Differential Thermal Analysis and Dielectric Studies on 2-Methyl-2-Nitro-Propane under High Pressure

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Differential thermal analysis and dielectric studies under pressures up to 300 MPa and temperatures of about 200 to 350 K have been performed on 2-methyl-2-nitro-propane (TBN). TBN displays an orientationally disordered phase (ODIC), solid I, and two non-plastic phases, solids II and III. The coexistence region of the plastic phase I increases with increasing pressure, whereas the low-temperature phase II apparently vanishes at a triple point I, II, III, above 300 MPa. The static permittivity increases on freezing, characterizing the solid I as an ODIC phase. In the frame of the Kirkwood-Onsager-Fröhlich theory the *g*-factor is about unity, discounting specific dielectric correlations. The dielectric behaviour of TBN is similar to previously studied related compounds, such as 2-chloro-2-methyl-propane or 2-brome-2-methyl-propane.

1. Introduction

In this paper we report on thermodynamic and dielectric measurements on 2-methyl-2-nitro-propane (TBN) under high pressure. TBN is part of a family of tertiary butyl compounds which exhibit a more or less globular shape, similar to the neopentane derivatives. They are typical representatives of so-called plastic crystals, revealing at least one orientationally disordered phase (ODIC) [1–3]. The solid phases of TBN have been studied in the past by various experimental methods. Urban et al. [4] describe three different solid phases of TBN with approximately equal entropy changes for the solid III/II and the solid II/I transitions. According to [4], the high-temperature plastic phase (solid I) is surprisingly not cubic but orthorhombic. However, this result is at variance with recent findings of Tamarit [5]. Dielectric [6–8], infrared [9], and NMR [10] studies confirm the ODIC character of solid I. The rotator phase was also simulated [11] in order to analyse the rotational dynamics.

The NMR study of Hasebe and Chihara [10] was extended up to 140 MPa with the aim to determine in detail the pressure dependence of the ^{1}H-spin-lattice relaxation time. The authors present also a sketch of the $p(T)$-phase diagram. It was felt that the phase behaviour should be analysed in more detail. Therefore we employed high-pressure differential thermal analysis (DTA) to elucidate more thoroughly the phase situation of TBN [12]. Molecular crystals display very often new pressure-induced phases [13], and only little attention was drawn to their structural investigation [14].

Furthermore we studied the rotator phase dielectrically [15]. The static permittivity will be discussed in terms of the Kirkwood-*g*-factor [16] that allows to examine preferred molecular correlations. Recently determined pVT data [5, 17] enable us to analyse in detail the density dependence of the Kirkwood-*g*-factor. The pressure dependence of the permittivity of TBN has not yet been reported in literature.

2. Experimental

The experimental devices for the high-pressure DTA [18, 19] and the dielectric measurements [13, 20, 21] have been described previously. We employed a Hewlett Packard 4192 A impedance analyser that allowed to vary the frequency up to 13 MHz. No dielectric relaxation was observed in this frequency range. TBN was obtained from Aldrich with a purity better than 99%. A glc-analysis yielded a purity of 99.5%. Therefore the sample was used without further purification.

3. Results

3.1. *Differential Thermal Analysis*

The phase diagram of TBN derived from DTA and pVT measurements is shown in Figure 1. The coexistence range of the plastic phase (solid I) is enlarged with increasing pressure, which is the normal behaviour of plastic crystals [22, 23]. However, the phase region of solid II seems to disappear at a triple point solid I, II, III beyond the experimental pressure range. An extrapolation of the phase boundaries yields an estimate of 370 MPa and 300 K for the triple point.

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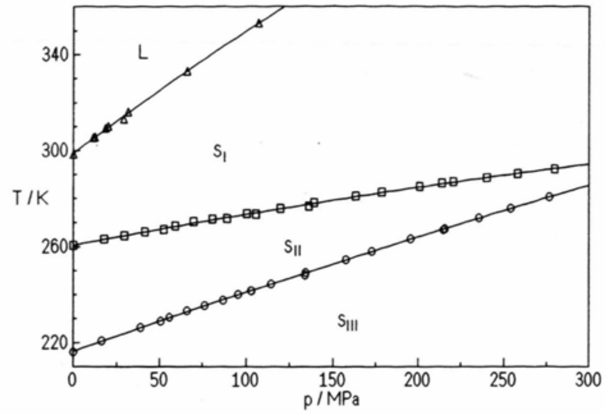

Fig. 1. Temperature-pressure phase diagram for 2-methyl-2-nitro-propane (TBN). L = liquid, $S_I \cdots S_{III}$ = solid phases.

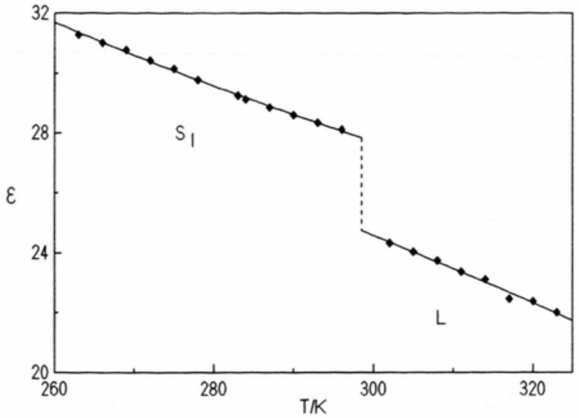

Fig. 2. Static Permittivity for TBN at ambient pressure as a function of temperature. L = liquid, S_I = plastic phase.

