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HIGH PRESSURE DIFFERENTIAL THERMAL ANALYSIS OF CYCLOHEXANOL-D_{11} ($C_6D_{11}OH$) AND CARBON TETRACHLORIDE (CCl_4)

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ABSTRACT

The phase behaviours of liquid and solid cyclohexanol-d_{11} ($C_6D_{11}OH$) and carbon tetrachloride (CCl_4) have been studied with the aid of differential thermal analysis for temperatures between 175 and 300 K and pressures up to 3 kbar. The transformations between the different liquid and solid phases and their metastability have been investigated.

INTRODUCTION

Molecular crystals often reveal so-called "plastic phases" due to orientational disorder. Such disorder is most readily observed with globular or cyclic compounds because of their relative ease of reorientational motion. Cyclohexane and its derivatives are typical representatives of "plastic crystals". Recent studies on cyclohexane have shown that deuteration causes a strong change in its phase behaviour [1]. The aim of the present work was to compare the phase behaviours of deuterated and "normal" cyclohexanol, especially regarding the so-called "exothermic anomaly" [2]. This phenomenon is observed when heating samples which are mixtures of stable and metastable phases. Furthermore the phase behaviour of carbon tetrachloride should be reinvestigated in order to compare its "dual melting" behaviour [3] with the metastability of cyclohexanol.

EXPERIMENTAL

All measurements were performed using the high pressure equipment described previously [2].

Commercially available deuterated cyclohexanol (Janssen Chimica, Beerse, Belgium) was purified by preparative gas chromatography (Carbowachs +

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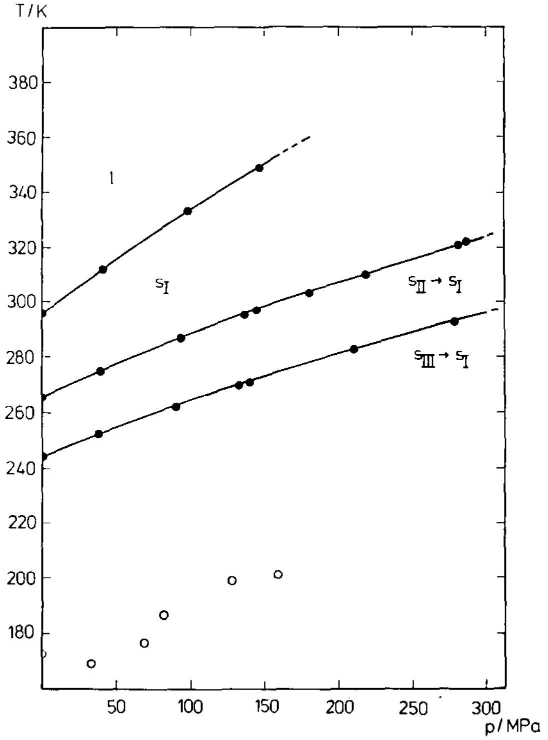

Fig. 1. Phase diagram of $C_6D_{11}OH$; the lower circles refer to annealing temperatures (see text).

KOH). Subsequent analysis with the aid of infrared spectroscopy revealed a protonation of the OD bond, but no CH vibration was detectable. Thus, the substance was identified as $C_6D_{11}OH$. Carbon tetrachloride was obtained from Riedel de Haen (Hannover, FRG). Gas chromatographic analysis demonstrated that its purity was better than 99.7%; therefore the sample was used without further purification.

RESULTS

Cyclohexanol-d_{11}

The phase behaviour of $C_6D_{11}OH$ (see Fig. 1) is quite similar to that of $C_6H_{11}OH$ [2]. If the sample is annealed at temperatures below 175 K, only the solid II–solid I transition is observed on reheating. Correspondingly, thermal treatment above 180 K leads to the solid III–solid I transition. The solid III–solid II transition is not visible on cooling but should occur at around 180 K. This is deduced from the fact that when the sample has been annealed at this temperature both solid–solid transitions are observed on

