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REENTRANT NEMATIC MIXTURES [+)]

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Binary mixtures of some terminal non-polar liquid crystals with the two terminal polar liquid crystals 4-cyano-4'-n-octyloxy-biphenyl ($\bar{8}$ CBP) and 4-cyano-benzylidene-4'-n-octyloxyaniline (CBOOA) exhibit reentrant nematic phases. The phase diagram of the system $\bar{8}$ CBP/CBOOA indicates that the pure components show this effect too. X-ray data on layer thickness and transition enthalpies are presented.

It is generally assumed that the nematic phase is the high-temperature phase with respect to the possible smectic modifications of a particular liquid crystal (1). However, recent investigations (2,3) at high pressure have shown that some terminal polar liquid crystals exhibiting bilayer smectic A phases produce a nematic phase upon cooling which is called reentrant nematic. At normal pressure only one binary mixture of two terminal polar liquid crystals has been reported so far to be reentrant nematic (4).

In our studies of mixtures of terminal non-polar and terminal polar liquid crystals we observed smectic A phases with enhanced thermal stability (induced smectic phases) (5-7). Some of these mixtures showed a nematic phase gap between the induced S_A phase and the S_A phase of the pure terminal polar component. A careful investigation of these diagrams using the contact method revealed that even at low temperatures two smectic regions exist. Furthermore, the nematic phase region broadens again producing a reentrant nematic at least for the more polar mixtures (table 1). In a few cases a reentrant nematic was found below the induced smectic A phase as well.

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TABLE 1

BINARY MIXTURES OF TERMINAL NON-POLAR AND TERMINAL POLAR LIQUID CRYSTALS EXHIBITING REENTRANT NEMATIC PHASES

	$\overline{8}$ CBP	CBOOA
$4\cdot0\cdot\overline{6}$	+++	++
$\overline{7}\cdot0\cdot5$	+	++
$\overline{8}\cdot0\cdot5$	+	+++
$\overline{7}\cdot S\cdot5$	+	++
$\overline{8}\cdot S\cdot5$	+	+
EBBA	++	++
7 ONE	++	++

\+ NO NEMATIC GAP ; REENTRANT NEMATIC OBSERVED BELOW THE S_A PHASE AT HIGH CONCENTRATIONS OF THE TERMINAL POLAR COMPONENT

\+ + NEMATIC GAP ; REENTRANT NEMATIC OBSERVED BELOW THE S_A PHASE ON THE POLAR SIDE

\+ + + NEMATIC GAP ; REENTRANT NEMATIC OBSERVED BELOW THE S_A PHASES ON BOTH SIDES OF THE GAP

$\overline{8}$ CBP : $C_8H_{17}O-\phi-\phi-CN$

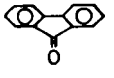
CBOOA : $NC-\phi-CH=N-\phi-O\,C_8H_{17}$

$4\cdot0\cdot\overline{6}$: $C_6H_9-\phi-COO-\phi-O\,C_6H_{13}$

$\overline{7}\cdot X\cdot5$: $C_7H_{15}O-\phi-COX-\phi-C_5H_{11}$

$\overline{8}\cdot X\cdot5$: $C_8H_{17}O-\phi-COX-\phi-C_5H_{11}$ } X=O,S

EBBA : $C_2H_5O-\phi-CH=N-\phi-C_6H_9$

7 ONE : $C_7H_{15}O-\phi-CH=N-$ 

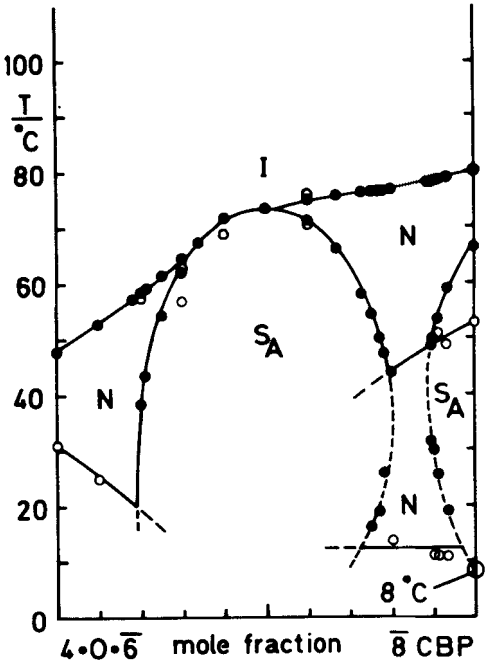


FIGURE 1

PHASE DIAGRAM OF THE SYSTEM $4\cdot0\cdot\overline{6}$ / $\overline{8}$ CBP OBTAINED BY DSC MEASUREMENTS (○) AND WITH A POLARIZING MICROSCOPE (●).

