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Differential thermal analysis (DTA) at high pressures: phase behaviour of pure and gas-saturated liquid crystals up to 270 MPa

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Abstract

The high-pressure phase behaviour of the liquid crystals 4-*n*-hexyloxy- and 4-*n*-decyloxy-4′-cyanobiphenyl (6OCB and 10OCB) has been studied pure as well as saturated with some gases or gas mixtures (helium, nitrogen, argon, Ar/CO_2 mixtures) at pressures up to 270 MPa with a high-pressure DTA apparatus.

Pure 6OCB shows a nematic phase, whereas 10OCB exhibits a smetic phase as well as an additional pressure-induced nematic phase above 35 MPa. The nematic and the smectic phases are destabilized under the influence of the gases mentioned above; in particular within the experimental pressure range the pressure-induced nematic phase of pure 10OCB is no longer observed under the influence of the gases and gas mixtures mentioned above with the exception of helium.

INTRODUCTION

The pressure dependence of the phase behaviour of liquid crystalline compounds has already been investigated intensively in the past [1–7].

In continuation of our earlier activities, measurements have been performed in the present work to obtain detailed information about the phase behaviour of liquid crystals in pure state as well as saturated with different gases and gas mixtures. Since the molecular interactions, and consequently the solubility, change from gas to gas, the gas content in the liquid crystal can be varied from very low to rather high values corresponding to very different concentrations of a completely inert substance (here, for example a rare gas such as helium or argon) dissolved in the liquid crystal. In the present work the influence of a dissolved gas on

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the stability range of a nematic or a smectic phase has been studied in detail.

The measurements were performed by differential thermal analysis (DTA), which turned out to be a quite unusual but useful experimental technique for high-pressure investigations of this type.

EXPERIMENTAL

The influence of dissolved gases on the phase behaviour of liquid crystals was investigated on the liquid crystalline model substances 4-*n*-hexyloxy- and 4-*n*-decyloxy-4′-cyanobiphenyl (6OCB and 10OCB). Both liquid crystals were purchased from BDH and used without further purification.

The measurements were carried out with a computer-assisted high-pressure DTA apparatus. Chromel–alumel thermocouples were used for the temperature measurements; the measuring cells were mounted onto the thermocouple junctions. Whereas the experiments on the pure substances were performed in closed cells made of lead, the measurements under gas pressure were carried out in open cells also made of lead, so that the pressure-transmitted gas was in direct contact with the substances. He, N_2, Ar and mixtures of Ar and CO_2 were used as pressurizing media up to 270 MPa. The accuracies of the temperature and pressure measurements were about ±0.5 K and ±0.5 MPa respectively. The DTA apparatus and the experimental technique have been described in detail elsewhere [6, 8].

RESULTS

6OCB

Figure 1(a) shows the phase behaviour of pure 6OCB between 330 and 440 K and at pressures up to 260 MPa. The pressure (p)–temperature (T) transition curve s/n corresponds to the melting pressure curve, i.e. to the transition of the crystalline solid to the nematic liquid crystalline state. The transformation curve n/l appearing at higher temperatures is associated with the transition of the nematic phase into the isotropic liquid. The pressure (p)–temperature (T) phase diagram of 6OCB shows that with rising pressure the nematic range increases and the nematic phase is stabilized.

Analogous phase behaviour has also been found for 6OCB saturated with helium (Fig. 1(b)). It has to be kept in mind, however, that here (as for all measurements with open cells) an additional gaseous phase coexists and that the $p(T)$ transition lines (e.g. in Figs. 1(b)–1(d), 2(b)–2(f)) correspond to three-phase lines with the coexistence of an additional gaseous phase;