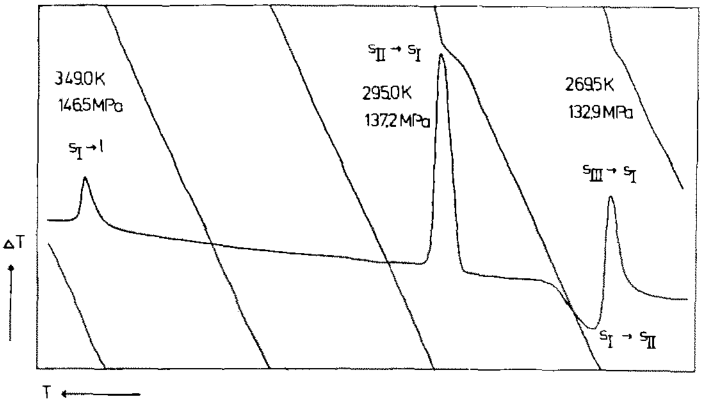

Fig. 2. DTA curves for $C_6D_{11}OH$ for a heating run after annealing the sample at 180 K.

further heating (Fig. 2). Immediately after the solid III–solid I transition, phase I is converted to solid II causing an exothermic peak. Solid phase II then transforms to solid I on further heating.

The transition temperatures are slightly lower compared to $C_6H_{11}OH$ but the differences are slight (Table 1). However, the exothermic anomaly seems to be less pronounced in the case of $C_6D_{11}OH$, probably due to the slower kinetics of the solid III–solid II conversion [4]. The higher the pressure the more difficult it is to adjust the correct annealing temperature in order to observe the exothermic anomaly on heating. The lower circles in Fig. 1 refer to these temperatures. Above 160 MPa, exothermic peaks were not detected.

Carbon tetrachloride

Carbon tetrachloride exhibits two plastic phases immediately below the melting curve, one of which (I_a) being metastable with respect to the other (I_b). Both phases melt directly; the I_a melting curve has been traced for pressures up to 100 MPa [3].

In the present work, the reported phase behaviour of CCl_4 was essentially confirmed. However, both the freezing to I_a and the melting of I_a were

TABLE 1

Transition temperatures at atmospheric pressure and slopes of the transition lines (K MPa^{-1}) for $C_6D_{11}OH$ and $C_6H_{11}OH$

Transition	$C_6D_{11}OH$		$C_6H_{11}OH$	
	T (K)	Slope	T (K)	Slope
Melting	295.5	0.425	298	0.426
Solid III–I	244.3	0.206	245	0.218
Solid II–I	265.4	0.232	265.7	0.239

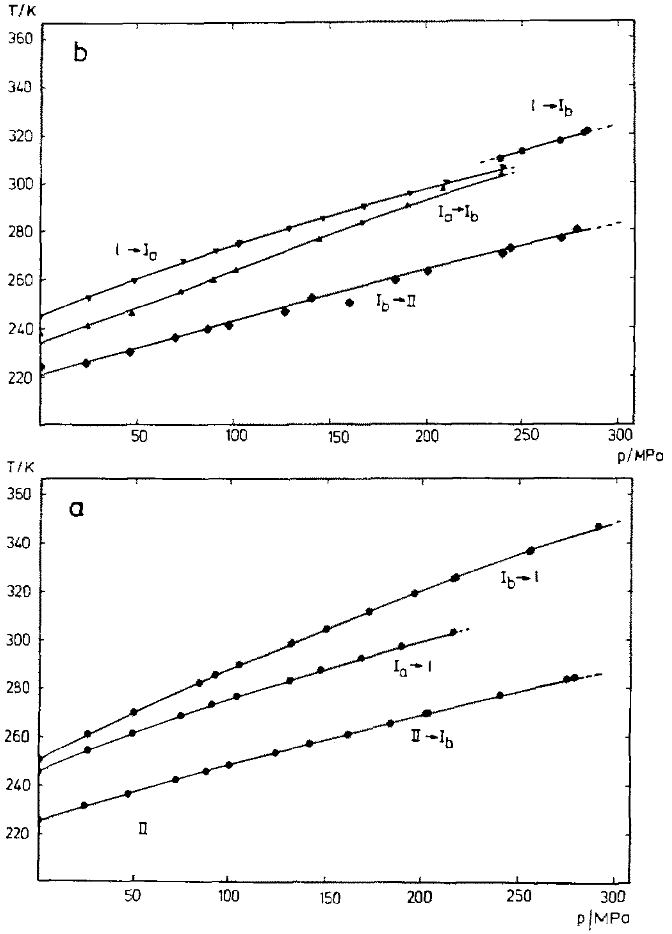

Fig. 3. Phase diagram of CCl_4 for (a) heating and (b) cooling runs.

