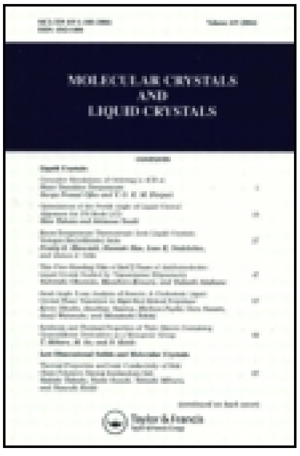

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Thermodynamic Anomalies Along the Isotropic-Nematic Phase Boundaries of two Component Systems

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Version of record first published: 20 Apr 2011.

To cite this article: Y. Guichard , G. Sigaud & F. Hardouin (1984): Thermodynamic Anomalies Along the Isotropic-Nematic Phase Boundaries of two Component Systems, Molecular Crystals and Liquid Crystals, 102:10, 325-330

To link to this article: http://dx.doi.org/10.1080/01406568408070547

Mol. Cryst. Liq. Cryst. 1984, Vol. 102 (Letters) pp. 325-330
0140-6566/84/10210-0325/$15.00/0

Printed in the United States of America

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

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(Received for Publication October 22, 1984)

The entropy and volume changes at the N-I transition have been determined in two binary systems (8OCB-6OCB and 8OCB-CBOOA). 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 ΔS_{NI} was revealed at the concentration for which a N A C multicritical point exists at low temperature[1].

More recently Shashidhar et al.[2-4] gave evidence for an anomaly of $\left(\frac{dT}{dP}\right)_{NI}$ at P = 1atm in two diagrams with a reentrant nematic (8OCB-6OCB and 8OCB-CBOOA). 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 8OCB-6OCB and 8OCB-CBOOA no significant singularity of ΔS_{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 $\left(\frac{dT}{dP}\right)_{NI}$ [2-4].

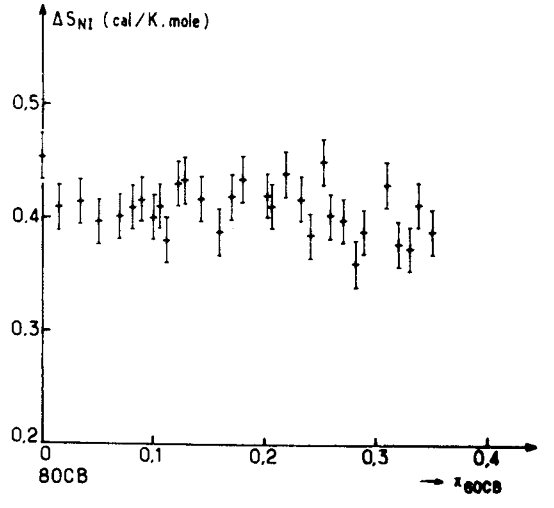

Figure 1 : 8OCB-6OCB system : variation of the nematic-isotropic transition entropy versus the molar fraction of 6OCB

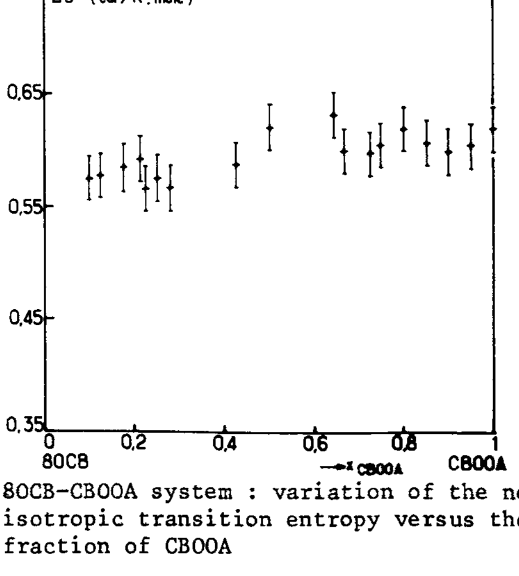

Figure 2 : 8OCB-CBOOA system : variation of the nematic-isotropic transition entropy versus the molar fraction of CBOOA

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.

