Differential Thermal Analysis and Dielectric Studies on Neopentanol under Pressure

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Differential thermal analysis (DTA) and dielectric measurements have been performed on 2,2-dimethyl-1-propanol (neopentanol) up to 200 MPa. Neopentanol exhibits at least one orientationally disordered (ODIC) phase (solid I) that transforms at lower temperatures to a non-plastic phase (solid II). There is evidence of a further ODIC phase denoted as solid I′. The pressure dependence of the phase transitions and the dielectric behaviour up to frequencies of 13 MHz are described. Activation enthalpies and volumes are derived from the dielectric relaxation time and compared with results for other alcohols.

Key words: High pressure, DTA, Phase transitions, Dielectric constant, and relaxation

1. Introduction

2,2-dimethyl-1-propanol (neopentanol) is an example of plastic crystals characterized by orientationally disordered phases (ODIC). According to X-ray studies [1] the ODIC phase obtained after freezing has a cubic structure (solid I) that transforms at lower temperatures to a monoclinic phase (solid II). The order-disorder transition (solid II–I) has been confirmed by NMR [2] and dielectric [3, 4] investigations at atmospheric pressure. However, high pressure studies have, so far, not been reported for neopentanol. But the application of pressure is a useful tool for varying the intermolecular distances; also a wealth of pressure-induced phase transitions have been found for many molecular crystals which are not present at ambient pressure [5, 6].

In the present work we report on the pressure dependence of the phase behaviour established with the aid of differential thermal analysis (DTA) [7] and dielectric investigations [8]. The dielectric measurements concern both the static and complex permittivity. The high symmetry of the molecular shape of neopentanol and its low molecular mass permit an interesting comparison with other related alcohols for which an account has been given recently [9].

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2. Experimental

For details of the high pressure equipment used for the DTA and dielectric measurements see [6] and [8–11], respectively. Neopentanol (99.0%) was obtained from Merck-Schuchardt, Germany, and distilled under a high reflux ratio, after which the water content was lower than 0.1%.

The static and dynamic permittivities $\varepsilon^* = \varepsilon' - i\varepsilon''$ were measured with a Hewlett Packard 4192 A impedance analyser in conjunction with a Commodore computer 8296. Different cylindrical capacitors of about 18 pF were mounted in a high pressure vessel made of copper beryllium alloy. The accuracy of the measurements for ε' is 0.1% after all corrections. Details of the impedance measurements and the data evaluation can be found in [8, 9].

3. Results

3.1 Phase behaviour

The phase diagram of neopentanol is shown in Figure 1. According to the DTA study the solid II–I transition was preceded by a heat effect that depended strongly on the annealing conditions. Figure 2 shows an example of DTA peaks whose areas change significantly in favour to the solid II–I transition with increasing annealing time (10 to 60 min). Obviously SII′ is a metastable phase. In the dielectric measurements longer times were needed to adjust the temperature,

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and therefore such a metastable SII′ was not observed. On the other hand, the dielectric measurements revealed a small step in the capacitance within the solid I phase, both with increasing and decreasing temperature. This is shown in Fig. 3, where the curves refer to three different runs performed at different pressures. The step is visible at about 15, 35, and 260 MPa in the upper, middle, and lower curve, respectively, showing also the shift of the temperature with pressure. This finding possibly indicates an intermediate transition between two ODIC phases. This phase transition (denoted in the following as solid I–I′) was also visible in a recent DSC study [12], but not observed in the DTA study [7].

