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P. Gorria [a], P. Barois [a], H. T. Nguyen [a], G. Sigaud [a], L. Navailles [b], C. W. Garland [c] & H. Haga [c]

[a] Centre de Recherches Paul Pascal, Ave. Schweitzer, F-33600, Pessac, France

[b] Groupe de Dynamique des Phases Condensées, Université Montpellier II, URA 233, F-34095, Montpellier, Cedex, 05, France

[c] Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, 02139

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Thermal and Structural Study Close to a SmecticA-SmecticA Critical Point

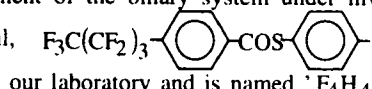
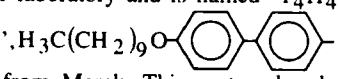
P. GORRIA[a], P. BAROIS[a], H.T. NGUYEN[a], G. SIGAUD[a], L. NAVAILLES[b], C.W. GARLAND[c] and H. HAGA[c]

[a]*Centre de Recherches Paul Pascal, Ave. Schweitzer, F-33600, Pessac, France,* [b]*Groupe de Dynamique des Phases Condensées, Université Montpellier II, URA 233, F-34095 Montpellier Cedex 05, France and* [c]*Department of Chemistry and Center for Materials Science and Engineering Massachusetts Institute of Technology, Cambridge, MA02139*

Two previous works[1,2] firstly evidenced the possible occurrence of gaps of miscibility in smectic A solutions of two non polymer mesogens and later demonstrated the connection of this phenomenon with the difference in layer spacing of the two pure components. In the present paper we provide a detailed thermal and structural analysis of the phase separation around the smecticA-smecticA consolute point of a selected system. It encompasses two high temperature resolution studies which give valuable information about the universality class to which this critical point is likely to be attached.

Keywords: smectic A; phase separation; critical point; critical exponents

I – GENERAL

The first component of the binary system under investigation ends with a perfluoroalkyl tail,  It has been prepared in our laboratory and is named 'F_4H_4' for short. The second component ,'10OCB',  from the nOCB series is purchased from Merck. This system has been chosen for its high

chemical stability and its low critical temperature which ensure no thermal degradation over the long periods required to run high resolution experiments, also for the enantiotropic character of the phase separation well below the consolute point which prevents any unexpected crystallization damaging to oriented samples. The figure 1 shows the full 'low resolution' phase diagram obtained from the observation of mixtures at fixed compositions with a light microscope equipped with a Mettler FP hot stage. The table 1 below gives useful characteristics of the two pure compounds.

II – DETERMINATION OF THE CRITICAL COORDINATES.

A classical method applied to locate the envelope of a gap of miscibility in the case of isotropic phase separation is the determination of the 'cloud points'. A light beam passes freely through an homogeneous sample which is slowly cooled. When the phase separation occurs the medium strongly scatters and the intensity of transmitted light drops abruptly. The technique is not so simple to adapt to our system. In the homogeneous state a liquid crystalline sample scatters light due to textural defects. This difficulty can be partly overcome by the use of oriented samples and thin cells. Well oriented planar samples appeared to be the best compromise (Focal-conics could be avoided in the homeotropic orientation; however the insufficient difference in the intensity of transmitted light when crossing the phase separation line in thin samples rules out this geometry). The light source is a low power He-Ne laser to prevent self heating of the sample (although the colorless samples are merely absorbing light). The detector is a photodiode. The main piece of the experimental set-up is the oven. The three wall chamber which we use allows scanning rates as slow as 0.2 $K.h^{-1}$ used for all experiments. Height samples with mole fractions ranging from ca. 0.400 to ca. 0.500 (prepared in such amount that the uncertainty on the mole fraction is ±0.003) have been run several times. A sample of the recorded curves is shown in figure 2. A fit of the

plot of the 'cloud point' temperatures as a function of temperature provides the coordinates at the maximum (Figure 3) especially the critical composition $x_{F,c} = (0.465 \pm 0.003)$ ($\equiv \varphi_{F,c} = (0.478 \pm 0.003)$) which was our main goal in this part of our work.

