Molecular Motion in Solid Tetraethyl- and Tetrabutylammonium Perchlorates

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The proton NMR second moment and spin-lattice relaxation time for polycrystalline tetraethyl- and tetrabutylammonium perchlorates have been measured over a wide range of temperatures. Solid-solid phase transitions related to the onset of cation tumbling were found for both compounds and confirmed by DSC. In the low temperature phases methyl-group reorientation was evidenced. For tetrabutylammonium cation a dynamic nonequivalence of one methyl group is found. The geared motion of the alkyl chains related with the onset of successive CH_2-group reorientations is suggested.

Key words: NMR, Molecular motions, Phase transitions.

Introduction

In our NMR studies of the molecular dynamics of symmetrical tetraalkylammonium cations embedded in different anion sublattices we have analysed various types of reorientation in relation to solid-solid phase transitions. For all investigated tetraethyl-, tetrapropyl- and tetrabutylammonium halides we have revealed C_3-reorientation of the methyl groups. The discovered solid-solid phase transitions appeared to be connected with the onset of whole cation tumbling [1–4]. We have also found that besides the mentioned reorientations, there are additional motions inside alkyl chains in spite of existing strong structural hindrances. In tetrabutylammonium tetrafluoroborate we have disclosed a dynamical nonequivalence of one methyl group [5].

The present study of tetraethyl- and tetrabutylammonium perchlorates was undertaken in order to analyse and compare the expected complex motions of smaller and bigger cations interacting with similar anion sublattices.

Experimental

The polycrystalline samples of tetraethyl- and tetrabutylammonium perchlorate (TEA ClO_4 and TBA ClO_4) (purum, Fluka AG) were recrystallized from anhydrous ethanol, evacuated for several hours and then sealed under vacuum in glass ampoules. Using a home-made wide-line spectrometer operating at a Larmor frequency of 28 MHz, proton NMR spectra were recorded from 110 to 480 K. The second moments were calculated by numerical integration of the spectra and corrected for the finite modulated field [6]. The accuracy was of about 10%. Proton spin-lattice relaxation times T_1 were measured at 60 MHz as a function of temperature using our home-made spectrometer with a saturation recovery pulse sequence. The temperature of the samples was controlled by means of a gas-flow cryostat and monitored to an accuracy of 1 K. Differential thermal analysis was made with a Derivatograph Unipan (typ DSC 605 M).

Results

a) *Second Moment*

Figure 1 shows the temperature dependences of the second moment M_2 of the ^1H NMR absorption line for both substances. For TEA ClO_4 the second moment between 110 and 270 K is about 15.0 G^2, and then it decreases to 0.5 G^2 at about 380 K, and this value remains constant up to 480 K. For TBA ClO_4 the second moment decreases from 18.2 G^2 at 133 K to 5.8 G^2 at 328 K. Above this temperature it jumps to about 0.6 G^2 and remains constant at higher temperatures.

DSC studies show heat capacity anomalies at 372 K for TEA ClO_4 (above 550 K the compound decomposes) and 333 K for TBA ClO_4 (melting point 484 K).

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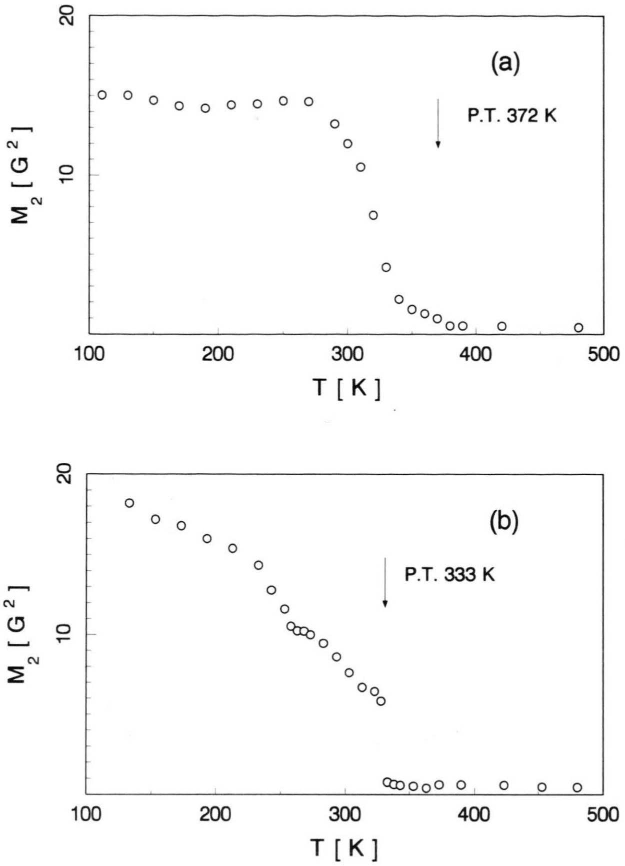