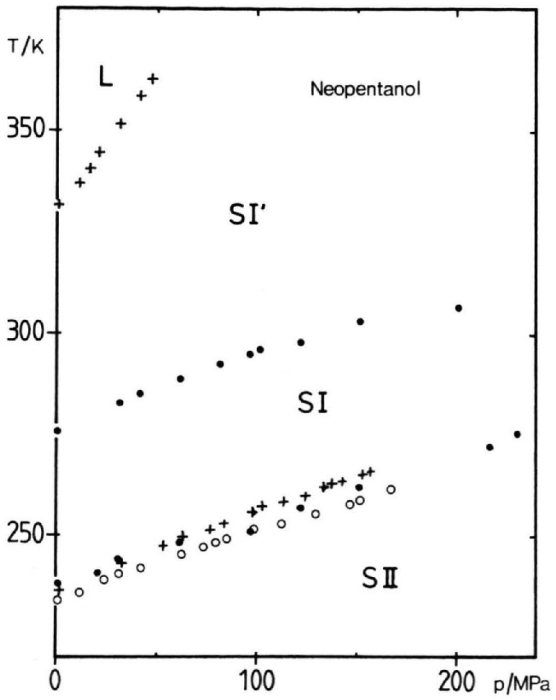

Fig. 1. Phase diagram for neopentanol, showing the solid II–I, solid I–I′ transitions, and melting. + = DTA [7], ● = dielectric measurements [8], ○ = DSC [13].

The DTA transition temperatures have been approximated by polynomials:

$$\text{Melting:} \quad T/K = 331.4 + 0.6722\,(p/\text{MPa}),$$

$$\text{Solid II–I:} \quad T/K = 236.2 + 0.2366\,(p/\text{MPa}) - 2.87 \cdot 10^{-4}\,(p/\text{MPa})^2.$$

The pressure dependence of the solid II–I transition has also been determined by Ellert (13), who found somewhat lower temperatures, see Figure 1.

3.2 Enthalpy and Volume Changes

The peak areas of the DTA traces enable us to calculate the enthalpy changes, which may be converted to volume changes with the aid of the Clausius-Clapeyron equation. Because a high pressure calibration entails too many uncertainties, only atmospheric pressure enthalpy changes are calculated and compared with literature data, see Table 1. The results show that even the transition temperatures scatter considerably. This is probably due to different degrees of purities of the very hygroscopic substance. Best agreement is obtained with Suenaga et al. [15], who applied adiabatic calorimetry for the determination of heat capacities of some neopentyl compounds. The

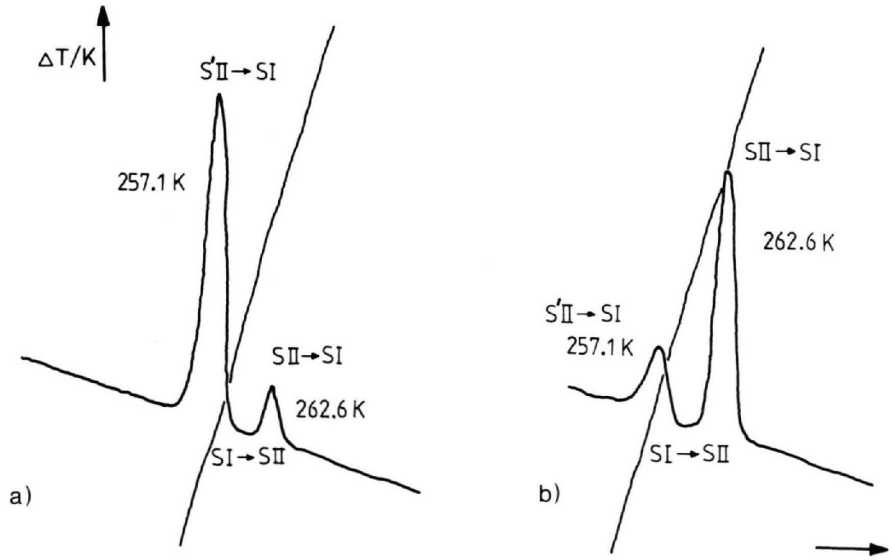

Fig. 2. DTA traces of neopentanol at 133 MPa, showing the influence of the annealing time on the metastable solid II′–I transition. a) 10 min, b) 60 min.