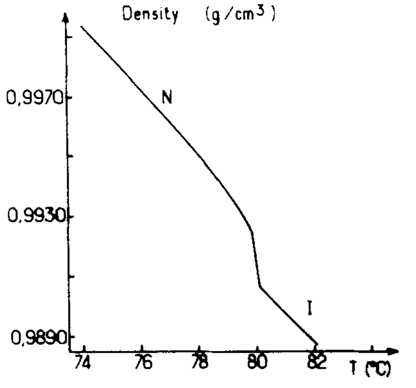

Figure 3 : Example of a thermal variation of the density.

Considering Klement and Cohen's equations[5] used to describe the molar volume near a first order NI transition for a not pure liquid crystal, we can extrapolate ΔV_{NI} at the transition (Fig. 4).

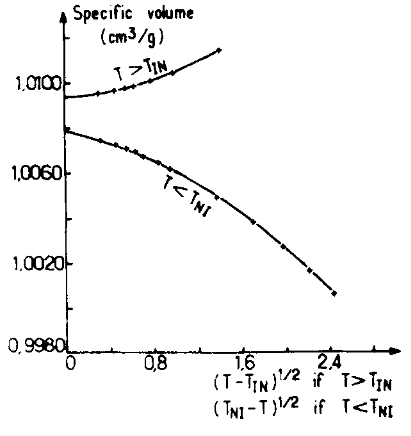

Figure 4 : $V_I - V_N$ extrapolation using the following equations :

$$V = V_N + \alpha_N(T - T_{NI}) - C_N(T_{NI} - T)^{1/2} \quad \text{if } T < T_{NI}$$

$$V = V_I + \alpha_I(T - T_{IN}) + C_I(T - T_{IN})^{1/2} \quad \text{if } T > T_{IN}$$

In the case of the 8OCB-6OCB system we observe a steep variation of $\Delta V_{NI} = f(x_{6OCB})$ located around $x_{6OCB} = 0.20$ (Fig. 5), that is to say in the region where the evolution of $\left(\frac{dT}{dP}\right)_{NI}$ is irregular.

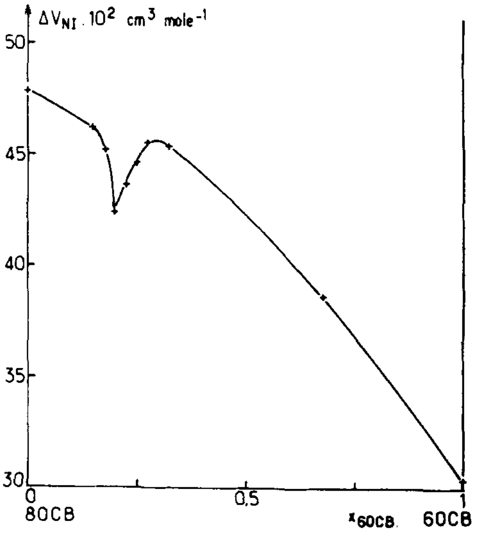

Figure 5 : 8OCB-6OCB system : volume changes at the nematic-isotropic transition

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).

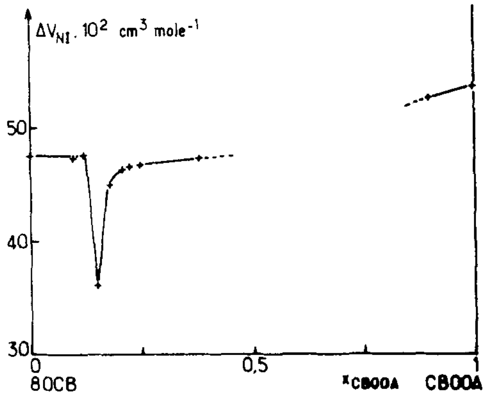

Figure 6 : 8OCB-CBOOA system : volume changes at the nematic-isotropic transition

DISCUSSION

The Clausius-Clapeyron's equation may be applied at the critical concentration. Referring to the 8OCB-6OCB system $\Delta(\Delta V_{NI})$ max $\simeq 4.2.10^{-2}$ cm^3. $mole^{-1}$ and we deduce :

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

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 ΔV_{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 ΔV_{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].

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