Fig. 1. Temperature dependences of proton second moments for TAE · ClO_4 (a) and TBA · ClO_4 (b).

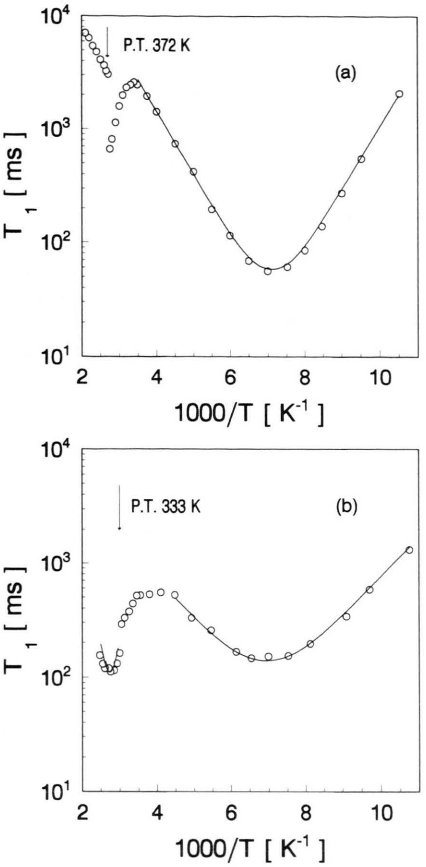

Fig. 2. Temperature dependences of proton spin-lattice relaxation times for TEA · ClO_4 (a) and TBA · ClO_4 (b). The solid lines are fits to the experimental data.

b) *Relaxation Time*

The temperature dependences of T_1 are shown in Figure 2. For TEA ClO_4 a minimum of $T_1 = 56$ ms appears at 143 K. At 295 K the relaxation time starts to decrease, above 364 K a sudden jump to higher T_1 values is observed, and then the relaxation time increases linearly in the $\log T_1$ vs. $1/T$ plot. For TBA ClO_4 a minimum of $T_1 = 150$ ms is observed at 143 K. Above 282 K the relaxation time starts to decrease. At 333 K a sudden jump to lower values takes place, and then the second minimum of $T_1 = 112$ ms appears at 364 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 [7]. Since no structural data of both substances are known, the calculations are made assuming the nitrogen atom at the centre of a regular tetrahedron with N–C bond length of 1.49 Å. The angles N–C–C and H–C–H have been taken to be 109.47°, and the bond lengths C–C and C–H to be 1.54 and 1.09 Å, respectively.

The rigid lattice second moment values for TEA ClO_4 and TBA ClO_4 can be calculated as a sum of respective intra- and interionic contributions. The intraionic part of M_2 for a substance containing protons in different functional groups is determined as [8]:

$$M_{2\,\text{intra}}^{\text{TEA}} = (2*4/20)\, M_2^{\text{I}}(\text{CH}_2) + (3*4/20)\, M_2(\text{CH}_3), \qquad (1)$$

and

$$M_{2\,\text{intra}}^{\text{TBA}} = (2*4/36)\,[M_2^{\text{I}}(\text{CH}_2) + M_2^{\text{II}}(\text{CH}_2) + M_2^{\text{III}}(\text{CH}_2)] + (3*4/36)\, M_2(\text{CH}_3). \qquad (2)$$

Table 1. The calculated second moments (in G^2).