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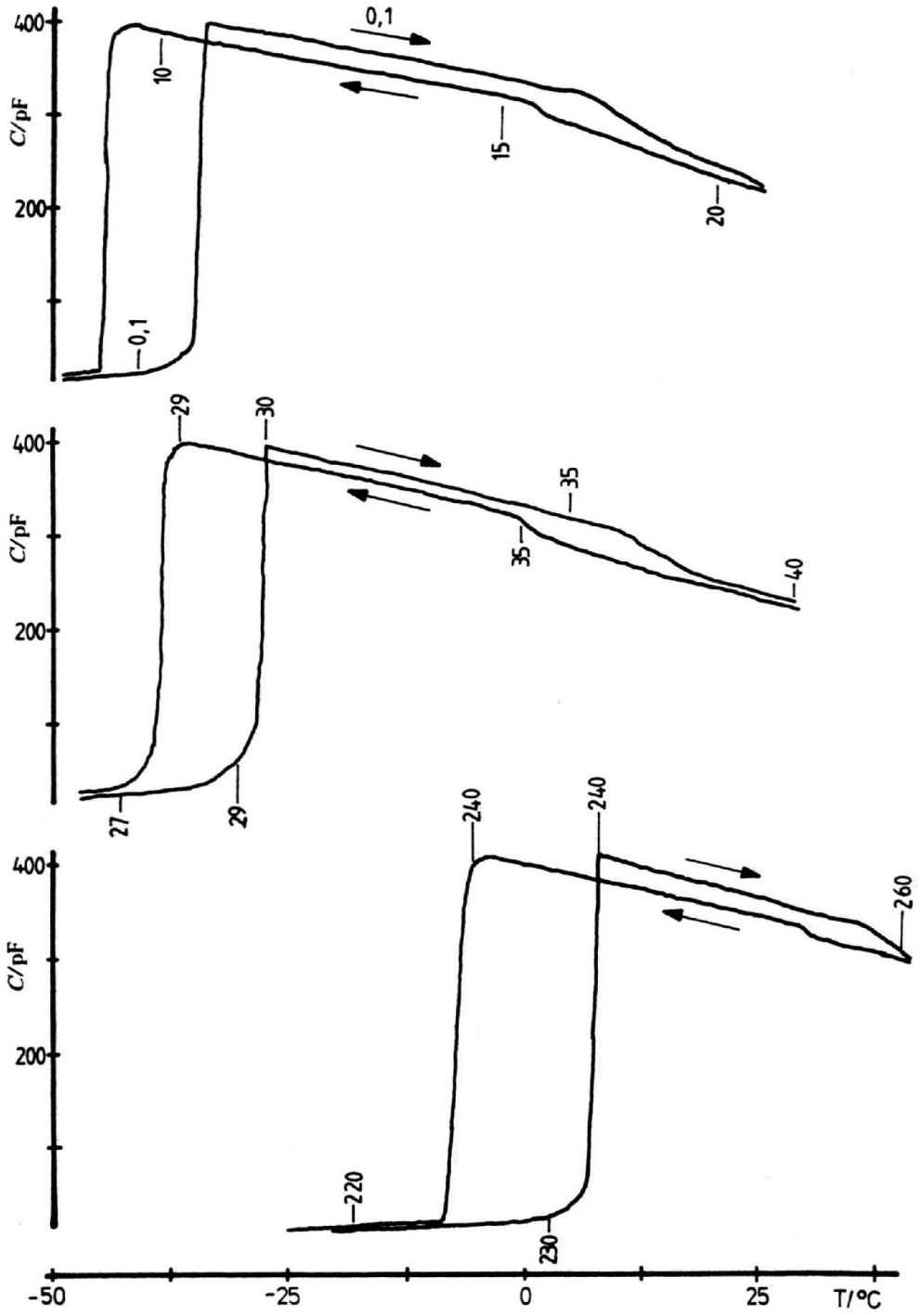

Fig. 3. Capacitance measurements for neopentanol as a function of temperature, showing the intermediate solid I–I′ transition at about 15, 35, and 260 MPa for the upper, middle, and lower curve, respectively. The numbers in the figure refer to pressures in MPa.

high transition temperature reported by Murrill et al. [14] is not well understood. They applied differential scanning calorimetry (DSC) for the investigation of various tetrahedral substances. A high pressure DSC calorimeter was used by Ellert, who calculated a somewhat smaller volume change, due to a significantly smaller slope of the transition line [13].

