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Dielectric Measurements at High Pressures and Low Ternperatures V. Dielectric and pVT data of t-Butylchloride

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Dielectric Measurements at High Pressures and Low Temperatures
V. Dielectric and pVT data of *t*-Butylchloride

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The static permittivity ϵ and pVT data of liquid and solid *t*-butylchloride (2-chloro-2methylpropane) have been determined as a function of temperature (233–313 K) and pressure (up to 3 kbar). From these data the Kirkwood correlation factor *g* has been calculated. The *g*-factor is somewhat larger than unity and decreases with increasing pressure and decreasing temperature. Furthermore, a recently found high-pressure induced solid phase transition has been confirmed and extended to higher temperatures and pressures.

1. INTRODUCTION

t-butylchloride (TBC) is a typical globular plastic crystal that has been thoroughly studied e.g. by dielectric measurements,[1] neutron scattering,[2] and differential scanning calorimetry.[3] There are three different solid phases at atmospheric pressure, denoted as solid I, II, and III on decreasing temperature. It might be interesting to compare the thermodynamic properties with *t*-butyl-bromide (TBB). Both substances have the same number of phase transitions at 1 atm. However, TBC has a much larger entropy change at the solid I/II transition (25.8 $J \cdot mol^{-1} K^{-1}$) than TBB (4.6), whereas TBB has a much larger one at the II/III transition (27.2) than TBC (10.2). This different behaviour is also reflected in dielectric measurements of Urban *et al.*,[1] according to which the large drop of the permittivity occurs at that transition where also the large entropy change is observed. This means, in the case of TBB there are two plastic phases, whereas TBC has only one at 1 atm, although TBC possesses a higher degree of globularity.[1] However, the DSC study of Wenzel *et al.*[3] suggest the existence of a second plastic phase (denoted as solid IV) at elevated pressures. It was the aim of the present work to extend the high pressure investigations with the aid of dielectric[4] and pVT measurements.[5]

2. EXPERIMENTAL

Details of the high pressure equipment used for the dielectric[6] and pVT measurements[7] have been described elsewhere. Commercially available TBC (Fluka AG, Buchs, Switzerland) was analyzed by gas chromatography, according to which the purity was 99.8%; it was therefore used without further purification.

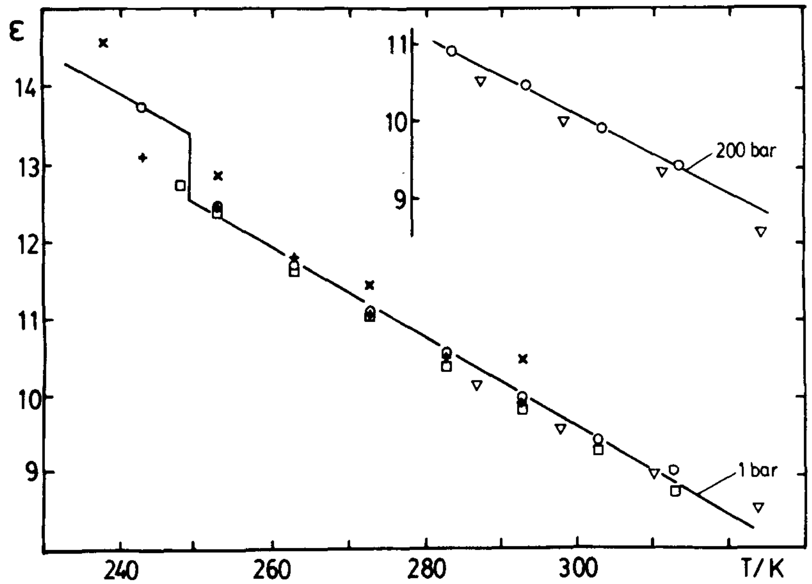

FIGURE 1 Permittivity of t-butylchloride in comparison with literature data ▽ ref. 8, × ref. 9, □ ref. 10, + ref. 11, ○ this work.

Most of the measurements have been performed isothermally, starting at the highest pressure attainable and then releasing the pressure step by step at constant temperature.

