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OPTICAL MICROSCOPY AT HIGH PRESSURE : p-T PHASE BEHAVIOUR OF 8OCB AND CBOOA AND THEIR MIXTURES

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ABSTRACT By direct texture observations under pressure in a diamond anvil cell, the phase behaviour of 8OCB and CBOOA and their mixtures have been investigated. The maximum pressure (p_M) of occurrence of the smectic A phase (smA) runs through a maximum value as a function of mole fraction, the highest p_M being observed at about 2.2 kbar for x(CBOOA)=0.284 .

INTRODUCTION While studying the p-T phase behaviour of 4-n-octyloxy-4'-cyanobiphenyl (8OCB) Cladis et al. (1) reported that the smectic A phase (smA) exists only up to a maximum pressure (p_M) of about 1.8 kbar. This phenomenon also corresponds with the so-called reentrant nematic behaviour. Since then values of p_M have been determined for some other compounds; e.g. for 4-n-cyanobenzylidene-4'-octyloxyaniline (CBOOA) at about 0.5 kbar (1). In other investigations mixtures were studied where one compound exhibits the reentrant phenomenon whereas the other does not; here especially the effect on p_M was investigated.

The present experiments on the 8OCB/CBOOA system have been carried out in order to study how two reentrant nematic phases (n_{re}) affect each other and how p_M varies with mole fraction in mixtures.

<u>EXPERIMENTAL</u> For the high pressure measurements an opposed diamond anvil cell following the principle of Piermarini and Block (2) was used. The diamond anvil cell was adopted to a polarizing microscope(Leitz, Ortholux II). Instead of a 1.0 mm thick aluminum gasket, which had been used by Shashidhar et al. (3) for x-ray and transmission studies, here the gasket was made from a 0.1 mm thick foil of hardened steel. Thus for the first time we were able to observe textures of liquid crystals under pressure of good quality in a diamond anvil cell. The same equipment has also been used for the investigation of a smectic A - smectic A transition in 4-n-hexyloxy-4'-decyloxybenzoate (4). Additionally the direct optical observation of the phase transitions was simultaneously monitored by recording the change of light intensity transmitted through the sample. The temperature was measured with a thermocouple and transition temperatures were obtained within $\pm$ 1 K. Rates of heating and cooling cycles were about 1 $Kmin^{-1}$. The pressure was determined with-

in ± 50 bar using an internal pressure calibration method. For experimental details; e.g. construction of the cell, pressure calibration etc. ; see reference 5 .

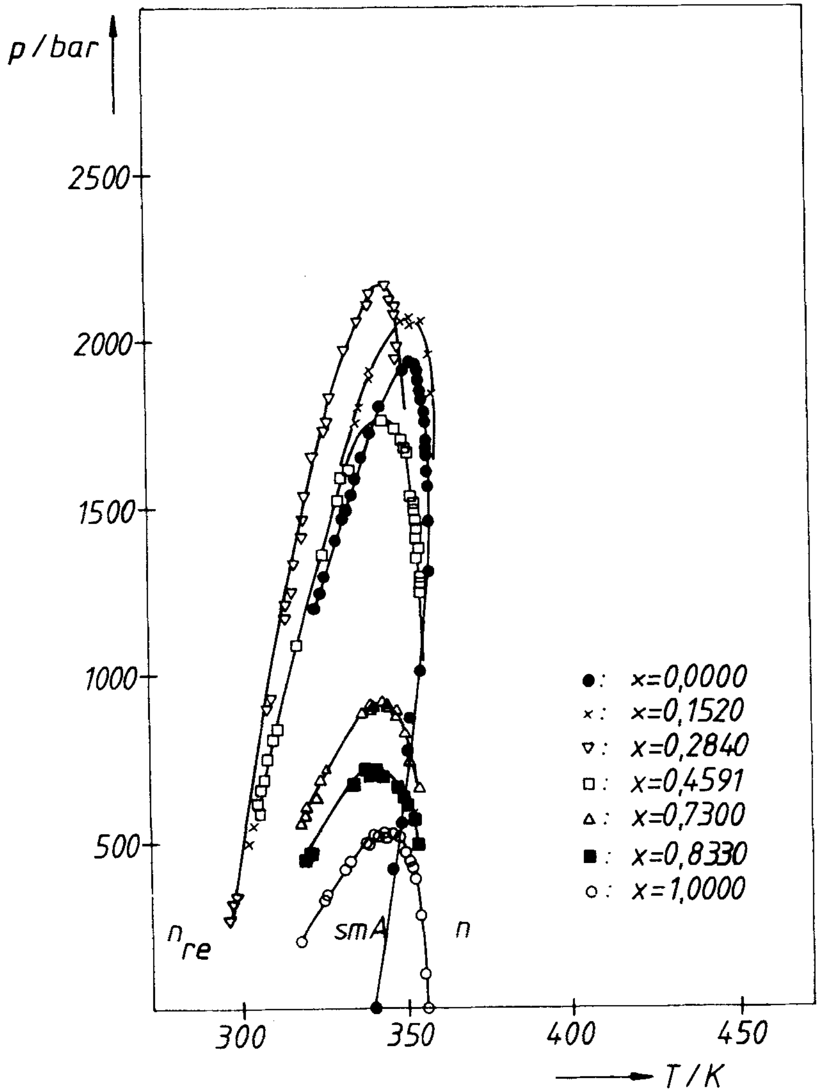

Figure 1 p-T transition lines of the bounded smA phase for all mixtures investigated