3.3 Static Permittivity and Kirkwood-g-Factor

Figure 4 presents the static permittivity, ε, as a function of temperature for different pressures. Both solid I and solid I′ show high values for ε, identifying these phases as orientationally disordered ones. Phase II certainly represents a non-rotational form. In general

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Table 1. Thermodynamic properties connected with the phase transitions of neopentanol at 1 atm.

Transition	T / K	ΔH / kJ mol^{-1}	dT/dp / K MPa^{-1}	ΔV / cm^3 mol^{-1}	Ref.
Solid I – liquid	331.4	3.9	0.672	7.9	[7]
	324–327	4.06			[14]
	328	4.42			[31]
	328				[4]
Solid I–I′	276		0.137		[8]
Solid II–I	236.5	4.0	0.237	4.0	[7]
	234.4	4.325	0.196	3.54	[13]
	242	4.47			[14]
	235.2	4.262			[15]
	234.2				[4]
Solid II′–I	235.4		0.192	3.3	[7]

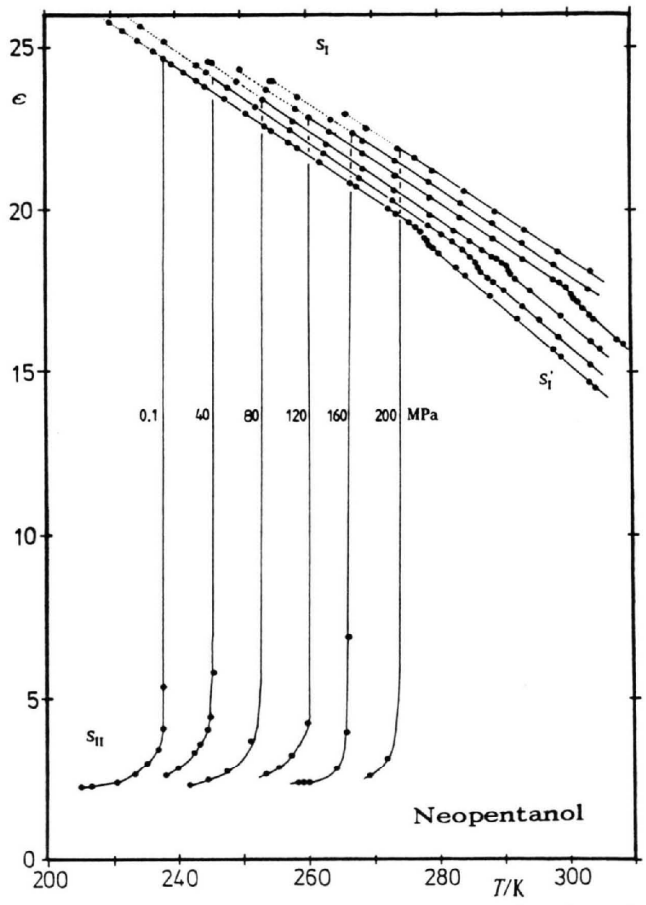

Fig. 4. Static permittivity of neopentanol as a function of temperature for different pressures, showing the solid II–I and the solid I–I′ transition.

when a polar plastic crystal exhibits several ODIC phases, large changes in the permittivity and enthalpy occur simultaneously at the order-disorder transition, whereas small changes are observed at the intermediate ODIC transitions, e.g. in t-butyl compounds [16, 17], cyclohexanone [18], cyclo-octanol [19] etc. In the present work no thermodynamic quantities are available for the intermediate solid I–I′ transition.

Some atmospheric pressure permittivities are plotted in Fig. 5, showing good agreement with data of Chan and Johari [4]. The dielectric constant passes continously the freezing point, a typical result for polar plastic crystals. The results for the static permittivity are listed in Table 2.

From the static permittivity we may derive the Onsager dipole moment. Its deviation from the moment in the gas phase can be expressed in terms of the Kirkwood-g-factor, using simplified assumptions as described previously [20]. At atmospheric pressure and room temperature $g \approx 3$, which is a typical result for alcohols indicating a preferred parallel correlation. The density dependence of the g-factor can not be discussed because extended P, V, T data are not known for neopentanol. Despite the limitations of the Kirkwood-Fröhlich theory the Kirkwood-g-factor remains a useful quantity to characterize orientational disorder in solid phases (21).

