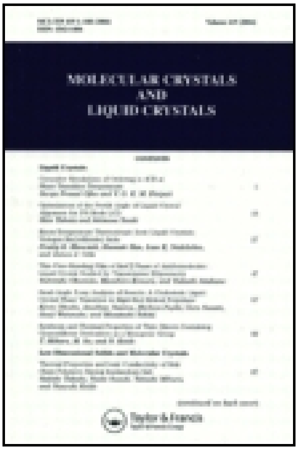


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# Evidence for a Smectic-A-Cholesteric Tricritical Point: Binary Mixtures

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# Evidence for a Smectic-A-Cholesteric Tricritical Point: Binary Mixtures.

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Differential scanning calorimetry measurements of the smectic-A-cholesteric latent heat of transition in binary mixtures: cholesteryl palmitate ($C_{16}$) and cholesteryl myristate ($C_{14}$), cholesteryl myristate and cholesteryl nonanoate ($C_9$), cholesteryl nonanoate and cholesteryl caproate ($C_6$); strongly suggest the existence of a tricritical point at approximately the reduced temperature $T_{AC}/T_{CI} \cong 0,90$ in mixture $C_9$-$C_6$.

## I. INTRODUCTION

The first or second order nature of the transitions in liquid crystals has been a matter of controversy, especially for the smectic-A(A)-nematic(N) or cholesteric(C) transition. The possibility that a second order transition exists thermodynamically, were the objective of the already submitted theories[1-4] based on a rigid molecule model, in the early 1970s. Specifically, these theories predict the second order changes to occur when the reduced temperature $T_{AC}/T_{CI}$ is at or below about 0.88, which ends a homologous series having short chain lengths. For $T_{AC}/T_{CI} = 0.88$ a tricritical point is thus predicted, where $T_{AC}$ and $T_{CI}$ are the smectic-A-cholesteric and cholesteric-isotropic transition temperatures, respectively.

In this letter, we report the results of the measured latent heat of the smectic-A-cholesteric transition in binary mixtures of some aliphatic cholesteryl esters: $C_{16}$-$C_{14}$, $C_{14}$-$C_9$, and $C_9$-$C_6$, where the concentration[5] serves as a convenient thermodynamic variable in mixtures. Based on the calorimetric measurements, we have obtained, within experimental resolution, strong evidence for tricritical behavior of the A-C transition in mixture $C_9$-$C_6$.

## II. EXPERIMENTAL

The liquid crystals used in these experiments were obtained from Aldrich Laboratory and recrystallized in ethyl acetate. The transition temperatures were determined using a polarizing microscope adapted to a hot stage, and a differential scanning calorimeter, model DSC-2. An indium calibration standard was used for calculating the latent heat of the A-C transition. A full scale range of 1.0, 0.5 or 0.2 mcal/sec was used during these measurements in order to facilitate more accurate estimates of the usually low latent heat of the A-C transition. The different mixtures studied and $T_{AC}/T_{CI}$ values are summarized in Table I.

TABLE I

Mixtures investigated and reduced temperatures for the A-C transitions

| | Concentration in mole % | | $T_{AC}/T_{CI}$ |
|---|---|---|---|
| | 0,0 | 100,0 | 0,9873 |
| | 20,8 | 79,2 | 0,9858 |
| $C_{14}$-$C_{16}$* | 41,3 | 58,7 | 0,9850 |
| | 60,9 | 39,1 | 0,9847 |
| | 80,9 | 19,1 | 0,9845 |
| | 100,0 | 0,0 | 0,9842 |
| | 21,7 | 78,3 | 0,9753 |
| $C_9^*$-$C_{14}$ | 43,5 | 56,5 | 0,9637 |
| | 63,5 | 36,5 | 0,9571 |
| | 81,5 | 18,5 | 0,9551 |
| | 100,0 | 0,0 | 0,9523 |
| | 31,8 | 68,2 | 0,9213 |
| | 42,0 | 58,0 | 0,9095 |
| $C_6^{**}$-$C_9$ | 49,1 | 50,9 | 0,9006 |
| | 52,1 | 47,9 | 0,8986 |

* exhibits smectic-A mesophase monotropic
** exhibits only a cholesteric mesophase

## III. RESULTS AND DISCUSSION

The experimental results are presented in Figure 1, in good qualitative agreement with Mcmillan's molecular theory extension proposed by Lee et al.[3] Our extrapoled data shows that the A-C transition would become second order for $T_{AC}/T_{CI} = 0.90 \pm 0.005$ in mixture $C_9$-$C_6$. The A-C transition in this case is observed only as a steep change in baseline of the DSC trace, thus indicating that the transition is of second order. Our $T_{AC}/T_{CI}$ value at the tricritical point is higher than that predicted by theory. Similar and strong deviations have been