The phase transition lines for TBN can be represented by polynomials:

$$\begin{aligned}
\text{solid III} \rightarrow \text{II:} \quad & T(\mathrm{K}) = 216.4 + 0.254\,(\mathrm{p/MPa}) \\
& \quad -8.02 \cdot 10^{-5}\,(\mathrm{p/MPa})^2, \\
\text{solid II} \rightarrow \text{I:} \quad & T(\mathrm{K}) = 260.6 + 0.137\,(\mathrm{p/MPa}) \\
& \quad -8.14 \cdot 10^{-5}\,(\mathrm{p/MPa})^2, \\
\text{solid I} \rightarrow \text{liquid:} \quad & T(\mathrm{K}) = 298.9 + 0.561\,(\mathrm{p/MPa}) \\
& \quad -5.1 \cdot 10^{-4}\,(\mathrm{p/MPa})^2.
\end{aligned}$$

The slope of the melting transition line differs significantly from that reported by Hasebe et al. [10]. Volume changes at atmospheric pressure have been calculated with the aid of the Clausius-Clapeyron equation using enthalpy changes from Urban et al. [4]: $\Delta H = 4.22$, 4.66, and 2.60 kJ/mol for solid III/II, solid II/I, and melting. The volume changes are 5.0, 2.5, and 4.9 $\mathrm{cm^3/mol}$ for the solid III/II, solid II/I, and melting, respectively. These values agree very well with results recently obtained by means of pVT- and X-ray measurements that will be published in a forthcoming paper [5, 17].

3.2. Dielectric Measurements

The static permittivity, ε, is presented in Figs. 2 and 3 at atmospheric and higher pressures, respectively. ε increases appreciably at the freezing temperature, identifying solid I as an ODIC phase. Furthermore, the slope of the melting curve is also confirmed by the dielectric measurements. However, $(\partial \varepsilon / \partial p)_T$ is in the solid phase I significantly smaller than in the liquid.

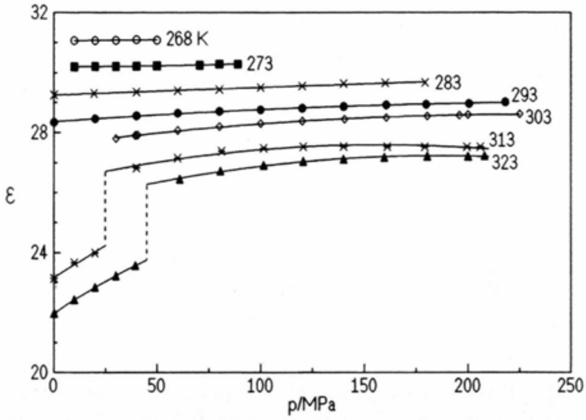

Fig. 3. Static Permittivity for TBN as a function of pressure and temperature. The dashed lines indicate the liquid-plastic phase transition.

Many runs have been performed which confirmed good reproducibility of the results. There was no indication of varying permittivities as has been observed for example for the non-cubic plastic phases of cyclopentanol, caused by changing growing conditions of the sample [24]. In other words, ε of TBN does not exhibit anisotropic features, supporting the assumed cubic structure for the plastic phase (solid I) [5].

Only few measurements have been performed in the non-plastic phase II, because the capacitor does not work well in the low-temperature brittle phases. In any case the static permittivity drops to low values comparable to the high frequency dielectric constant $\varepsilon_\infty \approx n^2$.

From the static permittivity we can calculate the Onsager dipole moment and compare it with the dipole moment in the gas phase $\mu = 3.71$ D [25]. Its deviation yields the g-factor, which is a rough measure of local ordering [16]:

$$g\,\mu^2 = \frac{9\,k\,T\,\varepsilon_0\,M\,(\varepsilon - \varepsilon_\infty)(2\,\varepsilon + \varepsilon_\infty)}{N_A\,\varrho\,\varepsilon\,(\varepsilon_\infty + 2)^2}\,.$$

The meaning of the quantities and the necessary simplifications in the frame of the Kirkwood-Fröhlich-Onsager theory have been described in [19, 23].

Figure 4 shows the Kirkwood-g-factor for different temperatures as a function of pressure. Values about unity for g discount specific correlations in TBN, in agreement with previous findings on other tertiary butyl compounds (TBCl [26] and TBBr [27]), and on cyclohexanone [23]. P, V, T-data [5, 17] enable us to distinguish between isochoric temperature changes and isothermal density changes, which is one of the principal advantages of high pressure studies [13]. Rough estimates yield

$$\left(\frac{\partial \ln g}{\partial \ln T}\right)_\varrho = 0.4\,, \quad \left(\frac{\partial \ln g}{\partial \ln \varrho}\right)_T = -\,1.4\,.$$

These derivatives show that the density dependence is more pronounced than the temperature dependence. Similar results have been found for t-butylchloride [26] and other non-hydrogen-bonded compounds, whereas for substances with strong dipolar interactions (alcohols) an opposite behaviour is observed [13].

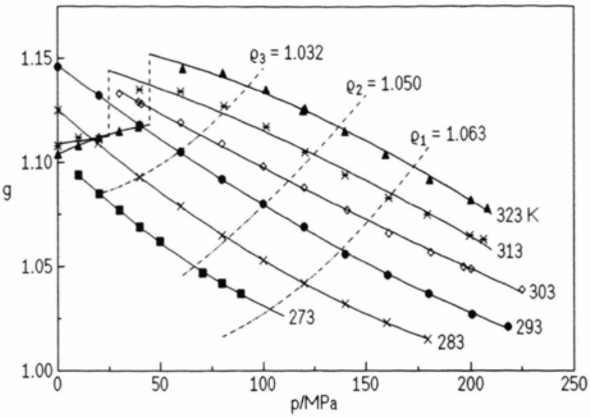

Fig. 4. Kirkwood-g-factor for TBN as a function of pressure for different temperatures and densities (in g/cm^3).

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