3.4 Dielectric Relaxation

Due to its hydrogen-bonded structure neopentanol reveals a dielectric absorption at comparatively low frequencies. Several functions are proposed for fitting the loss curves [22]. A detailed comparison of the fitting procedures has been given recently [9, 11]. We use the Jonscher equation [23] (with A, ω_p, m, and n as adjustable parameters, $\omega = 2\pi f$),

$$\varepsilon'' = \frac{A}{(\omega/\omega_p)^{-m} + (\omega/\omega_p)^{1-n}}, \tag{1}$$

to calculate the frequency of maximum loss, and hence the relaxation time $\tau = 1/\omega_{max}$. Also the Havriliak-Negami equation (HN) contains four adjustable parameters (ε_∞, α, β, and τ_0):

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon - \varepsilon_\infty}{(1 + (i\omega\tau_0)^{1-\alpha})^\beta}. \tag{2}$$

HN is preferred for an estimation of the high frequency permittivity, resulting in $\varepsilon_\infty \approx 3$, which is somewhat smaller than for other alcohols [11].

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Table 2. Static permittivity of Neopentanol. The solid lines in the right upper part of the Table separate the phases solid I and I′. The values below the solid lines in the left part concern the supercooled region of solid I.

p/MPa	T/K													
	238	243	248	253	258	263	268	273	278	283	288	293	298	303
0.1	24.71	23.98	23.25	22.51	21.78	21.05	20.32	19.59	18.71	17.84	16.98	16.12	15.25	14.39
10	24.83	24.10	23.36	22.63	21.90	21.17	20.44	19.71	18.98	18.01	17.18	16.30	15.44	14.59
20	24.95	24.21	23.48	22.75	22.01	21.28	20.56	19.83	19.11	18.17	17.37	16.52	15.63	14.79
30	25.07	24.33	23.59	22.86	22.13	21.40	20.68	19.95	19.23	18.49	17.59	16.71	15.83	14.99
40	25.19	24.45	23.71	22.98	22.24	21.52	20.79	20.07	19.36	18.65	17.86	16.96	16.05	15.19
50	25.32	24.57	23.83	23.09	22.36	21.63	20.91	20.19	19.48	18.78	18.08	17.18	16.24	15.40
60	25.44	24.69	23.94	23.21	22.47	21.75	21.03	20.32	19.61	18.91	18.21	17.37	16.44	15.60
70	25.56	24.81	24.06	23.32	22.59	21.86	21.15	20.44	19.73	19.04	18.35	17.57	16.63	15.79
80	–	24.92	24.18	23.44	22.70	21.98	21.27	20.56	19.86	19.17	18.48	17.73	16.83	15.99
90	–	25.04	24.29	23.55	22.82	22.10	21.38	20.68	19.98	19.30	18.62	17.95	17.07	16.19
100	–	25.14	24.41	23.67	22.93	22.21	21.50	20.80	20.11	19.43	18.76	18.10	17.28	16.40
110	–	–	24.52	23.78	23.05	22.33	21.62	20.92	20.23	19.56	18.89	18.24	17.49	16.60
120	–	–	24.64	23.90	23.16	22.44	21.74	21.04	20.36	19.69	19.03	18.38	17.75	16.80
130	–	–	24.76	24.01	23.28	22.56	21.85	21.16	20.48	19.82	19.16	18.52	17.90	17.01
140	–	–	–	24.13	23.39	22.68	21.97	21.28	20.61	19.95	19.30	18.67	18.05	17.22
150	–	–	–	24.24	23.51	22.79	22.09	21.40	20.73	20.08	19.44	18.81	18.20	17.59
160	–	–	–	24.36	23.62	22.91	22.21	21.53	20.86	20.21	19.57	18.95	18.35	17.76
170	–	–	–	–	23.74	23.02	22.33	21.65	20.98	20.34	19.71	19.10	18.50	17.92
180	–	–	–	–	23.85	23.14	22.44	21.77	21.11	20.47	19.84	19.24	18.65	18.08
190	–	–	–	–	23.97	23.26	22.56	21.89	21.23	20.60	19.98	19.38	18.80	18.25
200	–	–	–	–	–	23.37	22.68	22.01	21.36	20.73	20.12	19.53	18.95	18.41
210	–	–	–	–	–	23.49	22.80	22.13	21.48	20.86	20.25	19.67	19.11	18.57
220	–	–	–	–	–	23.60	22.92	22.25	21.61	20.99	20.39	19.81	19.26	18.73
230	–	–	–	–	–	–	23.03	22.37	21.73	21.12	20.52	19.95	19.41	18.89
240	–	–	–	–	–	–	23.15	22.49	21.86	21.25	20.66	20.10	19.56	19.05
250	–	–	–	–	–	–	23.27	22.61	21.98	21.38	20.80	20.24	19.71	19.21