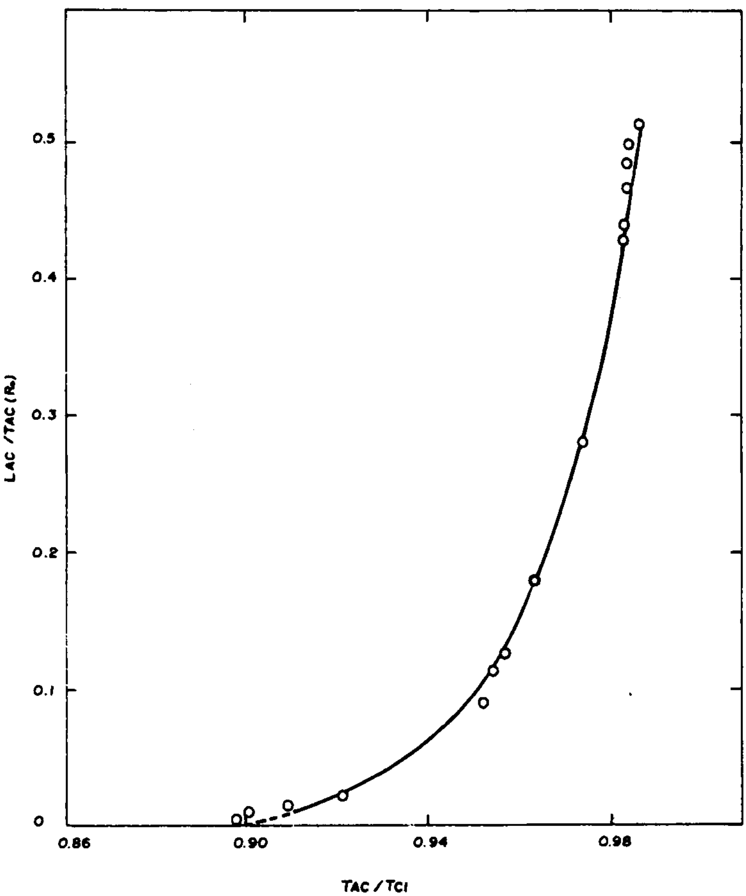


FIGURE 1 Variation of smectic-A-cholesteric transition entropies with the reduced temperature $T_{AC}/T_{CI}$. $R_o$ is the ideal gas constant.

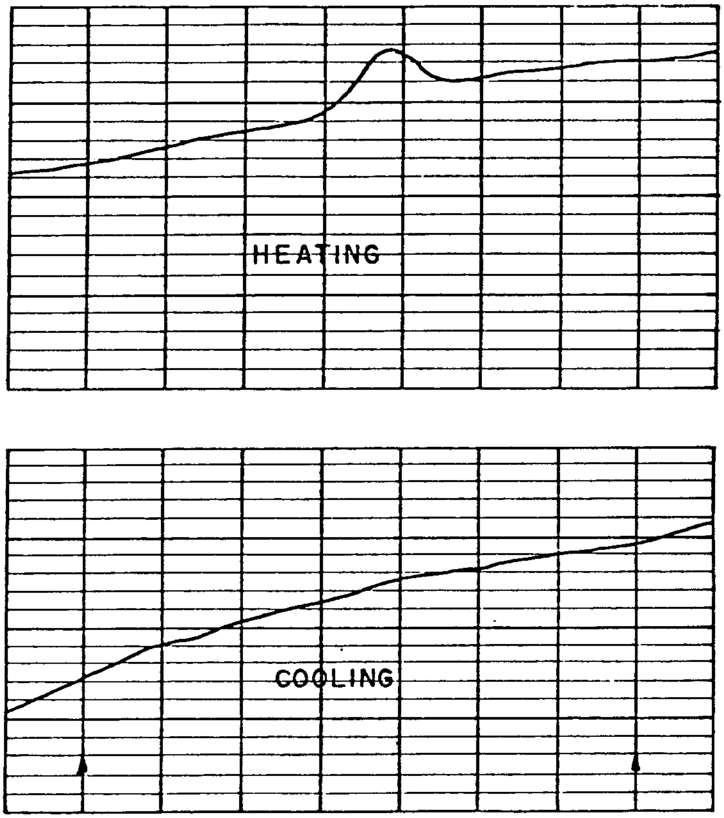


FIGURE 2 DSC-2 recorder trace for 58 mole% $C_9$ of the mixture $C_9$-$C_6$ in heating and cooling cycles. The recorder sensitivity and the time interval per unit length are not the same for the figures. ↑ ↑ smectic-A-cholesteric transition confirmed through microscopic observation.

reported earlier in a few other cases,[6-9] for example, in a range where the reduced temperature varies from 0.89 to 0.99, using the concentration of mixtures as a variable.[10] The discrepancies between the theory and the experiment, despite the theoretical[11-13] efforts, remain to be explained satisfactorily. However structural aspects of the molecules in different homologous series may be a relevant factor for explaining the true tricritical behavior observed in each series. The other feature of the present results is that the latent heat decreases much more abruptly with cooling cycles than heating cycles, see Figure 2 for mixture $C_9$-$C_6$. In conclusion, our calorimetric results on binary mixtures show a tricritical point in the A - C transition at a reduced temperature of ≅ 0.90. As a final remark, we find that the study of the critical exponents and order parameter (especially translational) in the vicinity of this tricritical point, would be of considerable interest.


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