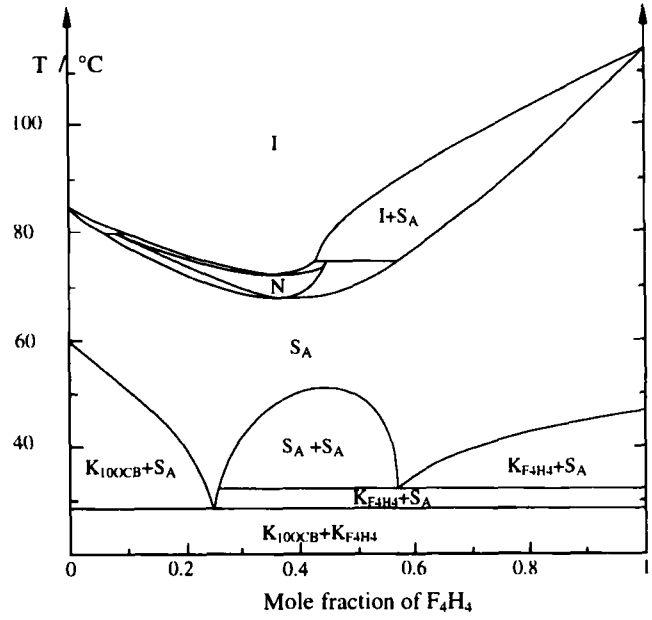


FIGURE 1. Isobaric (P=1 bar) phase diagram. Left : 10OCB; right : F_4H_4.

	Polymorphism						Layer spacing d, molecular length L and nature of the smectic A phase
	K		S_A		I		
F_4H_4	•	47	•	114	•		d =25.2 Å, L = 25.3 Å, S_{A1}
10OCB	•	59	•	84	•		d =34.8 Å, L = 27.1 Å, S_{Ad}

Table 1 : phase behavior and structural parameters for the pure components.

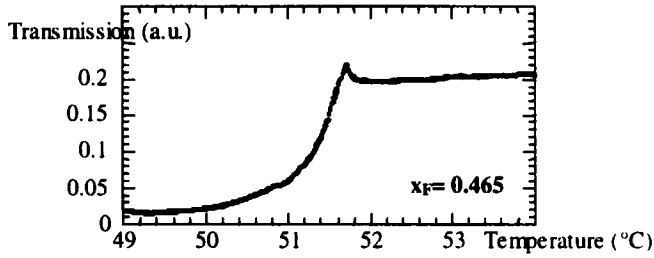


FIGURE 2. Transmitted light (arbitrary units) as a function of temperature for a near critical mixture (x_F : mole fraction of F_4H_4 component). Homogeneous planar orientation, cooling rate 0.2 $K.h^{-1}$, cell thickness (24±0.5) μm.

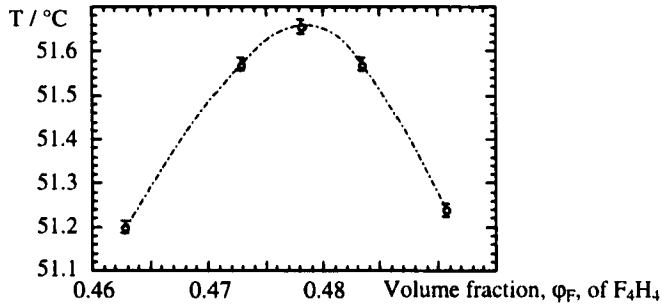


FIGURE 3. Upper part of the gap of miscibility as obtained from the cloud point method. The dash-dot line is a guide for the eye.