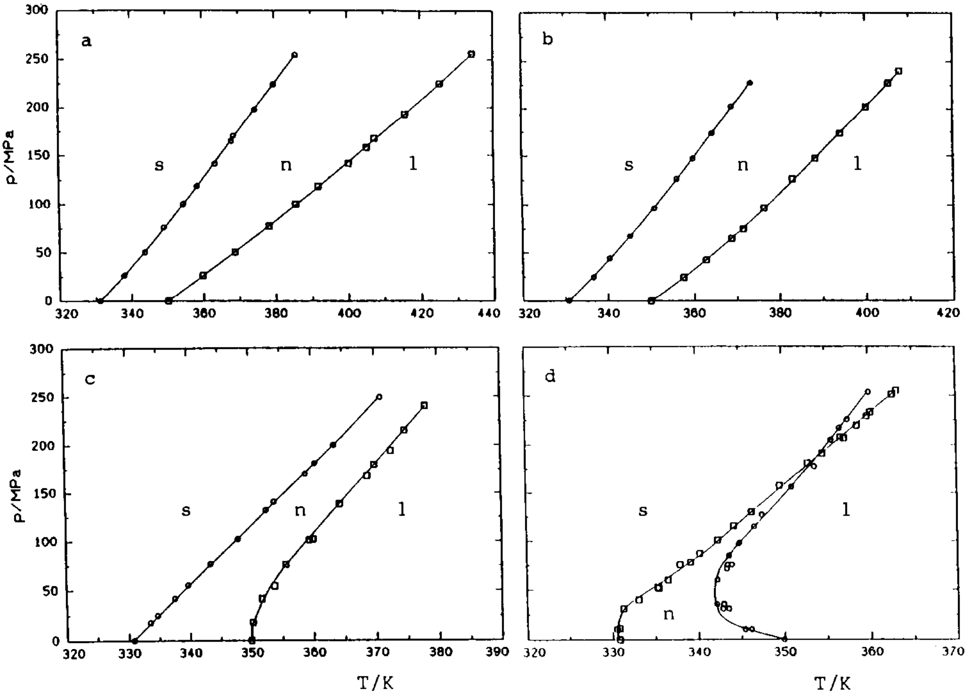

Fig. 1. $p(T)$ phase behaviour of 6OCB (pure (a) and saturated with helium (b), nitrogen (c) or argon (d)); see text.

consequently a triple point of a pure substance becomes a quadruple point in the gas saturated sample.

As can be seen from the $p(T)$ phase diagram of 6OCB under the influence of N_2 (Fig. 1(c)) the range of stability of the nematic phase becomes continuously smaller with rising pressure. Since the n/l phase transition temperatures were lowered much more by gas saturation than the melting temperatures, an intersection of the two coexistence curves could be expected. The extrapolation of the s/n and n/l phase transition curves in Fig. 1(c) would result in a quadruple point s/n/l/g at about 500 MPa and 410 K.

Under the influence of argon the s/n phase transition curve passes through a temperature minimum at about 330 K and 25 MPa (Fig. 1(d)) and the n/l transition curve also shows an even more pronounced temperature minimum at about 340 K and 50 MPa. Thus with rising pressure of argon, the existence range of the nematic phase is continuously destabilized. At about 355 K and 200 MPa the two coexistence curves intersect. At pressures above this quadruple point the nematic phase is metastable with respect to the solid phase and the phase transition of the isotropic liquid into the nematic phase can only be observed during cooling runs taking advantage of the pronounced supercooling of the solid phase.