Type of reorientation	TEA ClO_4			TBA ClO_4		
	$M_{2\,\mathrm{intra}}$	$M_{2\,\mathrm{inter}}$	$M_{2\,\mathrm{total}}$	$M_{2\,\mathrm{intra}}$	$M_{2\,\mathrm{inter}}$	$M_{2\,\mathrm{total}}$
rigid structure	26.2	1.0	27.2	26.3	1.0	27.3
CH_3 groups	14.7	0.8	15.5	20.5	0.8	21.3
$(CH_2)^{III}$ groups	–	–	–	16.0	0.6	16.6
$(CH_2)^{II}$ groups	–	–	–	10.8	0.6	11.4
$(CH_2)^{I}$ groups	4.6	0.6	5.2	5.5	0.6	6.1
cation tumbling	0	0.6	0.6	0	0.6	0.6

Here $M_2(CH_3)$ includes the interaction of protons of the four CH_3 groups; $M_2^{I}(CH_2)$ includes the interaction of protons of the first four CH_2 groups nearest to the nitrogen atom; $M_2^{II}(CH_2)$ and $M_2^{III}(CH_2)$ describe the interaction of protons attached to the second and the third carbon atoms in the butyl chain, respectively. This intracationic part was found to be 26.2 G^2 for TEA and 26.3 G^2 for TBA. The intercationic part of the second moment was estimated to be $M_{2\,\mathrm{inter}} = 1.0\ G^2$ for both compounds [1, 2]. Thus, the total rigid lattice values of the second moments equal 27.2 G^2 for TEA and 27.3 G^2 for TBA cations.

At low temperatures the experimental values of M_2 for both salts are much lower than the rigid-lattice values calculated. Therefore it must be assumed that the reorientations, reducing the rigid lattice values of the second moment, are taking place already below the measured temperature range. Calculations of the reduced second moments were performed for consecutive reorientations: of the CH_3 groups, successive CH_2 groups and finally, cation reorientation around its centre of gravity (Table 1).

For TEA ClO_4 the experimentally observed constant value M_2 of about 15.0 G^2 between 110 and 270 K is in full agreement with the value calculated for reorientation of all four CH_3 groups. The narrowing of NMR line observed above 270 K can be interpreted as due to the reorientation of all ethyl groups and the superposed whole cation reorientation around its centre of gravity. The reduced value of the second moment for an overall motion determined only by interionic cation-cation interaction would be about 0.6 G^2 [9], which is experimentally observed between 380 and 480 K. The aforesaid simple model of reorientation of the smaller TEA cation becomes more complicated considering the bigger TBA cation. The experimental M_2 at 133 K is lower than 21.3 G^2, the value calculated assuming methyl group C_3 reorientation (Table 1). This means that not only all methyl groups reorient with a frequency greater than 10^5 Hz but that additional motions must reduce the second moment. One can assume that the onset of successive reorientations of the methylene groups takes place with increasing temperature. The expected values of the second moment reduced due to successive onset of CH_2 group motions given in Table 1 are not distinctly manifested as discrete plateaux, except may be the last value corresponding to reorientation of all methylene groups in all butyl chains. The experimental value $M_2 = 5.8\ G^2$ observed just below the phase transition is in good agreement with the calculated value 6.1 G^2 given in Table 1. To explain fully the considered model of motion one should take into account that the freedom to reorient decreases for more internal methylene groups in the butyl chains of the cation. The Dreiding model shows that steric hindrances may prevent the reorientation of these internal groups. Therefore it seems reasonable to explain this controversy by assuming that the motions of the internal CH_2 groups in the butyl chains are to a certain extent correlated. A kind of geared motion giving freedom for particular chains to reorient would probably be an adequate model. Similar situations were observed in solid hexamethylene [10] and solid tetraethylammonium halides [1]. The abrupt decrease of the second moment at 333 K to 0.6 G^2 can be interpreted as a result of the phase transition conducting to whole cation reorientation around its centre of gravity.

