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DIFFERENTIAL THERMAL ANALYSIS (DTA) AND MICROSCOPIC STUDIES UNDER HIGH PRESSURE: PHASE BEHAVIOUR OF SOME TBAAs

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Abstract High pressure studies on the polymorphic phase behaviour of some members of the homologous series of the Terephthal-bis-(4-n-alkylanilines) (TBAAs) were performed using a high pressure differential thermal analysis equipment (DTA) and a diamond anvil cell (DAC). The substances show a complex T-p phase behaviour with pressure induced phases and tricritical phenomena.

Introduction At atmospheric pressure much experimental work has been carried out on the homologous series of the TBAAs (1,2), whereas high pressure investigations are still rather scarce. Until now TBBA and TBAA(5) were studied at high pressure in our laboratory (3,4). The interesting polymorphic

phase behaviour of these substances has initiated further experiments with other members of this homologous series; new results on the T-p phase behaviour of the octyl (TBAA(8)) and dodecyl (TBAA (12)) homologues are presented in this paper.

Experimental The substances were synthesized as described by Liebert (5) and were recrystallized several times from Chloroform/Ethanol until no further change of the clearing behaviour (i.e. of transition temperature and peak shape) could be observed.

High pressure measurements were carried out with a differential thermal analysis apparatus (DTA) to determine the T-p phase diagrams of TBAA(8) and TBAA(12). Experiments were performed up to 3 kbar and at temperatures between 300 K and 600 K. Transition temperatures were determined in heating runs with rates of 1 K min^{-1}. The DTA equipment and the experimental procedure are described elsewhere (6,7).

Additional optical measurements with a diamond anvil cell (DAC) under a polarizing microscope (7,8) were performed in order to investigate higher order transitions between mesophases and to identify pressure induced phases.

Results and Conclusions As the lower members TBBA and TBAA(5) of this homologous series, the investigated substances exhibit a complicated polymorphic phase behaviour.

TBAA(8)

TBAA(8) shows the following sequence of mesomorphic phases with increasing temperatures: smG/smF/smC/smA; the nematic phase is pressure induced and appears at a triple point at about 230 bar and 488 K.

The phase diagram of TBAA(8) has already been discussed in part in a preceding publication (4). Recent DTA-measurements (especially annealing experiments) have led to new results concerning the phase behaviour of the solid phases of TBAA(8). Figure 1 shows the T-p phase diagram of TBAA(8) with inclusion of the new findings. The transition curves I and II run within a temperature range of about 3 K; they are essentially parallel up to about 900 bar. Above 900 bar only transition I could be observed. The new phase s_y appears at about 450 bar. Optical observations indicate s_y to be a solid modification. Annealing experiments for several hours about 20 K below the freezing temperature followed by heating up again produced a variation of the peak areas: The peak area of transition I increased whereas the peak area of transition II decreased. This behaviour could be explained by a metastable character of the solid phase s_{II}.

In the pressure range from 450 bar up to 600 bar the s_y/smG transition curve could only be detected after annealing. Therefore the formation of the s_y phase seems to be a kinetically hindered process. Suitable thermal conditions or increase of pressure can evidently overcome this hindrance.

The smC/smA transition was detected by DTA and DAC up to 1100 bar, but above by DAC only. This effect can be explained by the existence of a tricritical point on the smA/smC transition line at about 1100 bar and 512 K where the transition changes from first to higher order. For both substances the smG/smF and smF/smI transitions are of higher order already at normal pressure and consequently not detectable by DTA.

TBAA(12)

Figure 2 shows the T-p phase behaviour of TBAA(12). At normal pressure four smectic phases are observed corresponding to the following transitions: s/smG (353.8 K), smG/smF (386 K), smF/smI (410 K), smI/smC (424.1 K) and smC/l (453.4 K). All but smG/smF and smF/smI which are of second order (9) were detectable by DTA. Above normal pressure the very weak changes in texture and light intensity occurring at these two transitions could even not be observed in the DAC experiments.

Beyond a triple point at about 805 bar and 492 K TBAA(12) exhibits a pressure induced phase. The phase diagrams of the lower members TBBA, TBAA(5) and TBAA(8) (3,4) show an increase of the temperature range of the smA and the nematic phases respectively. Therefore a pressure induced nematic and/or smA phase could be predicted for higher members of this homologous series. In the microscopic studies a fan-texture was found for the pressure induced phase mentioned above being characteristic for a smectic phase. Therefore this

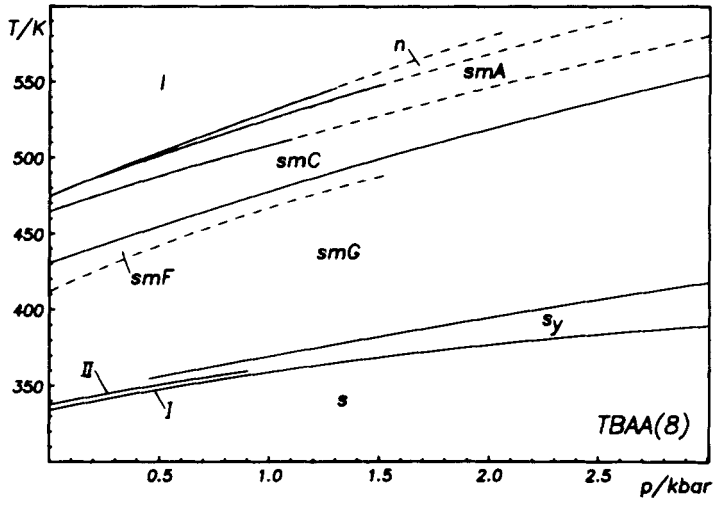

Figure 1: T-p phase diagram of TBAA(8)
(—— DTA results; --- DAC results)

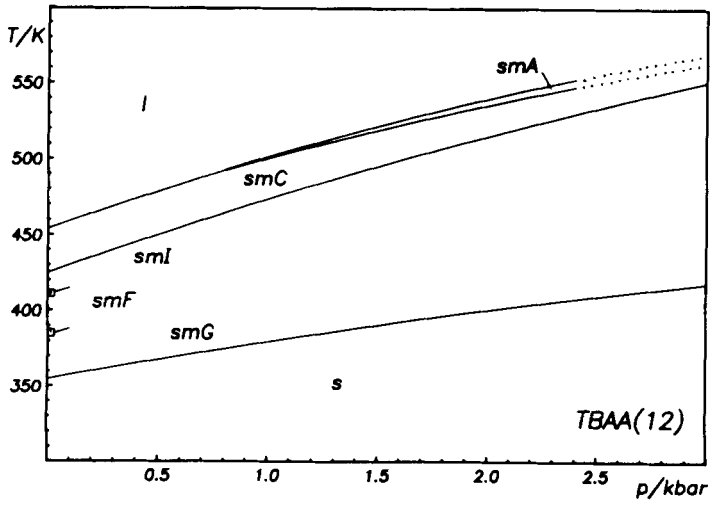

Figure 2: T-p phase diagram of TBAA(12)
(—— DTA results; ··· extrapolated data)

phase is suggested to be the smA phase.

Further investigations are underway. Financial support of the Fonds der Chemischen Industrie e.V. is gratefully acknowledged.

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