Molecular Motion in Solid Tetrabutylammonium Iodide

Barbara Szafrańska and Zdzisław Pająk
Institute of Physics, A. Mickiewicz University, Poznań, Poland

Z. Naturforsch. **42 a,** 253–257 (1987); received November 17, 1986

The temperature dependence of the ^{1}H second moment and the T_1 and $T_{1\varrho}$ spin-lattice relaxation times obtained for polycrystalline tetrabutylammonium iodide are interpreted in terms of the C_3 methyl group reorientation appearing together with cationic tumbling for which the activation parameters have been determined. IR spectra point to the existence of weak C–H...I hydrogen bonds. A structural phase transition evidenced at about 386 K is found to be related to the onset of cationic self-diffusion.

Introduction

Nuclear magnetic resonance techniques have revealed C_3 reorientation for the methyl groups and cationic tumbling for solid tetramethyl-, tetraethyl-, and tetrapropylammonium salts [1–10]. For the two last classes of compounds reorientations of the whole ethyl groups have also been discovered together with a number of phase transitions related to the onset of molecular tumbling [8–10]. Recently Köksal [9, 11] has reported ^{1}H spin-lattice relaxation data for tetra-n-butylammonium iodide TBA^+I^- between 100 and 333 K indicating C_3 reorientation for the methyl groups only. In order to obtain a more complete understanding of the molecular dynamics of this substance and to examine the existence of expected other types of motion we have measured ^{1}H second moments of the NMR line as well as spin-lattice relaxation times (T_1 and $T_{1\varrho}$) over a wider temperature range and we have given a detailed analysis of the results obtained.

Experimental

Using a home-made wide-line spectrometer operating at a Larmor frequency of 28 MHz, proton NMR spectra were recorded from 77 to 403 K. Proton spin-lattice relaxation times T_1 were measured with a pulse spectrometer operating at 25 MHz, using a saturation recovery pulse sequence, and $T_{1\varrho}$'s were measured at $H_1 = 15$ G by the spin-locking method [12]. The temperature of the sample was stabilized to within 1 K by a gas-flow cryostat. The polycrystalline sample of TBA^+I^- (Merck-Schuchardt – for synthesis) was recrystallized from anhydrous ethanol, evacuated for several hours and sealed under vacuum in a glass tube.

Results

a) Second Moment

The temperature dependence of the second moment of proton magnetic resonance lines of TBA^+I^- is shown in Figure 1. The second moment was determined with an accuracy of about 10%. The plot exhibits a decrease of the second moment M_2 in two temperature intervals: between 77 and 123 K,

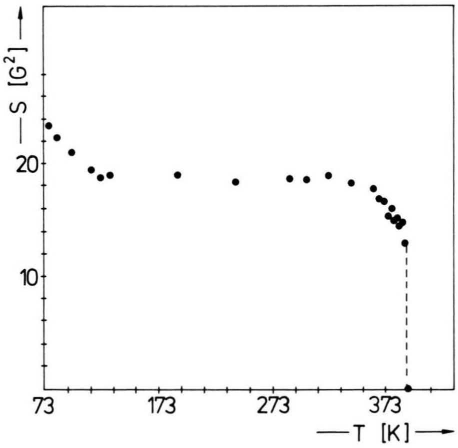

Fig. 1. The temperature dependence of the proton second moment of TBA^+I^-.

Reprint requests to Prof. Z. Pająk, Institute of Physics, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland.

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M_2 decreases from 23 to 19 G^2, then its value remains constant up to about 363 K where the next reduction starts. At 391 K M_2 changes abruptly to about 0.2 G^2. A DTA study shows a heat capacity anomaly at 383 K.

b) Spin-Lattice Relaxation Times T_1 and $T_{1\varrho}$

The temperature variation of the spin-lattice relaxation times T_1 and $T_{1\varrho}$ is shown in Fig. 2. The T_1 curve shows a minimum of 46 ms at 133 K. At about 386 K a considerable jump of T_1 takes place.

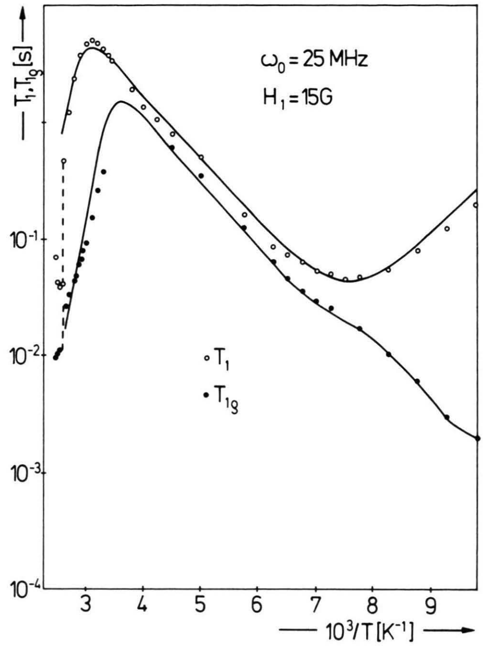

Fig. 2. The temperature variation of the spin-lattice relaxation times T_1 and $T_{1\varrho}$ of TBA^+I^-. The solid lines are calculated using motional parameters given in Table 2.

