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MICROSCOPIC AND THERMAL PHASE STUDIES AT HIGH PRESSURES: TBBA AND SOME OF ITS HOMOLOGUES

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Abstract The phase behaviour of some Terephthal-bis-(4-n-alkylanilines) (TBAAs) has been studied up to 5 kbar in the temperature range from 300 to 650 K using a differential thermal analysis equipment (DTA) and a diamond anvil cell (DAC) mounted on a polarizing microscope. All substances exhibit a complex T-p behaviour, which is discussed with respect to the stability of the different liquid crystalline phases.

Introduction At normal pressure TBAAs have been studied extensively by various experimental methods. To our knowledge, however, there do not exist any other high pressure investigations of

these substances besides former experiments carried out at our laboratory[1]. These experiments have been extended now to the pentyl (TBPA) and octyl (TBOA) homologues of TBBA the results being presented in this paper.

Experimental The substances were synthesized following Taylor et al.[2] and were recrystallized several times until no further improvement of the clearing behaviour could be detected in the experiments.

The high pressure measurements were performed using a DTA equipment and a high pressure polarizing microscope with a diamond anvil cell (DAC) making it possible to identify liquid crystalline phases and phase transitions by direct texture observations. Transition temperatures and pressures were determined in heating and cooling cycles with rates of about 1 to 5 K min^{-1}. The accuracy of the T-p data should be better than ±0.5 K and ±10 bar for DTA or ±1 K and ±50 bar for DAC. For further details of the experimental set ups and procedures the reader is referred to literature 4-6.

Results Figures 1-3 show the T-p phase diagrams of TBBA, TBPA and TBOA obtained in the experiments. The notation of the smectic phases (sm) follows the literature e.g. the work of Benattar et al.[3]

The phase diagram of TBBA has been discussed already[1]. Here some additional details are given.

The smA/smC transition, which is of higher order and could not be detected by DTA, has been observed by DAC as has also been done for the n/smA transition above about 1000 bar. These new results show that the smA temperature range increases with increasing pressure whereas pressure does not seem to affect the temperature range of the smC phase.

Direct optical observation of the former unidentified sX phase suggests it to be a solid like phase.

The T-p phase diagram of TBPA is given in figure 2. At normal pressure six liquid crystalline phases exist: I/n 507.0 K, n/smA 485.8 K, smA/smC 452.7 K, smC/smF 423.7 K, smF/smG 414.8 K, smG/smH 335.9 K, where all but smA/smC could be determined by DTA.

Under pressure the n/smA at about 1710 bar and the smF/smG transitions at about 1400 bar become undetectable by DTA. Thus at higher pressures both transitions have been observed by DAC, such as the smA/smC transition over the whole pressure range. It can be seen that the temperature ranges of n, smA and smG of TBPA increase with increasing pressure, the temperature ranges of smC and smF are nearly constant or decrease moderately, whereas smH vanishes at a triple point at about 340.1 K and 155 bar.

The T-p phase behaviour of TBOA is more complicated (Figure 3). At normal pressure four smec-

tic phases are found: l/smA 474.7 K, smA/smC 464.6 K, smC/smF 430.0 K, smF/smG 412.4 K, all but smF/smG being detectable by DTA.

An additional pressure induced n phase, however, could be identified above a triple point at about 230 bar and 488 K by texture observation, the l/n and n/smA transitions being determined by DTA and DAC. At pressures above about 1100 bar the smA/smC transition does not exhibit any detectable enthalpy change in our DTA experiments and could be followed to higher pressures by DAC only. An analogous effect was found for the smF/smG transition where the very modest changes in texture and light intensity occurring at this transition could not be observed at pressures higher than about 1400 bar. Another pressure induced phase (sY) is suggested to be a solid phase.

Conclusion The present measurements give a first interesting insight into the phase behaviour of the different liquid crystalline phases of some TBAAs under pressure. It can be deduced from the experiments that pressure has a stabilizing effect on the n, smA and smG phases, where the n phase can even be pressure induced. The smC and smF phases are only moderately affected by pressure; the temperature ranges of both phases are stable or slightly decrease with increasing pressure. However, pressure destabilizes the smH phase which vanishes at higher pressures.

The nature of the phase transitions n/smA,

smA/smC and smF/smG is another point in the phase behaviour of TBAAs attracting special attention. These transitions seem to exhibit so-called tri-critical points, which are shifted to higher pressures with increasing alkyl chain length. This is demonstrated by the DTA measurements. So the n/smA transition becomes undetectable by DTA at about 1000 bar for TBBA and at about 1710 bar for TBPA but exhibits a measurable enthalpy effect over the whole experimental T-p range for TBOA. The smA/smC transition is undetectable by DTA for TBBA and TBPA, but can be determined up to about 1100 bar for TBOA. A similar effect occurs at the smF/smG transition, which cannot be observed by DTA for TBPA and TBOA.

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Fig. 1

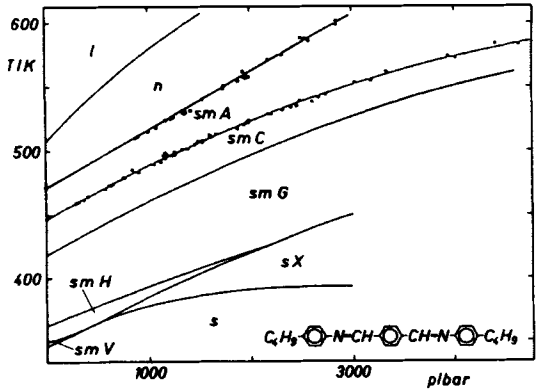

Fig. 2

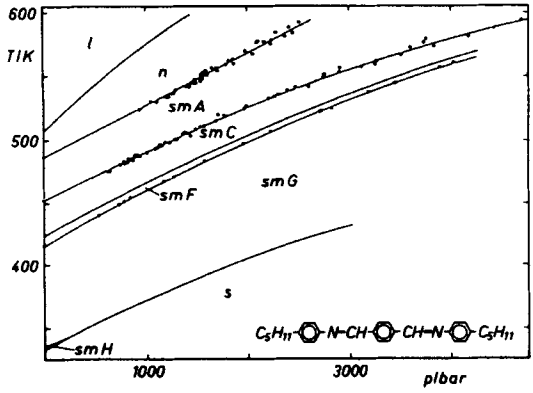

Fig. 3

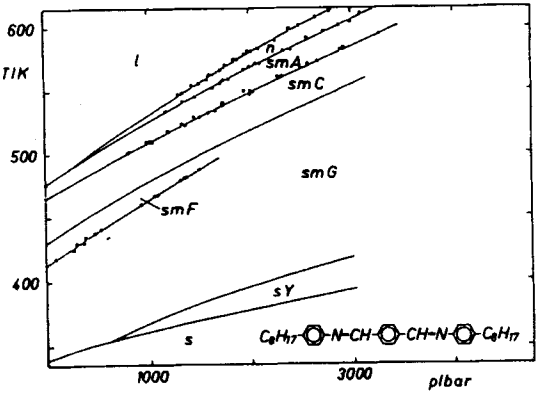

Fig. 1-3: Temperature-pressure phase diagrams of TBBA (Fig.1), TBPA (Fig.2), and TBOA (Fig.3) (data obtained from DAC measurements are indicated by o)