The curve in figure 3 is more likely the spinodal rather than the binodal since the experiments are conducted upon cooling at very slow rates which favors metastable states. However the value of $\varphi_{F,c}$ is not questioned since the spinodal and the binodal merge at the critical point.

III – THERMAL BEHAVIOR.

III – 1 – DSC experiments.

The same set of mixtures has been analyzed using differential scanning calorimetry (Perkin-Elmer DSC7). A typical thermogram is shown in the figure 4. The smeared peak results from both enthalpic and specific heat contributions

as usual with DSC. Hence no evidence of C_p fluctuations is given by these results. The useful information is in any case the weak but traceable signal which convinced us that high resolution were worth undertaking.

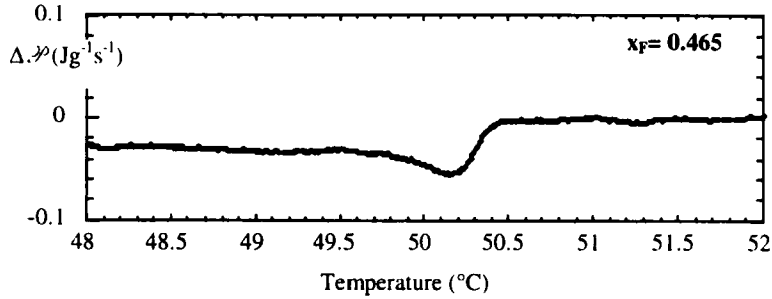


FIGURE 4. Normalized thermogram. Critical mixture. Cooling, 0.5 $K.min^{-1}$.

III – 2 – High temperature-resolution a.c. calorimetry.

The high resolution specific heat measurements have been made with an ac calorimeter at the MIT on a critical mixture.

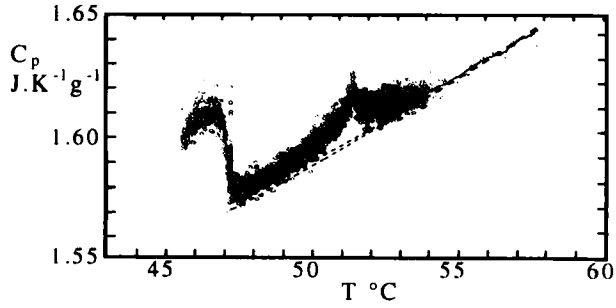


FIGURE 5. C_p as a function of T. Critical mixture, x_F= 0.465. Cooling, 1 $K.h^{-1}$ to 55°C, 40 $mK.h^{-1}$ below; a.c. calorimetry, frequency ω_h=0.196 s^{-1}.

The principles of the technique have been well described in [3]. The figure 5 shows a typical run recorded upon cooling at very slow rate. The excess heat capacity associated to the phase separation is extremely small (0.03 $J.K^{-1}.g^{-1}$).

The analysis is made possible owing to the accumulation of data points. The discussion of the fitting results (*using a power-law form* $\Delta C'_p = A^{\pm}|t|^{-\alpha}\left(1 + D_1^{\pm}|t|^{\Delta_1}\right) + B_c$) - too long to be presented in this brief paper see ref. [4]- concludes for a behavior characteristic of a second-order critical point but definitely not mean-field.

IV – STRUCTURAL BEHAVIOR :

IV – 1 – Low resolution X-ray scattering :

We used a Guinier chamber equipped with an oven regulated to ±0.1 K. The measure of the layer spacings as a function of temperature for a set of mixtures is shown in figure 5. For each mixture the system is represented by a single point as long as it remains homogeneous. When the system phase separates the scattering splits in two lines with different values of q, the reciprocal of layer spacings: it is then represented by two points at each temperature. The figure 5 shows that a common curve with the characteristic shape of a gap of miscibility results from the data points recorded in the inhomogeneous states. The observed curve is a representation of the binodal in the (d, T) diagram. These results served as preliminary to the high resolution study of a single critical mixture.

IV – 2 – High temperature resolution X-ray scattering.