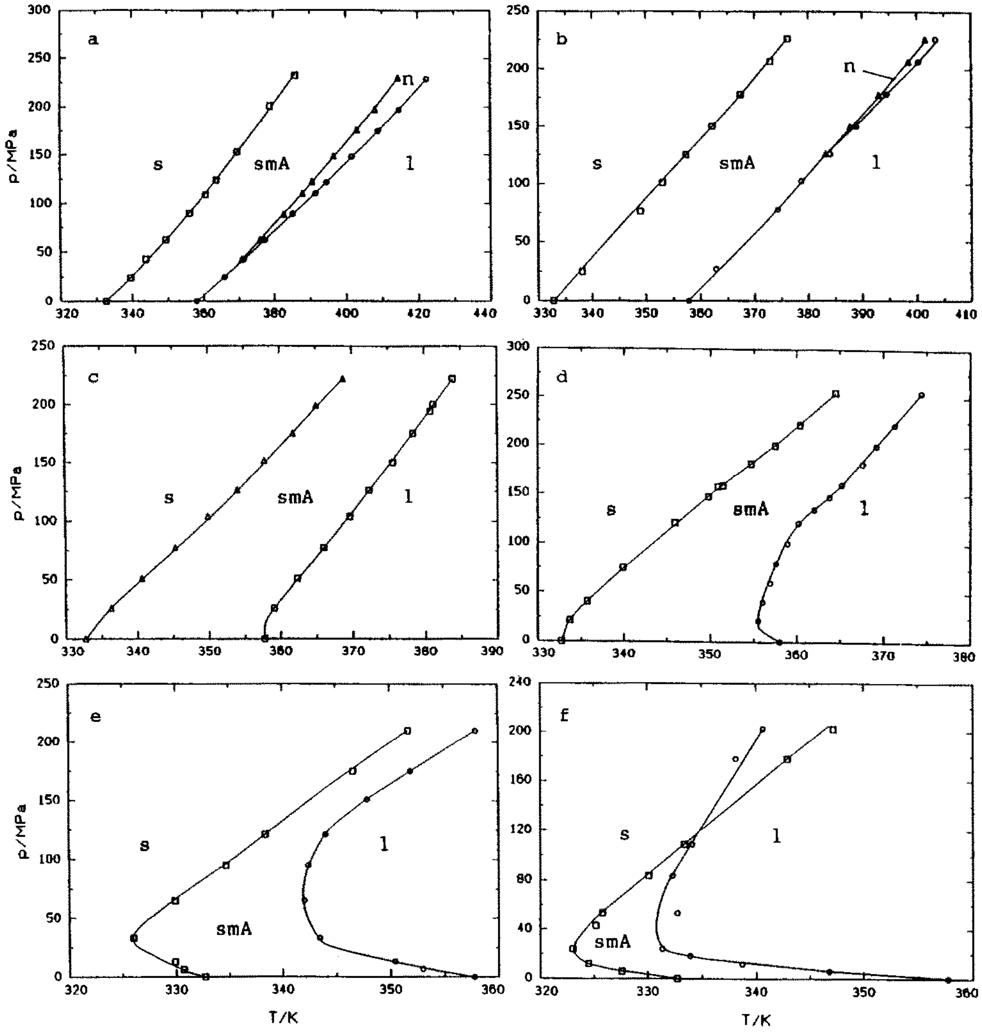

Fig. 2. $p(T)$ phase behaviour of 10OCB (pure (a) and saturated with helium (b), nitrogen (c), argon (d) as well as Ar/CO_2 mixtures 40:1 (e) or 30:1 (f)); see text.

10OCB

For investigations on a smectic phase 10OCB was used. The $p(T)$ phase diagram is shown in Fig. 2(a); it has already been measured by Hamm [7] and has been restudied in the present work [6].

At atmospheric pressure, 10OCB exhibits two phase transitions at 334 K and 358 K which could be attributed to s/smA and smA/l transitions respectively by polarizing microscopy studies [6]. Whereas there is only slight stabilization of the existence range of the smectic phase, the nematic phase becomes continously more stable and really appears with rising pressure at a triple point smA/n/l at 369 K and 35 MPa (Fig. 2(a)).

This pressure-induced nematic phase of 10OCB can still be observed when saturated with helium gas (Fig. 2(b)), the quadruple point smA/n/l/g (that corresponds to the triple point smA/n/l of the pure substance in Fig. 2(a)) being shifted to 383 K and 125 MPa.

