent heat of the S_A–Ch transition. The appropriate scales were chosen so as to maintain the thermal equilibrium of the system. As we have already mentioned, the measurements of the latent heat were made for cooling cycles of the sample for a wide range of relative concentrations of the binary mixture.

3. Results and discussion

We start by considering the phase diagram of the binary mixture of aliphatic cholesteryl esters, C_7–C_9 and C_6–C_9, exhibited in figure 1. The pure compounds, cholesteryl caproate (C_6) and cholesteryl heptanoate (C_7), exhibit only a cholesteric mesophase, while cholesteryl nonanoate also possesses a monotropic smectic A phase. As is well known, the concentration plays an important role as a thermodynamical variable in the study of phase diagrams of mixtures. The variation in concentration implies a change in the mean molecular length. This fact is crucial for the system to exhibit a richer phase diagram, as pointed out by Alben [6]. The behaviour exhibited in figure 1 is as expected [7]. The crystalline phase inhibits the formation [8] of the smectic A phase for concentrations of about 61·3 mol per cent of C_7 in the C_7–C_9 mixture. Thus, it is not possible to satisfy McMillan's criterion for second order behaviour. With this in mind we investigated the C_6–C_9 mixture that has revealed a wide range of reduced temperatures where the solid phase does not appear. Our extrapolated data provide evidence of a tricritical point in the cooling cycles (see figure 2, curve *b*) at the reduced temperature $T_{S_ACh}/T_{ChI} \cong 0{\cdot}92$, for a concentration of 63·1 mol

Temperatures of the Ch–I and S_A—Ch transitions for the C_7–C_9 and C_6–C_9 mixtures.

	Concentration/mol per cent			
System	C_n	C_9	Ch–I	S_A–Ch
C_7–C_9	100·0	0·0	365·7	—
	61·3	38·7	364·0	—
	41·3	58·7	363·5	339·6
	20·9	79·1	362·3	341·4
	0·0	100·0	362·8	345·5
C_6–C_9	21·4	78·6	363·0	338·3
	31·8	68·2	364·7	336·0
	36·9	63·1	365·0	334·6
	42·0	58·0	365·6	332·5
	52·1	47·9	366·9	329·7
	62·0	38·0	367·9	324·8
	100·0	0·0	371·9	—

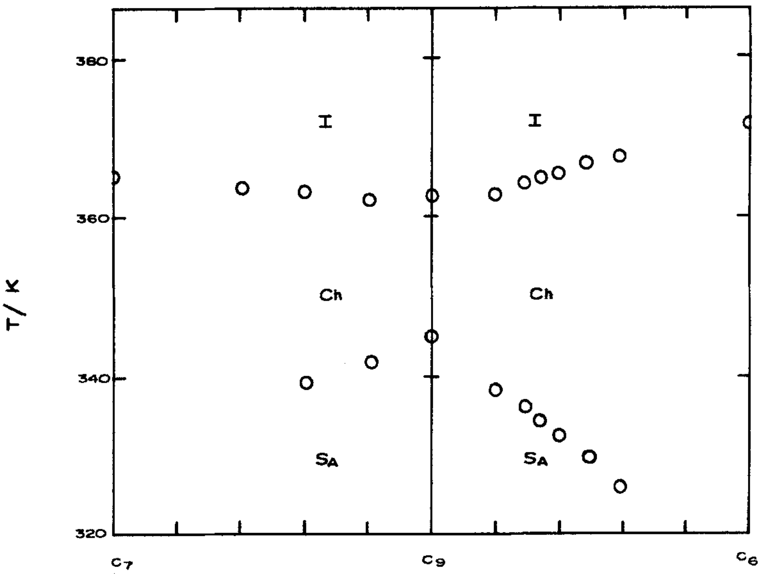


Figure 1. Binary diagrams for the mixtures C_7–C_9 and C_6–C_9.