3. RESULTS

3.1 Static dielectric constant

Values for the permittivity are shown in the Figures 1 and 2 and summarized in Table I. There is good agreement with atmospheric pressure data from literature (Figure 1), whilst high pressure data (> 200 bar) are not available for comparison. Figure 2 represents the

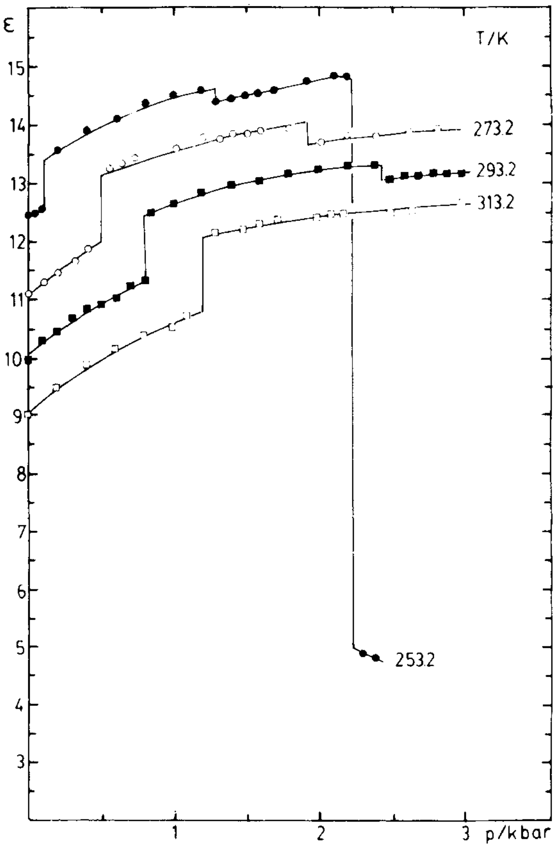

FIGURE 2 Permittivity of *t*-butylchloride as a function of temperature and pressure.

TABLE I

Permittivity of *t*-butylchloride, lines separate different phase transitions

	T/K							
p/bar	313	303	293	283	273	263	253	243
1	9.02	9.42	9.98	10.55	11.09	11.70	12.44	13.71
100	9.24	9.75	10.30	10.74	11.34	11.89	13.38	13.88
200	9.45	9.92	10.48	10.92	11.55	12.03	13.56	14.03
300	9.65	10.08	10.65	11.09	11.72	13.07	13.72	14.17
400	9.85	10.24	10.81	11.24	11.86	13.27	13.87	14.30
500	9.99	10.40	10.95	11.37	13.21	13.45	14.01	14.41
600	10.14	10.56	11.09	11.49	13.27	13.61	14.13	14.52
700	10.27	10.72	11.22	12.93	13.34	13.77	14.24	14.62
800	10.39	10.87	11.33	13.00	13.40	13.90	14.33	14.71
900	10.49	11.02	12.56	13.07	13.46	14.03	14.41	14.78
1000	10.57	11.17	12.64	13.14	13.52	14.14	14.48	14.85
1100	10.64	12.33	12.72	13.20	13.58	14.23	14.53	14.47
1200	10.70	12.38	12.80	13.26	13.65	14.31	14.56	14.52
1300	12.11	12.44	12.87	13.32	13.71	14.38	14.59	14.57
1400	12.15	12.50	12.93	13.38	13.77	14.43	14.41	14.62
1500	12.20	12.55	12.99	13.42	13.83	14.47	14.48	14.67
1600	12.24	12.60	13.05	13.47	13.89	14.50	14.54	5.33
1700	12.28	12.64	13.10	13.51	13.96	14.24	14.60	
1800	12.31	12.69	13.14	13.55	14.02	14.25	14.65	
1900	12.35	12.73	13.18	13.59	14.08	14.26	14.70	
2000	12.38	12.77	13.21	13.62	13.72	14.27	14.75	
2100	12.41	12.80	13.24	13.65	13.77	14.28	14.79	
2200	12.44	12.84	13.26	13.67	13.81	14.29	14.83	
2300	12.47	12.87	13.27	13.45	13.84	14.29	4.36	
2400	12.49	12.90	13.28	13.45	13.88	14.30		
2500	12.51	12.93	13.07	13.45	13.90	14.31		
2600	12.53	12.95	13.09	13.45	13.92	14.32		
2700	12.55	12.97	13.11		13.94	14.32		
2800	12.57	12.72	13.13		13.95	14.33		
2900	12.58	12.75	13.15		13.95	14.33		
3000	12.59	12.78	13.17		13.95			

pressure dependence of the permittivity at different constant temperatures. There is a small break at elevated pressures, due to the solid I–solid IV phase transition, where some part of the reorientational freedom must be frozen in. Obviously there exist two plastic phases at elevated pressures but only one at atmospheric pressure.