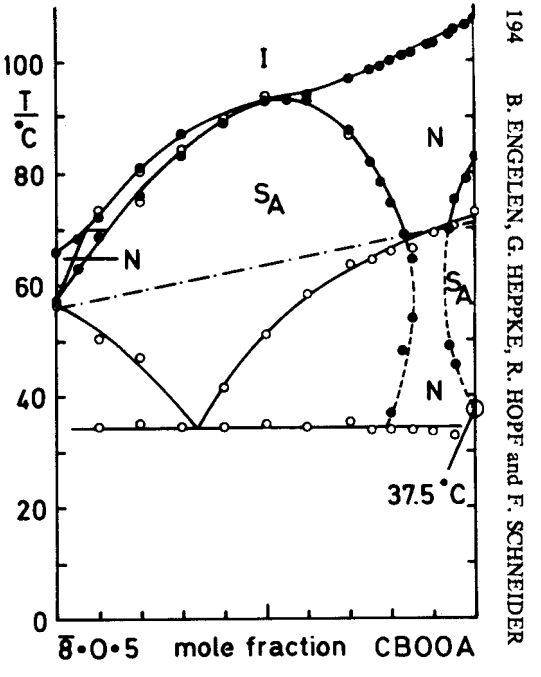


FIGURE 2

PHASE DIAGRAM OF THE SYSTEM $\overline{8}\cdot0\cdot5$ / CBOOA. THE DOT-DASH LINE (—·—·—·—) CORRESPONDS TO THE TEMPERATURES OF THE DETERMINATION OF THE LAYER THICKNESS (SEE FIG. 5).

The phase diagrams of the two systems 4·O·$\overline{6}$/$\overline{8}$ CBP and $\overline{8}$·O·5/CBOOA (for compounds see table 1) were studied in detail by DSC measurements (Perkin Elmer DSC-2) and with a polarizing microscope (fig. 1 and 2). The phase diagram of 4·O·$\overline{6}$/$\overline{8}$ CBP (fig. 1) was earlier presented in a paper by Oh (8) but no broadening of the nematic gap with decreasing temperature was reported. As in the other phase diagrams the transition temperatures to the reentrant nematic phase lie below the liquidus curve, so that only supercooled reentrant nematic samples can be investigated.

The extrapolation of the phase transition temperatures smectic-reentrant nematic to the pure $\overline{8}$ CBP (fig. 1) and the pure CBOOA (fig. 2) indicates that the terminal polar components themselves should exhibit monotropic reentrant nematics. This was confirmed by the observation of reentrant nematics in mixtures of the two terminal polar liquid crystals (fig. 3) which give a very simple phase diagram. The temperatures of all mesomorphic phase transitions are linearly dependent on the composition. An extrapolation gives 37.5 °C and 8 °C for the monotropic reentrant nematic-smectic A phase transitions of the pure CBOOA and $\overline{8}$ CBP, respectively.

Despite the fact that upon cooling there should be a loss of longe range smectic order we found the transition enthalpies to have the same sign as that of the normal nematic-smectic A phase transitions (fig. 4). The enthalpy values are of the same order of magnitude as that of the pure components which are known to exhibit nearly second order N-S_A phase transitions.

For the system $\overline{8}$·O·5/CBOOA (see fig. 2) the dependence of the smectic layer thickness on the mole fraction was obtained from X-ray measurements on magnetically ordered samples (fig. 5). In order to avoid strong supercooling of the samples we chose the temperatures indicated by the dot-dash line in fig. 2. At low concentrations the layer thickness is a linear function of the composition of the terminal polar component CBOOA. An extrapolation to pure CBOOA yields a value which corresponds closely to the molecular length l = 2.7 nm of CBOOA. This indicates a monolayer in the induced smectic A phase up to equimolar composition. At higher concentrations of CBOOA the layer thickness increases strongly towards the bilayer spacing of CBOOA (3.5 nm).