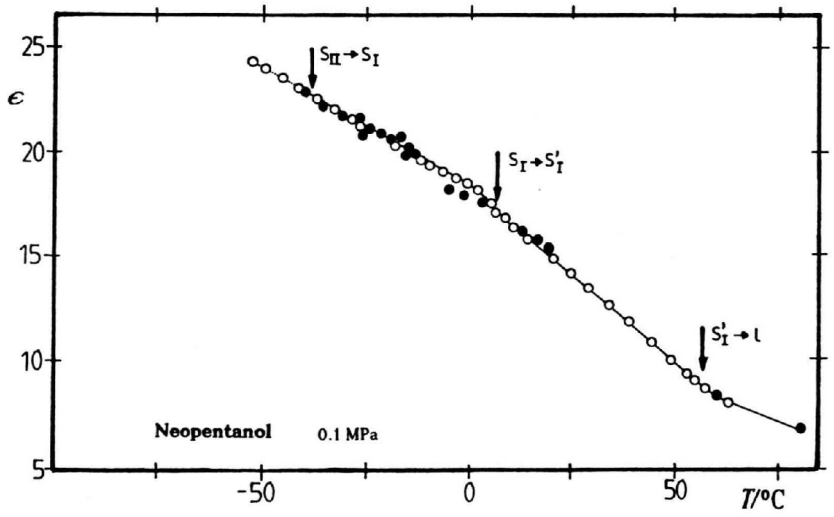

Fig. 5. Static permittivity of neopentanol as a function of temperature at atmospheric pressure. o = this work [8], ● = Ref. [4].

Detailed results for the Jonscher parameters m and n are listed in Table 3. The exponent m is very close to unity, corresponding to $\alpha = 0$ of the Havriliak-Negami fit. This result follows from the relations [24]

$$m = 1 - \alpha, \quad 1 - n = \beta(1 - \alpha).$$

Consequently, the dielectric relaxation is fairly well represented by the Cole-Davidson equation that is often used to describe the dielectric behaviour of other alcohols [9].

The Jonscher equation is related to the Dissado-Hill theory [25], in which the parameters m and n are