3.2 pVT data

Liquid specific volume data have been fitted with the Tait equation: $V_0 - V/V_0 = C \cdot \ln(B + p/B + p_0)$, yielding $B = 560$ bar and $C =$

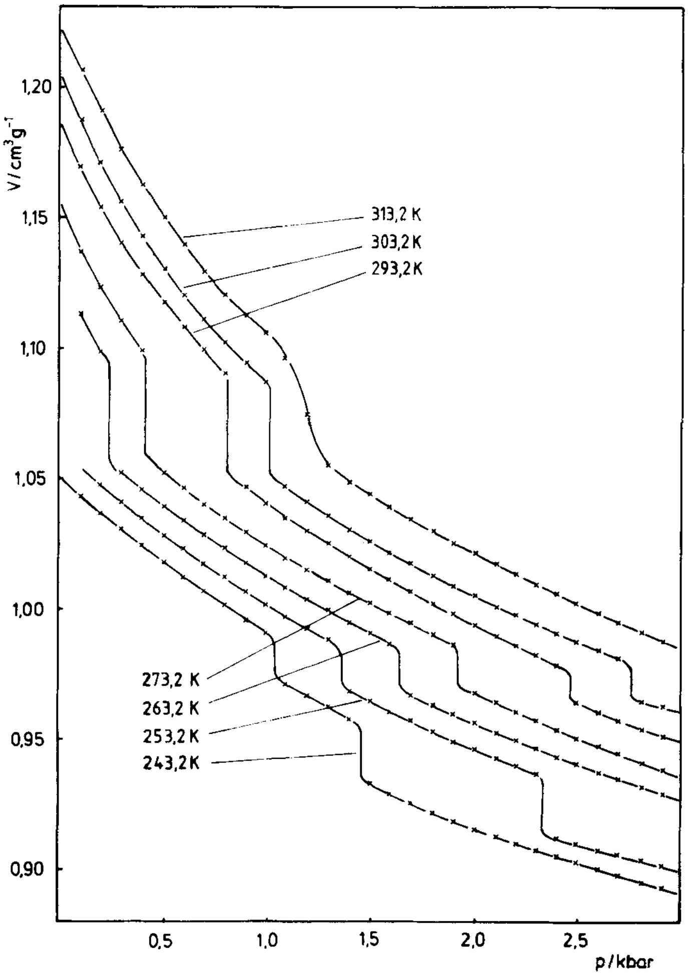

FIGURE 3 Specific volumes of *t*-butylchloride as a function of temperature and pressure.

TABLE II

Specific volumes, v/cm^3 g^{-1}, of *t*-butylchloride

	T/*K*						
p/bar	313.2	303.2	293.2	273.2	263.2	253.2	243.2
1	1.2225	1.2047	1.1872	1.1576			1.0511
100	1.2059	1.1871	1.1693	1.1373	1.1134	1.0540	1.0437
200	1.1902	1.1709	1.1538	1.1231	1.0983	1.0469	1.0357
300	1.1757	1.1562	1.1404	1.1102	1.0521	1.0410	1.0307
400	1.1623	1.1429	1.1286	1.0991	1.0463	1.0353	1.0250
500	1.1499	1.1309	1.1182	1.0526	1.0399	1.0288	1.0185
600	1.1388	1.1201	1.1086	1.0459	1.0328	1.0217	1.0113
700	1.1287	1.1104	1.0994	1.0397	1.0273	1.0161	1.0059
800	1.1197	1.1017	1.0902	1.0341	1.0227	1.0115	1.0013
900	1.1118	1.0940	1.0463	1.0288	1.0174	1.0063	0.9961
1000	1.1051	1.0871	1.0402	1.0236	1.0122	1.0012	0.9909
1100	1.0957	1.0468	1.0346	1.0190	1.0076	0.9964	0.9707
1200	1.0743	1.0412	1.0291	1.0146	1.0032	0.9921	0.9964
1300	1.0542	1.0358	1.0240	1.0104	0.9990	0.9880	0.9622
1400	1.0483	1.0307	1.0196	1.0063	0.9949	0.9684	0.9579
1500	1.0435	1.0259	1.0148	1.0023	0.9909	0.9646	0.9323
1600	1.0387	1.0213	1.0105	0.9982	0.9869	0.9607	0.9289
1700	1.0341	1.0169	1.0065	0.9942	0.9668	0.9568	0.9256
1800	1.0295	1.0128	1.0027	0.9900	0.9628	0.9532	0.9223
1900	1.0251	1.0088	0.9990	0.9856	0.9594	0.9495	0.9193
2000	1.0210	1.0050	0.9934	0.9676	0.9562	0.9461	0.9166
2100	1.0167	1.0013	0.9896	0.9640	0.9526	0.9429	0.9147
2200	1.0127	0.9977	0.9858	0.9604	0.9490	0.9394	0.9110
2300	1.0088	0.9942	0.9821	0.9568	0.9454	0.9363	0.9081
2400	1.0050	0.9908	0.9789	0.9533	0.9422	0.9119	0.9058
2500	1.0014	0.9875	0.9638	0.9499	0.9394	0.9097	0.9032
2600	0.9979	0.9842	0.9603	0.9466	0.9368	0.9075	0.9007
2700	0.9945	0.9808	0.9570	0.9435	0.9341	0.9053	0.8980
2800	0.9912	0.9648	0.9539	0.9406	0.9314	0.9033	0.8945
2900	0.9881	0.9625	0.9510	0.9379	0.9282	0.9009	0.8909
3000	0.9851	0.9606	0.9484	0.9355	0.9265	0.8989	0.8874

