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Thermochimica Acta 299 (1997) 33–36

thermochimica acta

# Differential thermal analysis under pressure on cyclohexanone-$d_{10}$ metatoluidine and bromocyclohexane

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## Abstract

Differential thermal analysis (DTA) measurements under pressure up to 300 MPa and temperatures of about 300 to 370 K have been performed on cyclohexanone-$d_{10}$, bromocyclohexane and metatoluidine. The p-T-phase diagrams of these compounds have been established. Cyclohexanone-$d_{10}$ exhibits the same sequence of phases as cyclohexanone-$h_{10}$; however, the solid III–II and solid II–I transitions are separated at normal pressure. For bromocylohexane no solid–solid transitions have been found in the range of the pressures studied. Metatoluidine shows a glass transition. The slopes $dT/dp$ of the phase transition lines have been determined and are used to calculate the volume changes with the aid of the Clausius–Clapeyron equation.

*Keywords:* Differential thermal analysis; High pressure; Phase transitions; Thermodynamics

## 1. Introduction

In our group we employ differential thermal analysis (DTA) up to pressures of 300 MPa, in order to study the phase behaviours of plastic and liquid crystals [1,2]. Plastic crystals form orientationally disordered phases (ODIC), in which the molecules may carry out rotational motions or reorientational jumps between preferred orientations. These molecules are often of globular shape and exhibit low entropies of fusion [3,4]. Typical representatives are cylohexane and its derivatives, such as chlorocyclohexane ($C_6H_{11}Cl$) and cyclohexanone ($C_6H_{10}O$). While chlorocyclohexane forms an ODIC phase, no additional solid phases are reported for the homologue bromocyclohexane ($C_6H_{11}Br$) [5]. However, it is well known that molecular crystals may display pressure-induced ODIC-phases [6,7]. Therefore, bromocyclohexane might be an interesting candidate for a high pressure investigation. In previous studies it was shown that deuteration can significantly change the polymorphism; for example, for cyclohexane [8] and 2,2-dinitropropane [2]. In the present work we extend these studies to cyclohexanone-$d_{10}$. The phase situation of molecular crystals is often intricate due to the occurrence of metastable phases and glass transitions [9]. Various monotropic phases have been noted for the glass-forming metatoluidine ($C_6H_4CH_3NH_2$) [10], whose polymorphism is now studied with the use of high pressure DTA.

## 2. Experimental

The experimental set-up for the DTA measurements under high pressure has been described previously [11,12]. The temperature and DTA signals are registered on-line with the aid of a personal computer. The transition temperatures are evaluated with recently developed programs [12]. Usually heating rates of

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*PII* S0040-6031(97)00133-0

0.5–1 K/min are applied. The highest cooling rate attainable is 6 K/min.

## 3. Results

The transition temperatures are recorded on heating as a function of pressure and fitted to polynomials, which are listed in Table 1. From the slope of the transition lines and literature enthalpy changes we calculate the volume changes with the use of the Clausius–Clapeyron equation. The thermodynamic results are collected in Table 2 together with some literature data.

Table 1
Transition temperatures as a function of pressure $T/\mathrm{K} = a + b(p/\mathrm{MPa}) + c(p/\mathrm{MPa})^2$

| Substance | Transition | a | b | $10^4$ c |
|---|---|---|---|---|
| Cyclohexanone-$d_{10}$ | melting | 214.8 | 0.313 | −2.14 |
| | SII → SI | 219.3 | 0.304 | −1.25 |
| | SII → SII | 216.8 | 0.190 | −0.912 |
| Bromocyclohexane | melting | 217 | 0.204 | −0.944 |
| Metatoluidine | melting | 242 | 0.243 | −2.18 |
| | glass transition | 185 | 0.104 | −0.163 |

Table 2
Thermodynamic properties at 1 bar

| | $T$ K | ΔH kJ/mol | ΔS R | ΔV $\mathrm{cm}^3/\mathrm{mol}$ | d$T$/d$p$ K/MPa |
|---|---|---|---|---|---|
| Cyclohexanone-$h_{10}$ ($C_6H_{10}O$) | | | | | |
| Melting | 242.4 | 1.19 [15] | 0.59 | 1.5 | 0.31 [13] |
| SII→SI | 220.3 | 0.44 [15] | 0.24 | 0.5 | 0.27 [13] |
| SIII→SII | 220.3 | 7.30 [15] | 4.0 | 6.3 | 0.19 [13] |
| Cyclohexanone-$d_{10}$ ($C_6D_{10}O$) | | | | | |
| Melting | 241.5 | (1.19) | 0.59 | 1.5 | 0.313 |
| SII→SI | 219.3 | 0.40 | 0.22 | 0.6 | 0.304 |
| SIII→SII | 216.8 | 7.10 | 3.94 | 6.2 | 0.190 |
| Bromocyclohexane ($C_6H_{11}Br$) | | | | | |
| Melting | 216.8 | 10.79 [5] | 6.0 | 10.15 | 0.204 |
| Metatoluidine ($C_6H_4CH_3NH_2$) | | | | | |
| Melting | 242.6 | 3.89 [3] | 1.93 | 3.91 | 0.243 |
| Glass transition | 185 | | | | 0.104 |