RESULTS Figure 1 shows the p-T transition lines for all mixtures investigated. Both pure substances exhibit the n_{re} behaviour, where p_M is found at about 1.9 kbar for 8OCB and at about 0.5 kbar for CBOOA. The smA/n_{re} transition, however, can only be observed in a limited pressure

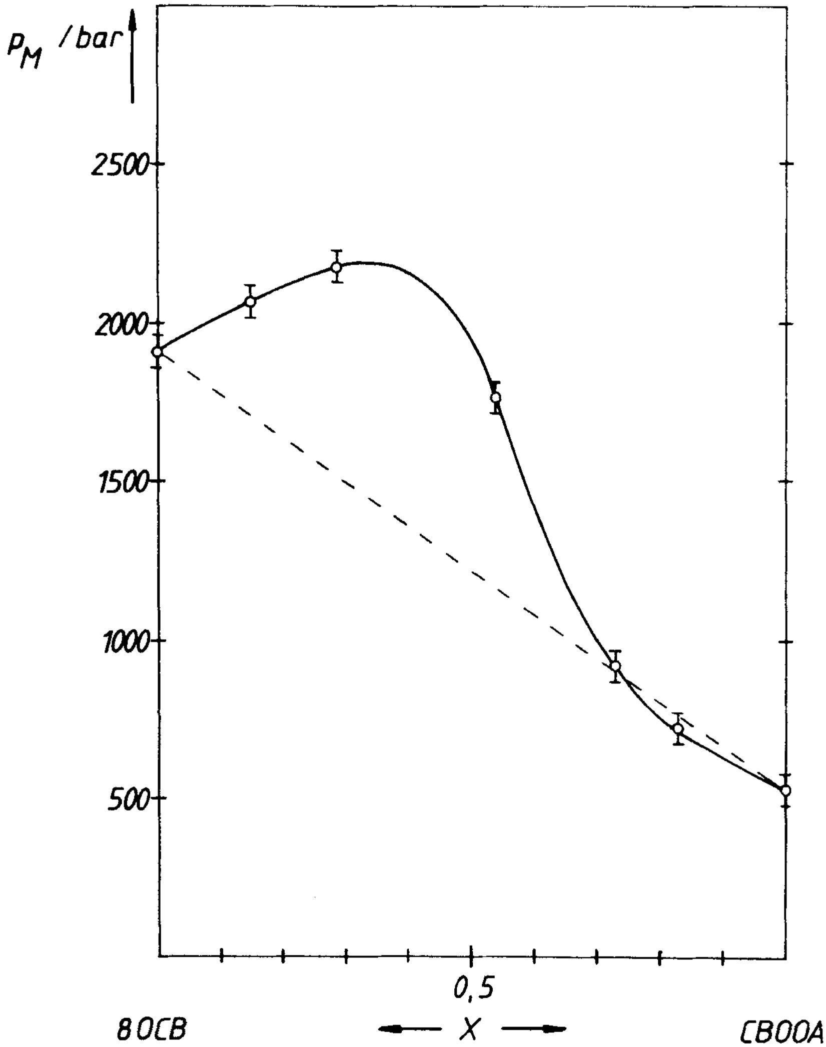

Figure 2 Variation of p_M with mole fraction (x)

range because of crystallization. For both substances the n_{re} phase is evidently stabilized by adding CBOOA to 8OCB and vice versa, i.e. p_M increases and the range of the smA/n_{re} transition is extended. The value of p_M is therefore increased from 1.9 kbar at x=0.000 to 2.2 kbar at x=0.284, where x is the mole fraction of CBOOA. For a further increase of the CBOOA concentration p_M decreases again until the value of pure CBOOA is reached at about 0.5 kbar.

This behaviour is also demonstrated in figure 2, where p_M is plotted versus mole fraction. The p_M versus x curve shows a maximum value at about x=0.3 . In CBOOA rich mixtures possibly a very slight minimum exists, which, however, is within the limits of experimental error.

Up to now only a monotonous change of p_M with mole fraction had been found, e.g. the 8OCB/6OCB system showed a monotonous decrease of p_M with increasing mole fraction of 6OCB, the stability range of the smA phase being below 1 bar for x>0.3 (6, 7). For the system 8OCB/4O8 (butyloxybenzylidene-octylaniline) an increase of p_M had been observed with increasing mole fraction of 4O8 (8).

This variation of p_M with changing composition had been explained on the basis saturation of molecular pairing and bilayer ordering (6). It is still unclear if the saturation of pairing hypothesis can explain the occurrence of the maximum value of p_M found in the present work. Additional investigations e.g. x-ray measurements at high pressure are necessary to clarify the situation.

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