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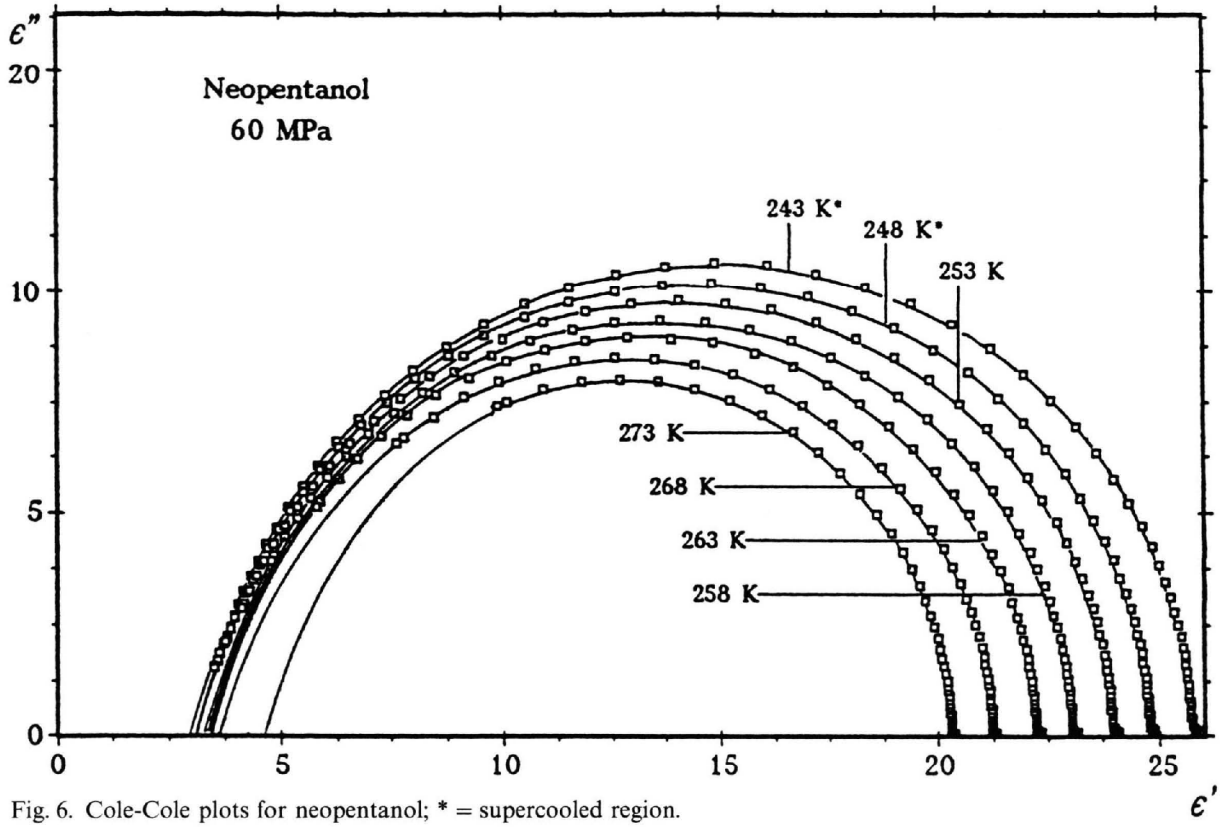

Fig. 6. Cole-Cole plots for neopentanol; * = supercooled region.

Table 3. Jonscher parameters m and $1-n$ for Neopentanol in the Solid I phase.

m	p/MPa					
T/K	0.1	30	60	90	120	150
243	0.973	0.980				
248	0.985	0.984	0.979			
253	0.978	0.992	0.990	0.987		
258	0.988	0.991	0.987	0.979		
263	0.995	0.987	0.987	0.981	0.975	
268	0.990	0.989	0.993	0.984	0.987	0.971
273	1.020	0.997	0.993	0.997	0.989	0.993
278	–	1.001	0.999	1.004	0.999	1.003
283	–	–	–	1.012	1.077	1.097
$1-n$	p/MPa					
T/K	0.1	30	60	90	120	150
243	0.799	0.849				
248	0.868	0.855	0.829			
253	0.899	0.874	0.856	0.851		
258	0.906	0.881	0.907	0.857		
263	0.975	0.923	0.915	0.870	0.868	
268	1.002	0.995	0.923	0.883	0.875	0.877
273	1.231	1.094	0.997	0.964	0.923	0.918
278	–	1.162	1.010	0.996	0.989	1.000
283	–	–	–	1.001	0.992	1.041

claimed to have physical significance. The exponent m describes the slope of the loss function in the low frequency region and is a measure of the exchange between neighbouring clusters. The closer m is to unity, the broader is the distribution of the form and size of local cluster structures, and the most probable cluster structure has little preferred orientation [26]. On the other hand, large values for the Kirkwood-g-factor should indicate specific correlations within a highly ordered local structure [27]. The parameter n is related to the slope of the loss curve in the high frequency limit and describes intracluster vibrations. Increasing values of n signify an increasing order of the local structure. Such tendencies are found for neopentanol with increasing pressure or decreasing temperature, in accordance with results previously found in related compounds [9, 28].