In the nematic phase region the X-ray reflections become slightly more diffuse but no discontinuity is observed at the nematic-smectic phase transitions. The curve is very similar

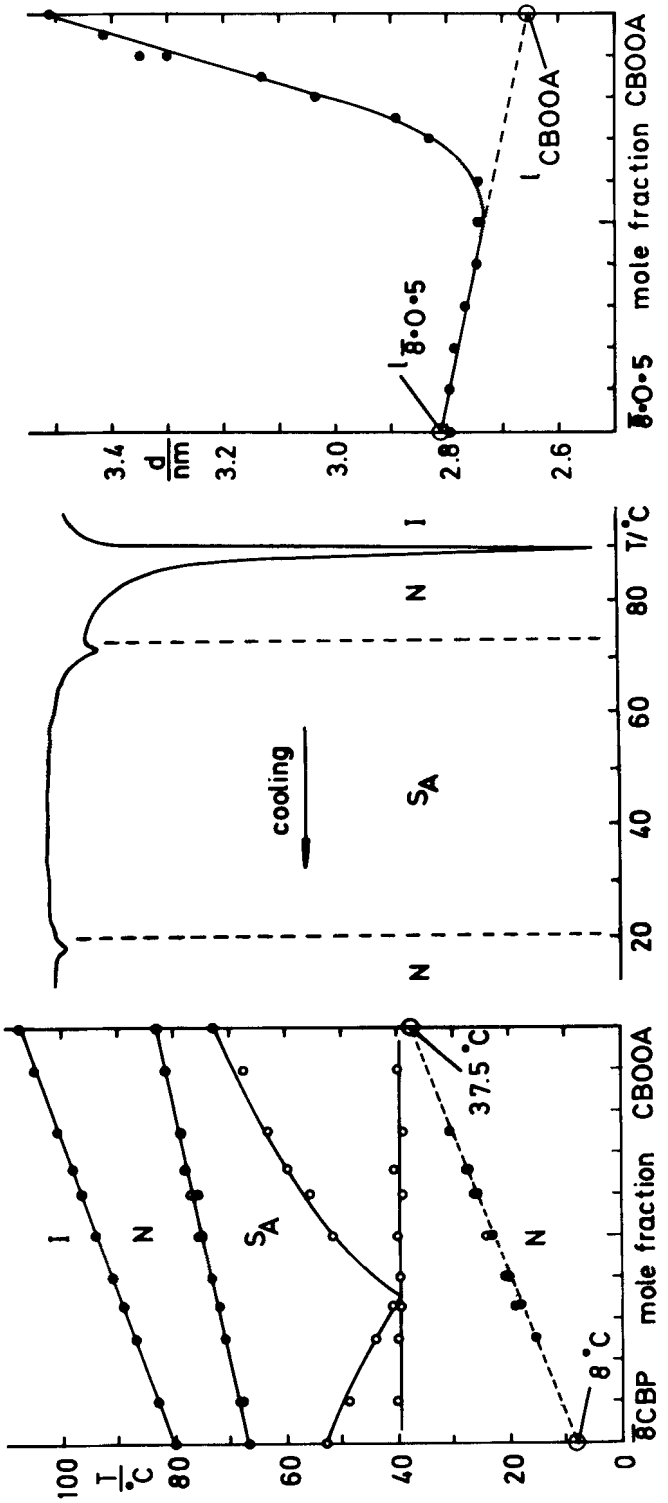


FIGURE 3

PHASE DIAGRAM OF THE SYSTEM $\bar{8}$ CBP / CB00A.

FIGURE 4

DIFFERENTIAL THERMAL ANALYSIS OF THE MIXTURE $\bar{8}$ CBP / CB00A WITH 40 MOLE % CB00A.

FIGURE 5

LAYER THICKNESS OF THE $\bar{8}$·0·5 / CB00A MIXTURES AS A FUNCTION OF THE MOLE FRACTION (FOR TEMPERATURES SEE FIG. 2).

to those obtained on systems with non-interrupted induced smectic phases (6,7). Obviously the size of the cybotactic groups in the nematic phase is rather large. Hence very weak transitions are anticipated and in fact we were not able to detect the N-S_A phase transitions by DSC measurements for compositions near the nematic gap. Furthermore, no temperature dependence of the layer thickness was found for samples with compositions corresponding to the nematic gap and to the maximum thermal stability of the induced smectic phase.

As regards the system $\overline{8}$ CBP/CBOOA a sample of equimolar composition was investigated by X-ray measurements. In agreement with the results obtained for the system $\overline{8}$·0·5/CBOOA (fig. 5) no temperature dependence of the layer thickness was found in the entire N-S_A-N temperature region of the $\overline{8}$ CBP/CBOOA mixture. The value obtained (3.35 nm) corresponds to the mean layer thickness of $\overline{8}$ CBP (3.1 nm) and CBOOA (3.5 nm) which shows that the smectic bilayer structure of the two components is maintained in these mixtures.

The investigation of other compounds with a tendency to produce reentrant nematics is in progress in order to obtain mixtures with enantiotropic reentrant nematic phases (9).

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