The observed decrease of $T_{1\varrho}$ with lowering temperature points to a minimum lying below the temperature range covered by our experiments. A discontinuity in the $T_{1\varrho}$ plot appears at 386 K.

Discussion

a) Second Moment

A theoretical value of the second moment for a rigid lattice structure can be calculated by Van Vleck's formula [13]. For a polycrystalline sample one obtains

$$M_2 = 358\,(1/N) \sum_{i,j} r_{ij}^{-6}, \qquad (1)$$

where N is the number of interacting spins and r_{ij} the distance between the spins.

When molecular reorientation occurs, the second moment is given by

$$M_2 = (1/4) \cdot 358 \cdot (1/N) \sum_{i,j} \frac{(1 - 3\cos^2 \gamma_{ij})^2}{\langle r_{ij}^3 \rangle^2}, \qquad (2)$$

where γ_{ij} is the angle between the interproton vector and the axis of reorientation.

The rigid lattice second moment value for tetrabutylammonium iodide can be calculated as a sum of intra- and interionic contributions. The intraionic part of M_2 for a substance containing protons in different functional groups can be calculated as [14]

$$\begin{aligned} M_{2\,\text{intra}} = (2 \cdot 4/36)\,[M_2^{\text{I}}(CH_2) &+ M_2^{\text{II}}(CH_2) \\ &+ M_2^{\text{III}}(CH_2)] \qquad (3) \\ + (3 \cdot 4/36)\, M_2(CH_3)\,. \end{aligned}$$

In this expression $M_2^{\text{I}}(CH_2)$ includes the interaction of protons of the four CH_2 groups nearest to the nitrogen atom; $M_2^{\text{II}}(CH_2)$, $M_2^{\text{III}}(CH_2)$ describe the interaction of protons attached to the second and the third carbon atoms in the butyl chain, respectively; $M_2(CH_3)$ includes the interaction of protons of the four CH_3 groups.

Since no structural data of the compound are known, $M_{2\,\text{intra}}$ was calculated assuming the nitrogen atom at the centre of a regular tetrahedron with N−C bond lengths of 1.49 Å. The angles N−C−C and H−C−H have been taken as equal to 109.47°, and the bond lengths C−C and C−H to 1.54 Å and 1.09 Å, respectively. The intraionic part of the second moment for the rigid lattice structure was found to be 26.3 G^2, neglecting the small heteronuclear contribution from nitrogen atom (~ 0.03 G^2).

The interionic part of the second moment, $M_{2\,\text{inter}}$, was estimated to be 1.0 G^2 only, like that for tetraethylammonium and tetrapropylammonium salts [10]. Thus, the total rigid lattice value of the second moment equals to at least 27.3 G^2, under the assumptions mentioned above.

Since the experimental second moment value for TBA^+I^- at liquid nitrogen temperature is lower than that calculated above, it must be assumed that certain reorientations take place at this temperature.

The calculations of the reduced second moment were performed for models with reorientations of the methyl groups, ethyl groups, and the cation around its centre of gravity. The values of the second moment obtained are given in Table 1.

Table 1. The calculated second moment [G^2].

Type of reorientation	$M_{2\,\mathrm{intra}}$	$M_{2\,\mathrm{inter}}$	$M_{2\,\mathrm{total}}$
Rigid structure	26.3	1.0	27.3
Methyl groups	20.5	0.8	21.3
Ethyl groups	15.9	0.6	16.5
Cation tumbling	0	0.6	0.6

The first decrease of M_2 to the constant value of about 19 G^2 is interpreted in terms of a motional narrowing process associated with the methyl groups reorientations about their C_3 symmetry axes, while all the CH_2 groups would remain rigid. For such reorientations M_2 is estimated to be 21 G^2 in agreement with the plateau value observed. For the interionic contributions the reducing factor 0.8 was used [15, 16].

In our previous studies on tetraethyl- and tetrapropylammonium halides it was found that, when the sample temperature is risen the methyl groups reorientation is followed by the ethyl groups reorientation and then by the cation tumbling. Therefore, calculating the second moment values we have considered these two types of motion.