The dielectric relaxation of neopentanol is much more Debye-like than that of cyclic alcohols or supercooled liquids. Some Cole-Cole plots are shown in Figure 6; they correspond to fairly close semi-circles. This has also been found recently for neohexanol, which exhibits several ODIC phases and metastable

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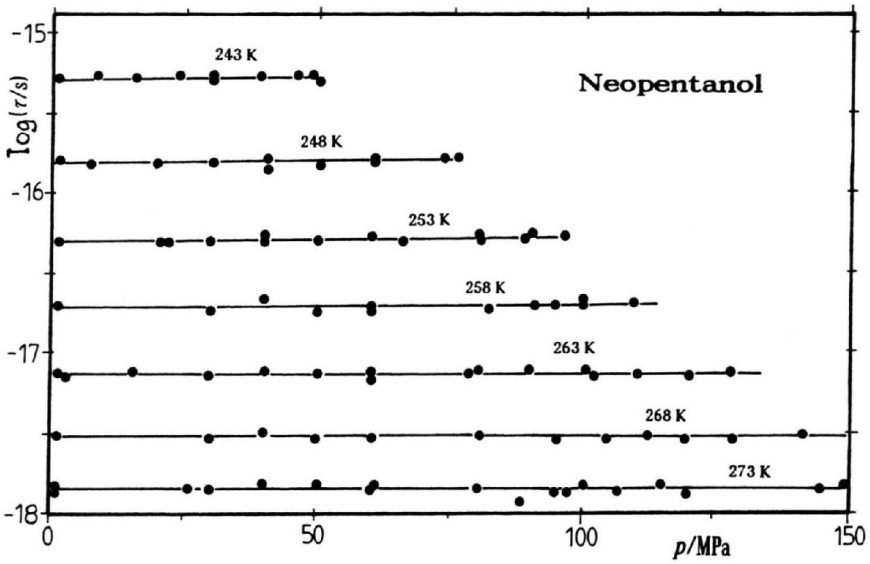

Fig. 7. Dielectric relaxation time for neopentanol as a function of pressure for different temperatures.

Table 4. Activation enthalpies and volumes for neopentanol in the solid I phase.

p / MPa	$\Delta H^{\#}$ / kJ/mol	T / K	$\Delta V^{\#}$ / cm³/mol
0.1	46.9	243	1.73
30	47.5	248	3.17
50	46.9	253	1.52
80	48.6	258	1.37
100	48.9	263	1.74
120	49.6	268	1.82
150	49.8	273	1.70
160	49.9	278	1.78

solid states [29]. Nevertheless, deviations from an exact Debye behaviour are visible as presented by the Jonscher parameters (Table 3). The dielectric behaviour of branched and cyclic alcohols is certainly modified by the various motions caused by the flexible parts of the molecules [9].

3.5 Relaxation Time and Activation Parameters

Relaxation times are calculated from the frequency of maximum loss and plotted in Fig. 7 as a function of pressure for different temperatures. The temperature and pressure dependences of the relaxation times allow to calculate the (Arrhenius) activation enthalpy ($\Delta H^{\#}$) and activation volume ($\Delta V^{\#}$), respectively.

$$\Delta H^{\#} = R\left(\frac{\partial \ln \tau}{\partial (1/T)}\right)_p, \tag{3}$$

$$\Delta V^{\#} = RT\left(\frac{\partial \ln \tau}{\partial p}\right)_T, \tag{4}$$

In Table 4 activation parameters are compiled. There is only a very small increase of the activation enthalpies with pressure, whereas the activation volumes are practically independent of the temperature. This is also visible from Fig. 7, which shows essentially parallel lines of $\log \tau$ against p. For other alcohols, such as cyclopentanol [30], a much more pronounced pressure dependence of the activation enthalpy has been found. The relatively high activation enthalpies agree with results in other hydrogen-bonded plastic crystals [9, 11, 20, 29], whereas the values for $\Delta V^{\#}$ are unusually small. This is probably due to the fact that the globular shape of neopentanol requires much less extra space for a reorientation compared with other alcohols, whose shapes are less spherical.

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