detectable at pressures above 200 MPa. Figures 3a and 3b show the pressure dependence of the phase transitions on heating and cooling, respectively. The freezing line to I_a and the transition I_a–I_b converge and meet at about 250 MPa. Above that pressure, only the freezing to I_b is observed.

TABLE 2

Transition temperatures at atmospheric pressure and constants of the polynomial $T = a + bp + cp^2$ for CCl_4, where p is in MPa

Cooling		Heating		a	b	$c \times 10^4$
Transition	T (K)	Transition	T (K)			
Liquid–I_a	245.2	I_a–liquid	245.7	246	0.324	−2.74
I_a–I_b	236.8	I_b–liquid	250.5	251	0.386	−1.92
I_b–II	224.1	II–I_b	225.6	225.8	0.234	−0.842

TABLE 3

Some calorimetric data for CCl_4

Transition	T (K)	ΔH (kJ mol^{-1})	dp/dT (K MPa^{-1})	ΔV (cm^3 mol^{-1})
I_a-liquid	245.7	1.77	0.324	2.36
I_b-liquid	250.5	2.45	0.386	3.95
II-I_b	225.5	4.43	0.234	4.78

The transformation to the low temperature form solid II is also associated with a supercooling effect. Table 2 lists the transition temperatures at atmospheric pressure as well as the polynomials expressing the pressure dependence. There is good agreement with the reported results of Bean and Wood [3].

In addition, enthalpy and volume changes (using the Clausius–Clapeyron equation) have been calculated after calibration against substances of known transition enthalpies. Some results are shown in Table 3; all data refer to atmospheric pressure. The enthalpy changes agree well with those cited in the literature (5,6), whereas volume changes have not yet been reported.

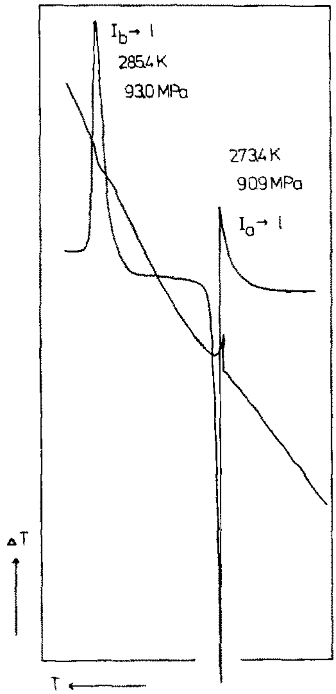

Fig. 4. DTA curves for CCl_4 showing an exothermic anomaly.

CONCLUSIONS

In the present work, it has been shown that the metastability of solid phase III for $C_6D_{11}OH$ is very similar to that of $C_6H_{11}OH$. But there is also a certain similarity to the metastable phase I_a of CCl_4. We note some features that are common to both cases; there is of course one important difference: the solid II–solid III transition corresponds to the transition liquid–solid I_b.

The upper limit of the temperature range where the metastable phase exists is lower than the transition temperature between the two corresponding stable phases; that is the transition solid III–solid I occurs at 244.3 K which is lower than that for solid II–solid I which occurs at 265.4 K; also the I_a–liquid transition at 245.7 K is lower than that for I_b–liquid which occurs at 250.5 K. Suitable annealing procedures lead in both cases to exothermic anomalies, as shown in Figs. 2 and 4. However, the exothermic peak of the formation of I_b is much more pronounced than the exothermic anomalies observed for cyclohexanol (whether deuterated or not). This is obviously due to the presence of the liquid phase in the case of CCl_4.

It seems that the exothermic anomalies previously described for cyclohexanol [7,8] are also detectable for many other compounds, provided that the appropriate thermal treatments have been determined.

ACKNOWLEDGEMENT

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