With rising pressure of N_2, however, a destabilization of the smectic and even a disappearance of the nematic phases are found in the pressure range of the experiments (see Fig. 2(c)); the formation of a pressure-induced nematic phase could no longer be detected either in heating or in cooling DTA runs.

In analogy to 6OCB (Fig. 1(d)) the transition curve smA/l of 10OCB passes through a slight temperature minimum at about 25 MPa and 355 K under the influence of dissolved argon (Fig. 2(d)). With rising pressure the existence range of the smectic phase is strongly destabilized. In contrast to the smA/l coexistence curve the s/smA transition curve does not show any temperature minimum and an intersection point of these two curves at about 410 K and 500 MPa is to be extrapolated. The formation of a pressure-induced nematic phase could not be observed.

Measurements with Ar/CO_2 gas mixtures in a molar ratio of 40:1 and 30:1 respectively also demonstrate a strong influence on the s/smA and smA/l transition curves (Fig. 2(e, f)). Both $p(T)$ curves run through pronounced temperature minima. With rising pressure a strong destabilization of the smectic range is again to be seen. Whereas the two lines do not intersect in the experimental pressure range for the 40:1 gas mixture (Fig. 2(e)), an intersection point of the s/smA and smA/l transition curves at about 120 MPa and 334 K is found for the 30:1 mixture (Fig. 2(f)); at pressures above this intersection point the smectic phase can only be observed in cooling DTA runs and the smectic phase becomes metastable with respect to the crystalline solid.

DISCUSSION

The phenomena described above can be understood at least qualitatively taking into account two competing pressure effects: (i) the transition temperatures have the tendency to increase with rising pressure (as is already well known for the pure substances (see Figs. 1(a) and 2(a)) (effect I); (ii) the solubility of the gas (and by this the concentration of an inert impurity) in the liquid crystalline phases increases with rising pressure resulting in a decrease of the transition temperatures (see, for example, Figs. 1(d), 2(d)–(f) (effect II).

For helium, which is only slightly soluble in liquids effect I dominates and the $p(T)$ phase diagrams (Figs. 1(b) and 2(b)) resemble those of the pure substances (Figs. 1(a) and 2(a)). In the sequence nitrogen, argon and even more carbon dioxide (here as a component of the binary gas mixtures) the gas solublity is essentially higher and the temperature decrease is more important according to effect II. With further increasing pressures even temperature minima on the transition curves can appear where both effects approximately balance each other; at pressures below the temperature minimum effect II dominates over and above effect I.

