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THERMODYNAMIC ANOMALIES ALONG THE ISOTROPIC-NEMATIC PHASE BOUNDARIES OF TWO COMPONENT SYSTEMS

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The entropy and volume changes at the N-I transition have been determined in two binary systems (80CB-60CB and 80CB-CB00A). We give evidence for an anomaly of Δv_{NI} as a function of the concentration directly related to $\left(\frac{dT}{dP}\right)_{NI}$ at P = 1 atm. This result might be due to the influence of a critical smectic-like compacity.

INTRODUCTION

Some experimental studies concerning (x,T) phase diagrams of two component systems suggest that the smectic layering order has an effect upon the thermodynamic behaviour of the isotropic-nematic phase transition.

For example a discontinuity of the entropy change $\Delta S_{\rm NI}$ was revealed at the concentration for which a NAC multicritical point exists at low temperature $^{\rm l}$.

More recently Shashidhar et al. $^{2-4}$ gave evidence for an anomaly of $\left(\frac{dT}{dP}\right)_{NI}$ at P = latm in two diagrams with a reentrant nematic (80CB-60CB and 80CB-CB0OA). Such anomaly occurs at the concentration where the temperature range of the smectic A phase is maximum. Studying these latter cases we have found a modification of the difference of the volume between the isotropic and nematic phases ΔV_{NI} instead of a discontinuity of the entropy of transition ΔS_{NI} .

EXPERIMENTAL RESULTS

Indeed, for both systems 80CB-60CB and 80CB-CB0OA no significant singularity of $\Delta S_{\rm NI}$ versus concentration is detected from accurate and systematic Dupont 990-DSC measurements (Fig. 1 and 2) in the regions corresponding to the

irregular variations of $\left(\!\frac{dT}{dP}\!\right)_{\rm NI}^{2-4}$.

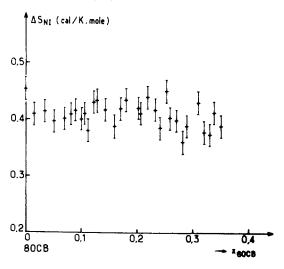


Figure 1: 80CB-60CB system: variation of the nematicisotropic transition entropy versus the molar fraction of 60CB

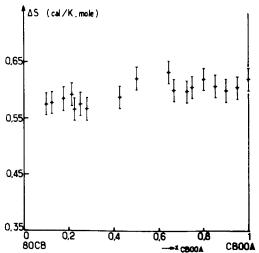


Figure 2: 80CB-CB00A system: variation of the nematicisotropic transition entropy versus the molar fraction of CB00A

Furthermore, the density as a function of temperature and close to the N-I transition is measured by means of a P.A.A.R. Density Meter (sensitivity 10^{-5} g.cm⁻³). For a given mixture this experiment is depicted in figure 3.

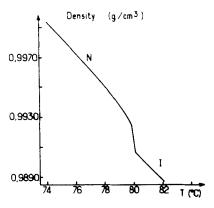


Figure 3: Example of a thermal variation of the density.

Considering Klement and Cohen's equations used to describe the molar volume near a first order NI transition for a not pure liquid crystal, we can extrapolate $\Delta V_{
m NI}$ at the transition (Fig. 4).

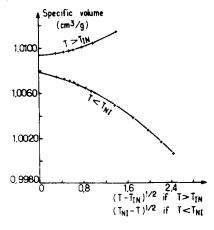


Figure 4 : $V_{\rm I}$ - $V_{\rm N}$ extrapolation using the following equations :

$$\begin{array}{l} V = V_{N} + \alpha_{N}(T - T_{NI}) - C_{N}(T_{NI} - T)^{1/2} & \text{if } T \leq T_{NI} \\ V = V_{I} + \alpha_{I}(T - T_{IN}) + C_{I}(T - T_{IN})^{1/2} & \text{if } T \geq T_{IN} \end{array}$$

In the case of the 80CB-60CB system we observe a steep variation of Δv_{NI} = $f(x_{60CB})$ located around x_{60CB} = 0.20 (Fig. 5) , that is to say in the region where the evolution of $\left(\frac{dT}{dP}\right)_{NI}$ is irregular.

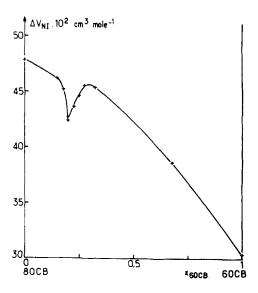


Figure 5: 80CB-60CB system: volume changes at the nematic-isotropic transition

In the second system, the part of the diagram corresponding to 0.4 < x_{CBOOA} < 0.9 has been excluded from our analysis because the two-phase (N+I) region is too large. Nevertheless for x_{CBOOA} < 0.4 we confirm that as for $\left(\frac{dT}{dP}\right)_{NI}$ a sharp discontinuity of ΔV_{NI} appears (Fig. 6).

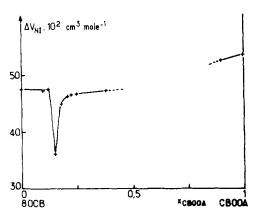


Figure 6: 80CB-CBOOA system: volume changes at the nematicisotropic transition

DISCUSSION

The Clausius-Clapeyron's equation may be applied at the critical concentration. Referring to the 80CB-60CB system $\Delta(\Delta V_{NI})$ max = 4.2.10⁻² cm³, mole⁻¹ and we deduce :

$$\Delta \left[\left(\frac{dT}{dP} \right)_{NI} \right]_{max} = 2.4 \pm 0.2 \text{ K(Kbar)}^{-1}$$

This calculated value closely agree with the experimental one obtained by Shashidhar et al. $^{2-4}$: 2.1 K(Kbar) $^{-1}$.

It is somewhat surprising to note that $\Delta {\rm V}_{\rm NI}$ plays a bigger role than ΔS_{NI} in this molecular effect. Nevertheless ΔS_{NI} integrate a large part of the excess heat-capacity which could mask some very weak perturbation of the latent heat.

At last, if the anomalies of $\Delta V_{\rm NI}$ actually are related to a maximum of the smectic temperature range, the existence of a critical smectic-like compacity is raised as well as its influence on the I-N phase transition 6 .

REFERENCES

- 1 M.F. Achard, G. Sigaud, F. Hardouin, "Liquid Crystal of one- and two-dimensional order", Springer Verlag, Berlin, 149 (1980)
- 2 R. Shashidhar, H.D. Kleinhans, G.M. Schneider, Mol. Cryst. Liq. Cryst. Lett. <u>72</u>, 119 (1981)
- 3 H.D. Kleinhans, G.M. Schneider, R. Shashidhar, Mol. Cryst. Liq. Cryst. Lett. 82, 19 (1982)
- 4 H.D. Kleinhans, G.M. Schneider, R. Shashidhar, Mol. Cryst. Liq. Cryst. 103, 255 (1983)
- 5 W. Klement, L.H. Cohen, Mol. Cryst. Liq. Cryst. <u>27</u>, 359 (1974)
- 6 C.S. Johnson, P.J. Collins, J. Chem. Phys. 79, 4056 (1983)