These experiments have been performed at the GDPC in Montpellier. The oven allows a temperature control to $\pm 2\ 10^{-3}$ K and the settings of the experiment provide a resolution characterized by the width at middle height of the direct beam ($3.15\ 10^{-4}$ Å^{-1}). A typical X-ray diagram in the separated mixture is shown in figure 6. The values of q (homogeneous solution), q_1 and q_2 (separated systems) have been plotted in figure 7. The first evidence in this graph is that we missed the goal to prepare the 'exact critical composition' for

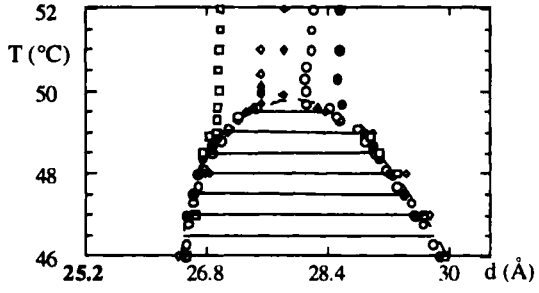


FIGURE 5. Layer spacing in the smectic A phase as a function of temperature. x_F = 0.480 (▫), 0.460 (●), 0.439 (●); 25.2 Å is the layer spacing of the pure F_4H_4. Exposure time : three hours at each stabilized T.

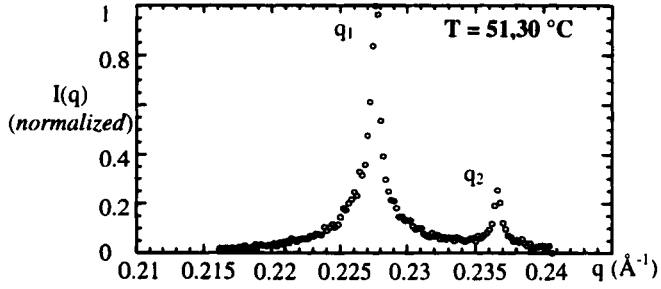


FIGURE 6. High resolution profile showing SA-SA coexistence for a near critical mixture. Recording one such diagram may take several days

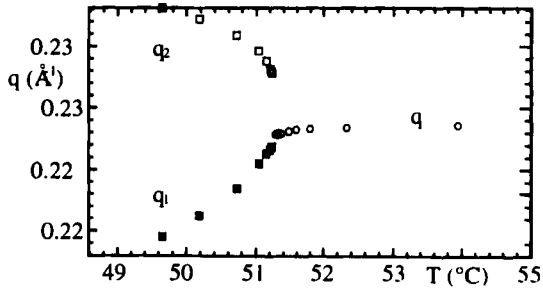


FIGURE 7. Evolution of the q-vectors in an 'almost critical' mixture.

the branch q is attached to the branch q_1 leaving an open gap with the branch q_2. However two separate fittings of the q_1 and q_2 branches yield a common value of the critical coordinates T_c and q_c which have been used to plot the reduced layer spacings $\partial_1 = \frac{d_1 - d_c}{d_c}$ $\left(d_c = \frac{2\pi}{q_c}\right)$ and $\partial_2 = \frac{d_2 - d_c}{d_c}$ as a function of the reduced temperature $t = \frac{T - T_c}{T_c}$. Both plots are satisfactorily described by a power law $\partial_i = t^{\beta}$ with a similar exponent $\beta \approx 0.3$ significantly away from the mean field theoretical value, $\beta_{MF} = 0.5$.

V – CONCLUSION.

The critical behavior of the smectic A-smectic A phase separation is definitely not mean field. A detailed analysis of the results to appear in a more extensive paper suggests that this critical point would be of Ising type. If so this phenomenon occurring in an anisotropic solution would not be much different from phase separation in isotropic liquids (as already observed for the dynamics of phase separation[5]). The special character of this point, if any, could be revealed by experiments, yet to come, with an applied electric field.

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