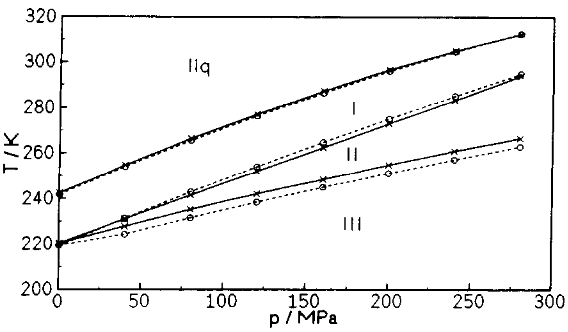

Fig. 1. Phase diagram of $C_6H_{10}O$ (x) and $C_6D_{10}O$ (o).

### 3.1. Cyclohexanone-$d_{10}$

Cyclohexanone-$h_{10}$, $C_6H_{10}O$, is a typical plastic crystal, displaying an ODIC-phase with low enthalpy of fusion and high permittivity. Previously, an additional pressure-induced phase has been detected [13], which is supposed to be plastic as well due to its high permittivity [14]. The small volume and enthalpy changes at the intermediate solid phase transition [15] and a recent neutron scattering study [16] supports the ODIC-character.

In the present work we investigate the deuterated cyclohexanone, $C_6D_{10}O$, whose phase diagram is shown in Fig. 1 in comparison with $C_6H_{10}O$. For the deuterated sample the solid III–II transition temperatures are a little bit lower and the solid II–I transition temperatures are somewhat higher. Thus the p-T range for the solid II phase is broader and the two solid–solid transitions are well separated at normal pressure. In the case of cyclohexane the effect of deuteration is just the opposite [8]. For deuterated cyclohexanol a decrease of the transition temperatures was found [2].

In Fig. 2 we present some selected DTA signals for different pressures. There is some indication of a further transition immediately before the III–II transition, as revealed by a shoulder, which is better separated at higher pressures. The ratio of the peak areas referring to solid III–II and solid II–I transitions is 16 and does not change with pressure. With the use of DSC Masberg found 7500 J/mol for the sum of the two enthalpy changes at 1 bar [17]. Correspondingly, we assign $\Delta H(\mathrm{III}-\mathrm{II}) = 7100$ and $\Delta H(\mathrm{II}-\mathrm{I}) = 400$ J/mol. The enthalpy change of melting could

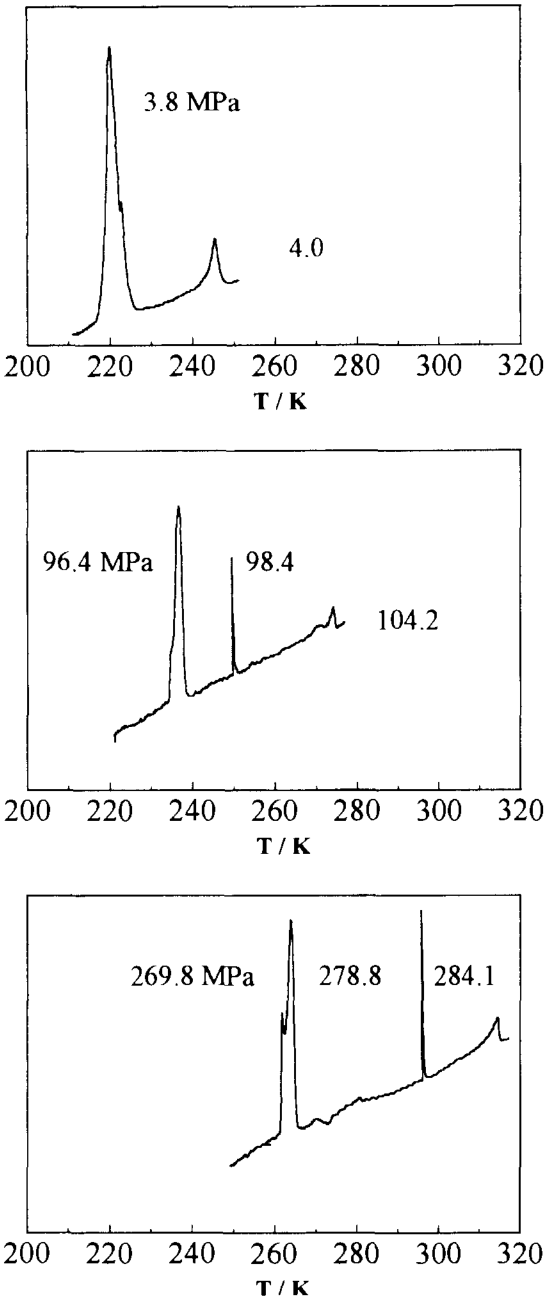

Fig. 2. Selected DTA peaks for $C_6D_{10}O$ at different pressures, showing the solid III–II and the solid II–I transitions.

not be accurately measured, and therefore we take the value for $C_6H_{10}O$ ($\Delta H = 1190$ J/mol [15]) for the calculation of the volume change, (see Table 2).