0,095 at 300 K. The specific volumes for the liquid and solid phases of TBC are plotted in Figure 3 and summarized in Table II. The steps in the isotherms correspond to the volume changes accompanying the phase transitions. The pressure dependence of these transitions is shown in Figure 4 in comparison with results from dielectric, DTA,[12] and DSC measurements. On the whole there is good agreement, however, a somewhat different slope has been found for the recently detected pressure-induced solid I–IV transition.

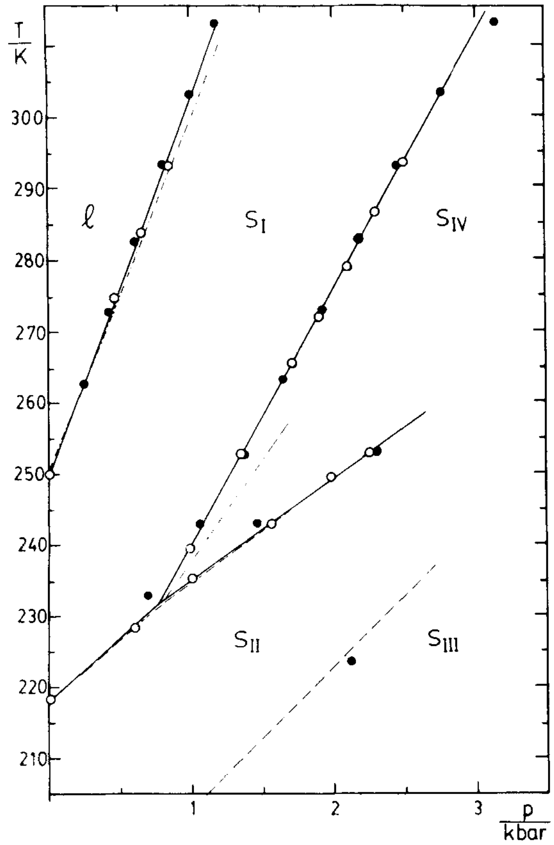

FIGURE 4 Phase diagram of *t*-butylchloride - - ref. 3, ----- ref. 12, ○ ref. 4, ● ref. 5.

4. DISCUSSION

4.1 Thermodynamic properties

The volume changes which have been determined as the discontinuities in the $v(p)$-plot are converted to enthalpy changes using the equation of Clausius Clapeyron. The thermodynamic data are collected in Table III including also data of TBB. Regarding the sequences of the solid phases, the high pressure modification IV of TBC should be related to solid II of TBB and correspondingly solid II of TBC to solid III of TBB. Indeed the thermodynamic (and also the dielectric) changes at the phase transitions correspond much better in this sense. The rather low changes associated with the melting and the

TABLE III

Thermodynamic properties of TBB and TBC at the phase transitions

Substance	Transition	$\frac{\text{Pressure}}{\text{bar}}$	$\frac{T}{K}$	$\frac{\Delta S}{\text{J mol}^{-1}\text{ K}^{-1}}$	$\frac{\Delta V}{\text{cm}^3\text{ mol}^{-1}}$	Author
TBB	melting	1	256.2	7.53		1
	solid II/I	1	231.5	4.60		1
	III/II	1	208.7	27.2		1
TBC	melting	1	248.4	8.0		1
		500	276.3	7.96	4.2	5
		1000	302.6	6.28	3.4	5
	solid II/I	1	219.4	25.8		1
		500	226	23.5		3
	IV/I	1000	240	4.7	1.7	5
			239	4.2		3
		2000	276	3.8	1.45	5
	II/IV	1000	234	19.0	2.7	5
			235	17.0		3
		2000	248.6	16.1	2.2	5
	III/II	1	183.1	10.2		1
		1000	206	7.3	1.5	5
			204	10.0		3

solid I–IV transition are typical for plastic phase transitions. Furthermore a distinct decrease of the volume and entropy change of melting is observed on increasing pressure that has also been found in previous studies for other substances.[13]

