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PHASE BEHAVIOUR OF TBBA UNDER HIGH PRESSURE BY DIFFERENTIAL THERMAL ANALYSIS (DTA)

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Abstract The phase behaviour of TBBA has been studied by high-pressure differential thermal analysis (DTA) up to 3 kbar in the temperature range from 300 to 600 K. The T-p phase diagram of TBBA is very complex. At normal pressure a new metastable solid phase has been found. At higher pressures the smectic VI and the smectic VII phases vanish and another new phase is pressure induced. The enthalpy of the smectic A/nematic transition decreases drastically with increasing pressure suggesting a tricritical point at about 1000 bar and 515 K.

Introduction In a research program on the thermodynamic properties of liquid crystals under high pressure[1,2] the phase behaviour of TBBA has been studied up to 3 kbar by differential thermal

analysis (DTA). This substance has been chosen because of its interesting polymorphism at normal pressure and it was expected that similar effects to those observed before with other liquid crystals (e.g. tricritical phenomena, pressure induced phases[1,2]) would be found.

Experimental The DTA equipment and the experimental procedure are described elsewhere.[1,3] Some additional details are given below.

The substance was synthesized as described by Taylor et al.[4] and was recrystallized several times from ethanol/benzene until no further change of the transition temperature and of the peak shape of the nematic/isotropic liquid phase transition could be observed.

For the measurements the substance was encapsuled in lead cells[3] to prevent a contact between the surroundings and the sample. Thus the thermal decomposition of TBBA was strongly hindered. Nevertheless after each measurement at higher pressures the transition temperatures and the transition peaks were remeasured at 1 bar and the cell was replaced if any change could be observed.

Results Figure 1 shows the T-p phase diagram of TBBA obtained when the substance was heated from the solid crystal (s). At normal pressure two solid/smectic G (s1/smG, 384.2 K; s2/smG, 386.7 K), the smectic G/smectic C (smG/smC,

418.1 K), the smectic A/nematic (smA/n, 471.9 K) and the nematic/isotropic liquid (n/l, 510.8 K) transitions have been found. Figure 2 shows the T-p phase diagram obtained when the substance was cooled until the solid phase appeared. Here the smectic VI (smG/smVI, 360.4 K) and the smectic VII (smVI/smVII, 347.6 K) phases have additionally been observed in the supercooled region at atmospheric pressure. In both diagrams the smC/smA transition was not detected by DTA. These results have been confirmed by optical microscopy where the smC/smA transition (445.0 K) has also been observed. All results are in good agreement with the data given in the literature (e.g. see references[4,5,6]).

The influence of pressure on the phase behaviour of TBBA is very complex. All transition temperatures increase with increasing pressure. This increase is drastic for the n/l transition and as a consequence this transition could only be observed up to about 1000 bar. At a triple point sX/smVI/smG (about 2250 bar, 427 K) the smVI phase and at another triple point s/smVII/smVI (about 335 bar, 358 K) the smVII phase vanish, respectively. A new phase (sX) is pressure induced at about 535 bar and 366 K. In the following some additional pecularities of the T-p diagrams are discussed.

The s1/smG and the s2/smG transitions occur within a temperature range of about 2 K and the transition lines are essentially parallel over the

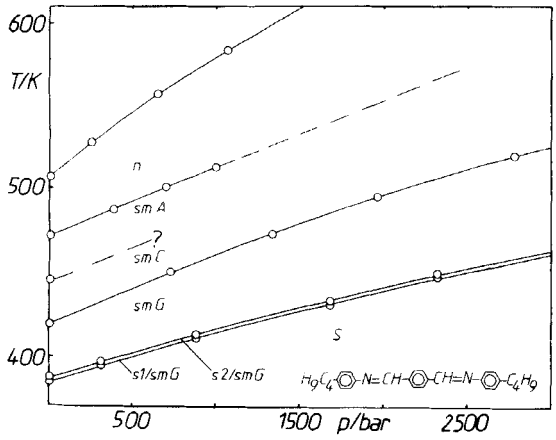

Figure 1: T-p phase diagram of TBBA obtained in heating runs

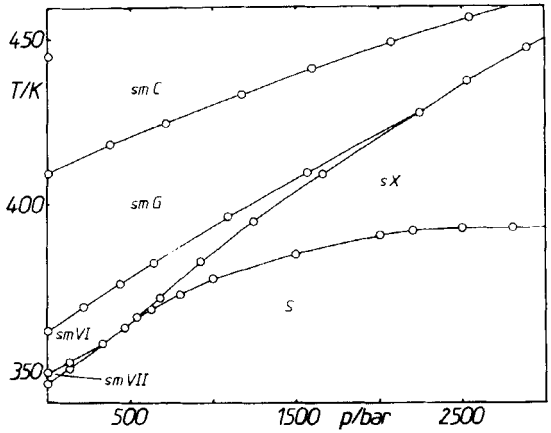

Figure 2: T-p phase diagram of TBBA obtained in cooling runs

whole pressure range up to 3 kbar. The ratio of the peak areas of the two transitions varies with each new measurement; the sum of the peak areas, however, was always constant. This behaviour could be explained by the metastable character of one of the two solid phases.

The transition enthalpy of the smA/n transition is about 160 J mol^{-1} at 1 bar and decreases rapidly with increasing pressure. Thus no transition enthalpy could be detected above about 1000 bar and 515 K. This suggests a change of the transition order from first to higher order.

In the supercooled region the smG/smVI transition is enantiotropic, whereas the smVI/smVII and the smVII/s transitions are monotropic. At higher pressures this behaviour is more complicated because of the pressure induced sX phase. The sX phase appears either at a monotropic (smVI/sX, from 535 bar to 2250 bar) or at an enantiotropic transition (smG/sX, above 2250 bar). The sX/s transition is monotropic over the whole experimental pressure range. The transition line of the sX/s transition exhibits an unusual curvature at low pressure. At higher pressures the slope as well as the curvature of the coexistence line become zero; this suggests that there is no volume change at the sX/s transition, the densities of the two phases being identical.

Conclusion TBBA exhibits interesting high pressure phenomena, which are similar to those studied in former experiments.[1,2] The effects concerning the sX phase, however, are not well understood and further investigations will be necessary to explain the structure and behaviour of this phase.

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