### 3.2. *Bromocyclohexane*

The thermodynamic properties of bromocyclohexane have been thoroughly investigated at normal pressure [5], according to which this compound displays only fusion. However, according to the Pople–Karasz theory [18] a plastic phase can be expected at higher pressures, when the molecular shape does not deviate too much from globularity. This has been quantitatively treated by introducing an asymmetry parameter $\nu$ that is related to the ratio of the energy barrier against reorientation and the energy barrier against the diffusion to an interstitial site.

DTA measurements have been performed up to 300 MPa, without any evidence of pressure-induced rotator phases. The melting temperature at atmospheric pressure (216.8 K) is very close to the solid II–I transition temperature of chlorocyclohexane (220.0 K [5]). This is a typical feature of plastic crystals, that they often display a transition to a disordered phase at the melting point of a non-ODIC homologue. Even the slopes are very similar: $dT/dp = 0.204$ K/MPa (melting of $C_6H_{11}Br$) and 0.180 K/MPa (II–I transition of $C_6H_{11}Cl$ [19]), respectively. The volume change of melting has been calculated with the aid of the enthalpy change reported by Kobashi and Oguni [5], (see Table 2).

### 3.3. *Metatoluidine*

This compound freezes at 242 K and transforms to a glass at 185 K. Legrand et at. [10] report a monotropic transition between two solid phases $\alpha$ and $\beta$. However, in our DTA study we did not find any solid–solid transitions (Fig. 3). Probably the high pressure DTA device is not sensitive enough in order to detect transitions of second or weakly first order, which only cause a shift in the base line.

The slope $dT_g/dp$ of the glass transition (0.104 K/MPa) is lower than previously reported values for similar compounds [20], but higher than for hydrogen-bonded systems [21]. The latter authors discuss the slope with Eq. (1), assuming

$$\left(\frac{\partial p}{\partial T}\right)_T = \frac{\Delta H^{\neq}}{T\Delta V^{\neq}} \tag{1}$$

that the glass transition is related to a state of constant

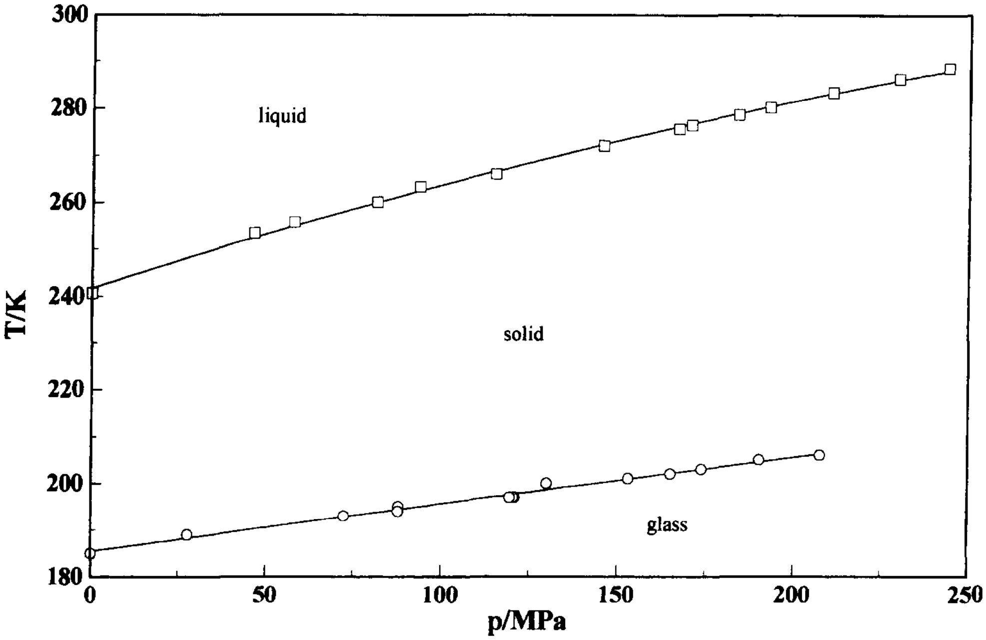

Fig. 3. Phase diagram of metatoluidine, melting curve (□), glass transition (o).

relaxation time. In fact, it is well known that for the dielectric relaxation of hydrogen-bonded plastic crystals the ratio $\Delta H^{\neq}/\Delta V^{\neq}$ is distinctly larger compared with other ODICs [6,11].

## Acknowledgements

The authors thank Stefan Masberg for the DSC measurement on cyclohexanone $d_{10}$, and Prof. Descamps for stimulating the investigation of metatoluidine. Financial support of the Fonds der Chemischen Industrie is gratefully acknowledged.

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