In Fig. 3(a)–(f) some original DTA thermograms are given. Figure

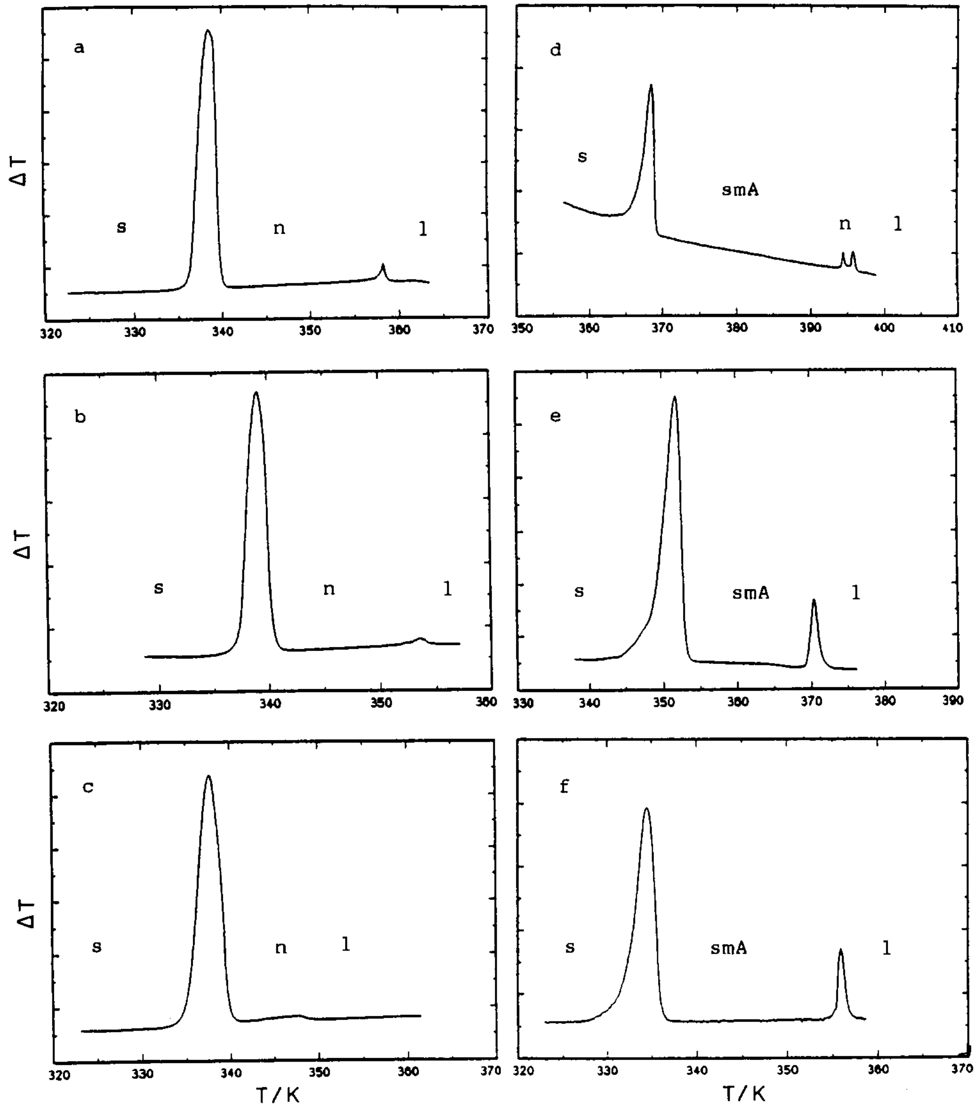

Fig. 3. DTA thermograms of 6OCB ((a)–(c)) and 10OCB ((d)–(f)) saturated with helium at 24.5 MPa (a) or 178.0 MPa (d), nitrogen at 42.0 MPa (b) or 104.0 MPa (e), and argon at 52.5 MPa (c) or 21.5 MPa (f); see text.

3(a)–(c) shows that for 6OCB an increasing flattening of the n/l peak is found. Here the n/l transition at argon pressures above 50 MPa can only be determined from a small baseline shift; this gives a hint of decreasing first order contributions to the transition and even from a change to higher order. On the contrary the DTA peaks of the smA/l transition of 10OCB are not influenced very much by helium (Fig. 3(d)), nitrogen (Fig. 3(e)) or argon (Fig. 3(f)). Here well-resolved peaks result which do not differ greatly from the peaks obtained for the pure substance in a closed cell except that the pressure-induced nematic phase is no longer found under nitrogen or argon pressure (see above); evidently the gas solubility in a smectic phase is lower and/or its structure more stable against inert gas inpurities than in the case of a nematic state.

These findings show that the properties and the structure of the mesomorphic phases are influenced by the saturating gases used in a quite individual and characteristic manner; here the use of other measuring techniques (e.g. X-ray scattering, DSC) will be indispensable. In addition some information can be obtained about the reliability of high-pressure measurements on liquid crystals when performed in (even very slightly) leaky cells using a pressure-transmitting gas; the present study again demonstrates that with the use of helium the approach to the pure component properties is best.

The investigations are continuing, with the especial aim of obtaining more quantitative knowledge about the gas solubilities and their influence on the structure of the different mesomorphic phases.

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