4.2 Dielectric properties

The dielectric results are discussed in terms of the Kirkwood–Fröhlich–Onsager theory.[14] The Kirkwood-g-factor is calculated from the equation:

$$g = \frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)9kTM\epsilon_0}{\epsilon(\epsilon_\infty + 2)^2 N_A \rho \mu^2}.$$

M is the molecular mass, ρ the density,[5] N_A Avogadro's constant, k Boltzmann's constant, $\epsilon_0 = 8.854 \cdot 10^{-12}$ C^2 J^{-1} m^{-1}, $\mu = 7,14 \cdot 10^{-30}$ Cm, $\epsilon_\infty = 2{,}016$ at 293 K and 1 bar, T the temperature. The Lorenz–Lorentz equation was used to take into account the density dependence of ϵ_∞. Details of the calculation procedure have been described in previous papers.[6,15]

Figure 5 shows the Kirkwood-g-factor as a function of temperature, pressure and density. There is a discontinuous change on freezing that

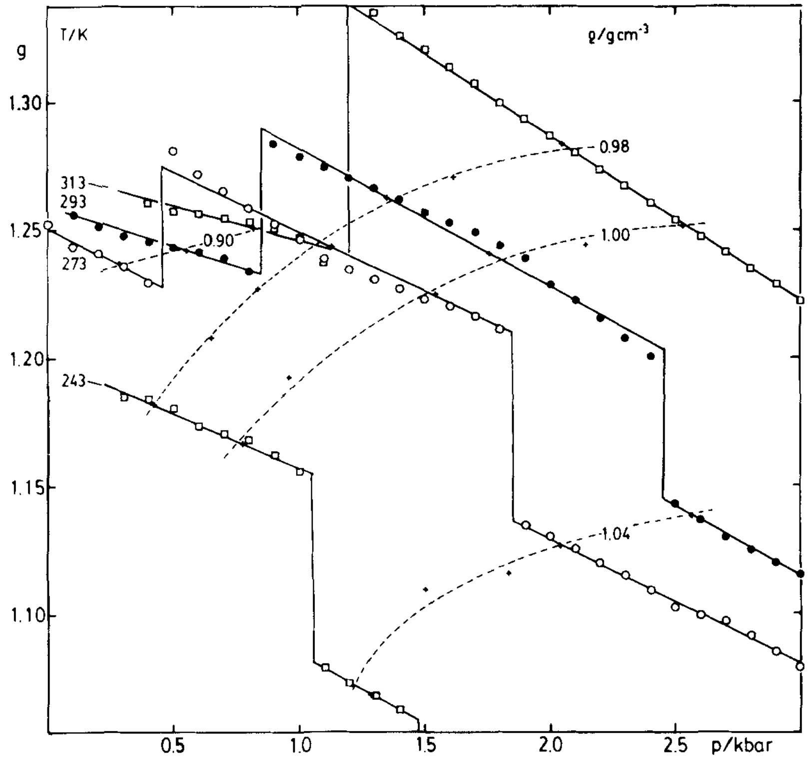

FIGURE 5 Kirkwood-*g*-factor of *t*-butylchloride as a function of temperature and pressure.

has been observed for most of the polar plastic crystals so far studied.[15] With increasing pressure the *g*-factor decreases, showing a break at the intermediate solid transition. The values in the second plastic phase (solid IV) are approaching unity and do not indicate specific dipolar interactions. However, in the case of TBB Urban found *g*-factors below 1 and a decrease of the permittivity with decreasing temperature for the second plastic phase, whereas the plastic phases of TBC show an opposite temperature dependence. Furthermore it might be interesting to discuss the density dependence of the *g*-factor. It is one of the main advantages of high pressure studies that they allow to separate the different influences of temperature and density. In the case of TBC—and similar results have also been found for cyclohexanone[15]—the *g*-factor does not seem to be sensitive to isochoric temperature changes. However, for substances with strong dipolar interactions due to hydrogen bonding—such as methanol[16]—a large temperature dependence is observed.

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