For the case of superposed reorientations of the methyl and ethyl groups the calculations performed (adopting the procedure as in [10]) give M_2 reduced to 16 G^2. However, in our experiment no plateau of this value is observed. The steady decrease of the second moment from 19 to about 13 G^2 is interrupted by the phase transiton at 391 K. Thus it seems reasonable to ascribe the motional narrowing process observed to the cation reorientation around its centre of gravity. Using the Waugh-Fiedin expression [17], the activation energy for the motion considered was found to be about 54.5 kJ/mol. The reduced value of the second moment for such reorientations would be about 1 G^2 [18]. It is not observed below the phase transition, which indicates that overall molecular motion taking place is still not frequent enough to average the intraionic dipolar fields to zero. Above the phase transition, the observed M_2 value of 0.2 G^2 can be interpreted as a result of self-diffusion of the cation, the linewidth being determined by the magnetic field inhomogeneity only.

b) Spin-Lattice Relaxation Times

The analysis of the second moment data indicates that the low temperature T_1 minimum can be associated with the methyl group reorientation. The high temperature behaviour of T_1 and $T_{1\varrho}$ points clearly to the existence of another motional mechanism dominating relaxation. Since the relaxation dependences undergo a discontinuity before reaching the second minimum, it is not possible to obtain unambiguous information on the nature of this mechanism. It might consist in ethyl group reorientation or in cation tumbling. The last motion seems to be favoured by the second moment analysis.

The relaxation rate of the nuclei from different molecular groups CH_3 and CH_2 for the structure with superposed reorientations of the methyl and ethyl groups can be expressed as [19]

$$1/T_1 = (12/36)\,(1/T_1)^{CH_3} + (8/36)\,(1/T_1)^{CH_2}, \tag{4}$$

for the structure with the reorientations of the methyl groups and cation reorientation around its centre of gravity as

$$1/T_1 = (12/36)\,(1/T_1)^{CH_3} + (24/36)\,(1/T_1)^{CH_2}. \tag{5}$$

The relaxation rates $(1/T_1)^{CH_3}$ and $(1/T_1)^{CH_2}$ were calculated using the formula of Dunn and McDowell [20]

$$1/T_1 = (9/80)\,(\gamma^4 \hbar^2/r^6) \cdot [A f(\tau_{c1}) + B f(\tau_{c3}) + C f(\tau_{c4}) + D f(\tau_{c5})], \tag{6}$$

where r is the distance between protons in CH_3 and CH_2 groups, τ_{c1} is the correlation time for the isotropic reorientation of the whole cation, τ_{c2} the correlation time for the ethyl group reorientation around the $C_{II}-C_{III}$ bond and τ_c the correlation time for the methyl group reorientation around its three-fold symmetry axis:

$$1/\tau_{c3} = 1/\tau_{c1} + 1/\tau_c, \quad 1/\tau_{c4} = 1/\tau_{c1} + 1/\tau_{c2},$$

$$1/\tau_{c5} = 1/\tau_{c1} + 1/\tau_c + 1/\tau_{c2},$$

$$A = (1/3)\,(1 - 3\cos^2\delta)^2, \quad B = (3/2)\sin^4\delta,$$

$$C = \sin^2 2\delta + \sin^4\delta, \quad D = (1/2)\,(8 - 3\sin^4\delta).$$

δ is the angle between the $C_{II}-C_{III}$ and $C_{III}-C_{IV}$ bonds,

$$f(\tau_{ci}) = \tau_{ci}/(1 + \omega_0^2\,\tau_{ci}^2) + 4\tau_{ci}/(1 + 4\omega_0^2\,\tau_{ci}^2). \tag{7}$$

Table 2. The best fitted parameters τ_{0i} and $E_{\mathrm{A}i}$.

	Methyl groups reorientation		Ethyl groups reorientation		Cation tumbling	
	τ_0 [s]	E_{A} $\left[\frac{\mathrm{kcal}}{\mathrm{mol}}\right]$	τ_0 [s]	E_{A} $\left[\frac{\mathrm{kcal}}{\mathrm{mol}}\right]$	τ_0 [s]	E_{A} $\left[\frac{\mathrm{kcal}}{\mathrm{mol}}\right]$
T_1:	$3.25 \cdot 10^{-13}$	2.5	$5.21 \cdot 10^{-15}$	12.9	$1.42 \cdot 10^{-14}$	13.1
$T_{1\varrho}$:	$3.50 \cdot 10^{-13}$	2.6	$3.17 \cdot 10^{-12}$	12.6	$6.40 \cdot 10^{-12}$	13.0