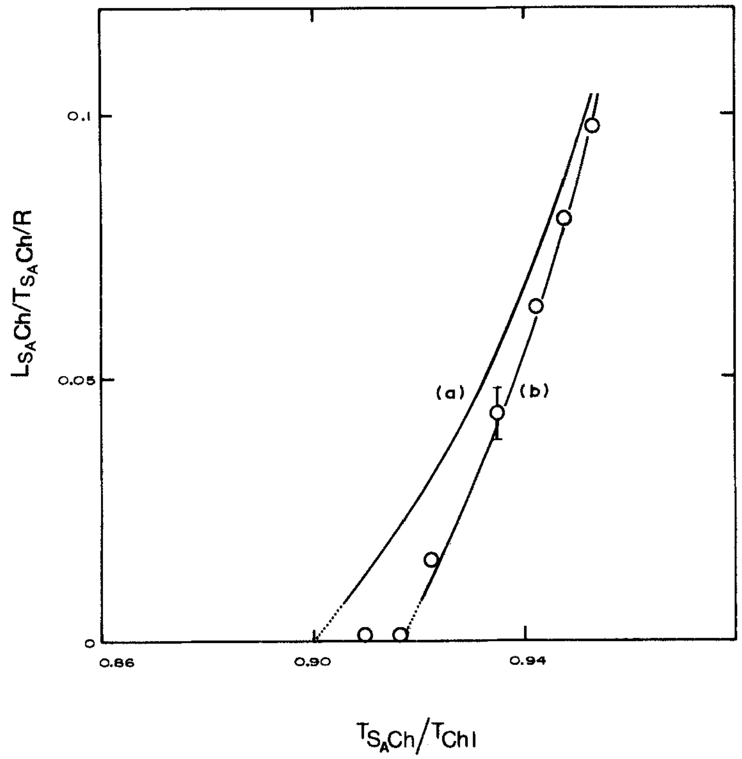
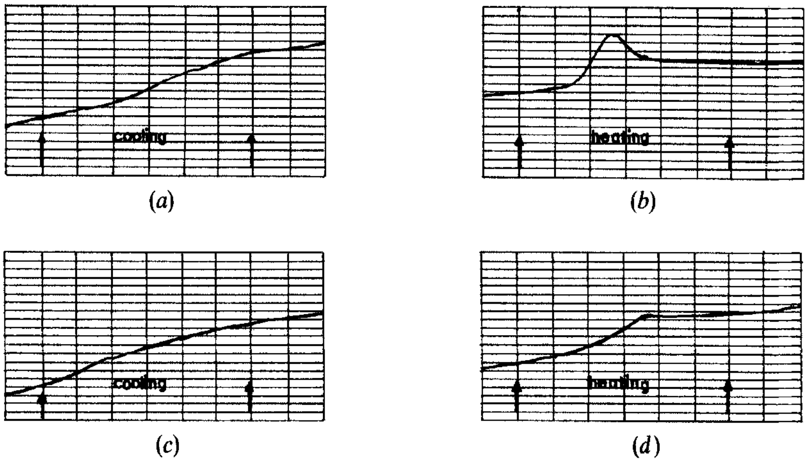


Figure 2. Variations of smectic A-cholesteric transitional entropies with the reduced temperature T_{S_ACh}/T_{ChI}; (*a*) for heating cycles [1] and (*b*) for cooling cycles. *R* is the gas constant.

per cent C_9 in the C_6–C_9 mixture, where T_{S_ACh} and T_{ChI} are the smectic A–cholesteric and cholesteric–isotropic transition temperatures, respectively. The S_A–Ch transition, in this case, is observed only as a steep change in the baseline of the DSC trace, as shown in figure 3 (*a*). This effect is confirmed for a concentration of 58·0 mol per cent C_9 of the same mixture as shown in figure 3 (*c*) (see also [1]). These transitions were also confirmed using a polarizing microscope. Many independent measurements of the latent heat were made for the same samples, taking into account the reproducibility of the experiment.

On the other hand, for the heating cycles, the tricritical point occurs at a reduced temperature $T_{S_ACh}/T_{ChI} \cong 0{\cdot}90$, in the same binary mixture, for a concentration of 47·9 mol per cent C_9. As can be seen in figure 3 (*d*), the baseline of the DSC trace also indicates the vanishing of the latent heat for the heating cycles. Outside these two points, the DSC-2 machine simply measures heat capacity [9], (see figure 3 (*a*) and (*d*)). On the contrary, figure 3 (*b*) clearly exhibits a finite amount of latent heat, indicating a first order smectic A–cholesteric transition at a concentration of 63·1 mol per cent of C_9. This is the same concentration as for the data reported in figure 3 (*a*) for the cooling cycles, where a second order transition is detected. Note that figures 3 (*a*) and (*b*) refer to the same sample, thus indicating that, within the experimental resolution, this behaviour is a property of the system and not a consequence of sample preparation. Hence, there is a pronounced difference in the localization of the tricritical point in the heating and cooling cycles. This is our central result. The entropy of the transition presents a loop which is similar to the hysteretic loop in magnetic systems [10]. The area covered by this loop gives the difference in the entropy of transition between the two cycles. This difference in the entropy of transition may be tentatively understood following the X-ray scattering intensity measurements performed by McMillan [3] for C_9 in both cycles. These measurements show that in the vicinity of the smectic A phase a kind of smectic A domain is formed in the cholesteric phase, before the transition. This



(*a*) (*b*)

(*c*) (*d*)

Figure 3. DSC spectra for the following concentrations of C_9; (*a*) 63·1 mol per cent for cooling cycles; (*b*) 63·1 mol per cent for heating cycles. These measurements were performed for the same sample. (*c*) 58·0 mol per cent for cooling cycles, and (*d*) 47·9 mol per cent for heating cycles. The recorder sensitivity and the time interval per unit length are not the same for the figures. ↑↑, smectic A–cholesteric transition confirmed through microscopic observations.

effect is attributed to the so called 'order parameter fluctuations' in the neighbourhood of the smectic A phase. We believe that this effect must be much more pronounced in the mixture, and is the main cause of this marked difference in the entropy of transition we are reporting.

This work opens some possibilities that could be exploited in future investigations. It would be interesting to study the critical exponents and the order parameter (especially translational) in the vicinity of these tricritical points. In this respect, light scattering and X-ray measurements for the mixture would be helpful to investigate the nature of the coupling between concentration and smectic order fluctuations [11, 12]. The results reported here were obtained by differential scanning calorimetry, which normally furnishes static values for the parameters. However, for a more detailed study, heat capacity (C_p) [13] could be measured in the vicinity of these critical points in a high resolution photo-acoustic experiment. Another interesting experiment could be the measurement of the densities [14] of systems near the smectic A–cholesteric transition for both cycles.

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