Using $r = 1.7976$ Å, $\delta = 109.47°$ and inserting (6) into (4) and (5) we obtained

$$1/T_1 = 7.50 \cdot 10^8 f(\tau_\mathrm{c}) + 15.95 \cdot 10^8 f(\tau_{\mathrm{c}2}) + 17.82 \cdot 10^8 f(\tau_\mathrm{c}, \tau_{\mathrm{c}2}), \quad (8)$$

$$1/T_1 = 5.96 \cdot 10^9 f(\tau_{\mathrm{c}1}) + 2.53 \cdot 10^9 f(\tau_\mathrm{c}, \tau_{\mathrm{c}1}) \quad (9)$$

for the reorientations of methyl and ethyl groups and for the reorientations of methyl groups and cation reorientation around its centre of gravity, respectively. Equations (8) and (9) can be applied to describe $T_{1\varrho}$ with different functions $f_\varrho(\tau_{\mathrm{c}i})$ only:

$$f_\varrho(\tau_{\mathrm{c}i}) = (3/2)\, \tau_{\mathrm{c}i}/(1 + \omega_1^2 \tau_{\mathrm{c}i}^2) + (5/2)\, \tau_{\mathrm{c}i}/(1 + \omega_0^2 \tau_{\mathrm{c}i}^2) + \tau_{\mathrm{c}i}/(1 + 4\omega_0^2 \tau_{\mathrm{c}i}^2), \quad (10)$$

where $\omega_1 = \gamma H_1$ ($H_1 = 15$ G) and $\tau_{\mathrm{c}i}$ are described by the Arrhenius equation

$$\tau_{\mathrm{c}i} = \tau_{0i} \exp(E_{\mathrm{A}i}/RT), \quad (11)$$

where τ_{0i} is an inverse frequency factor and $E_{\mathrm{A}i}$ is the activation energy. The best fitted parameters τ_{0i} and $E_{\mathrm{A}i}$ for the structure with reorienting methyl and ethyl groups and for the structure with reorienting methyl groups together with superposed cation reorientations are listed in Table 2. The fittings for T_1 and $T_{1\varrho}$ shown by solid lines in Fig. 2 for both alternatives are not distinguishable.

We can thus conclude that besides the C_3 reorientation of the methyl groups another type of molecular reorientation takes place yet below 391 K. Taking into account the performed analysis of the second moment we interpret the observed diminishing of T_1 and $T_{1\varrho}$ at higher temperature as an evidence for the onset of cationic tumbling with the activation energy of about 54.5 kJ/mol.

Our results concerning C_3 reorientation of the methyl groups are in agreement with the data published by Köksal [9, 11]. The calculated value of $(T_1)_{\mathrm{min}}$ for CH_3 groups reorientation about their C_3 axes is 44 ms, which agrees well with the experimentally observed value. The $(T_{1\varrho})_{\mathrm{min}}$ value calculated for such reorientation ($H_1 = 15$ G) equals to 422 µs and would lie below the temperature range covered by our experiment. Above the phase transition point the temperature dependences of T_1 and $T_{1\varrho}$ are evidently influenced by two different mechanisms of reorientation, since T_1 increases while $T_{1\varrho}$ decreases with the rise of temperature. $T_{1\varrho}$ seems to reflect a slow self-diffusion process, leading to a small value of the second moment ($M_2 = 0.2\ \mathrm{G}^2$) observed, whereas T_1 is dominated by faster isotropic cation reorientation, starting below the phase transition.

Summarizing, we would like to emphasize the similarity of the molecular dynamics observed for tetramethyl-, tetraethyl- and tetrapropylammonium salts as well as for tetrabutylammonium iodide under study: the C_3 methyl group reorientation is followed by cationic tumbling at higher temperatures. However, the ethyl group reorientation observed for tetraethyl- and tetrapropylammonium salts is not revealed for tetrabutylammonium iodide. The phase transition, evidenced for tetrabutylammonium iodide, is related with the onset of cationic self-diffusion.

It is interesting to note that tetrabutylammonium iodide is not a purely ionic crystal. Our complementary IR study has proved that weak hydrogen bonds of the type C−H...I are essential for the crystal structure.

The evidence for hydrogen bonds in tetramethylammonium halides has been reported [21]. It can be argued that weak hydrogen bonds exist also in tetraethyl- and tetrapropylammonium halides.

The hydrogen-bond contribution to the barrier for the cation reorientation has been estimated for guanidinium salts [22]. It would be interesting to estimate it for tetraalkylammonium halides too, and therefore further tetrabutylammonium salts are under study.

Acknowledgements

The present work has been supported by the Polish Academy of Sciences under project CPBP 01.12. The authors are grateful to Dr. E. Szcześniak for his assistance in performing numerical calculations.

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