b) *Relaxation Time*

The relaxation rate of the nuclei from the different molecular groups CH_3 and CH_2 of the tetraalkylammonium ion is given [11] as

$$1/T_1 = (n_1/N)(1/T_1)^{CH_3} + \sum_{i=2}^{4} \frac{n_i}{N} \left(\frac{1}{T_1}\right)^{CH_2^i}, \tag{3}$$

$$n_1 + n_2 + n_3 + n_4 = N, \tag{4}$$

where n_1 is the number of relaxing nuclei in the methyl group, n_2, n_3, n_4 are the numbers of relaxing nuclei in successive CH_2 groups and N is the total number of relaxing nuclei in the cation. The relaxation rates $(1/T_1)^{CH_3}$ and $(1/T_1)^{CH_2^i}$ were calculated similarly as in [1] and [2], using the formula of Dunn and McDowell [12].

The analysis of the second moments data for TEA ClO_4 indicates that the observed minimum of T_1 can be associated with the methyl group reorientation.

The best-fitted activation parameters for all reorienting methyl groups are $E_a = 10.6$ kJ/mol, $\tau_0 = 1.9 \cdot 10^{-13}$ s. The diminishing of T_1 at higher temperatures (above 295 K) could be explained as due to the onset of superposed ethyl group reorientations and cation tumbling. The estimated activation energy for this complex motion would be about 25.9 kJ/mol. The phase transition revealed by DSC at 372 K, though not evidenced markedly in the second moment temperature behaviour, leads to a distinct jump of T_1. Above the phase transition T_1 describes the cation tumbling with an activation energy 10.4 kJ/mol. This motion yields the reduced value of the second moment 0.6 G^2 (see Figure 1a).

The analysis of the second moment data for $TBA\,ClO_4$ suggests that the low temperature minimum of T_1 should be also associated with the reorientation of the methyl groups. However, the experimental $T_{1\,min} = 150$ ms is markedly higher than the value $T_1 = 105$ ms calculated for all four reorienting methyl groups. This controversy can be explained assuming that one methyl group in the cation is dynamically not equivalent to the three others. Thus we interpret the observed minimum as related with only three reorienting methyl groups since the calculated minimum of T_1 equals 140 ms. A very similar inequivalence we have already observed for tetrabutylammonium tetrafluoroborate [5] and tetrapropylammonium iodide [3]. The best-fitted activation parameters for this model of reorientations are $E_a = 6.8$ kJ/mol and $\tau_0 = 5.5 \cdot 10^{-12}$ s. The nonequivalence of the methyl groups is not manifested in the temperature dependence of the second moment since its value in the low temperature range is already lowered and obscured due to the onset of the above mentioned additional motions in the butyl chains. These motions affect markedly T_1 above 282 K, but it is difficult to interpret this effect due to the discontinuity of the relaxation time-temperature dependence at the phase transition. One can try to interpret the observed diminishing of T_1 as an evidence for the successive motions of CH_2 groups in the butyl chains (geared motion). The distinct minimum of T_1 observed for the high temperature phase can be associated with the isotropic cation reorientation around its centre of gravity. The change of the second moment associated with this reorientation equals $\Delta M_2 = 5.2$ G^2. The T_1 minimum, calculated from relation

$$\frac{1}{T_1} = \frac{2}{3} \Delta M_2 \gamma^2 f(\omega, \tau), \tag{5}$$

equals 110 ms in full agreement with the experiment and the situation observed in $TBA\,BF_4$ [5]. The best-fitted activation parameters for the tumbling evidenced are $E_a = 43.8$ kJ/mol and $\tau_0 = 9.4 \cdot 10^{-16}$ s.

Conclusions

At low temperatures the existence of C_3 methyl-group reorientations with typical activation energies is proved for both salts. In $TBA\,ClO_4$, similarly as in $TBA\,BF_4$, the dynamical nonequivalence of one CH_3 group is found. At higher temperatures the isotropic reorientation of the whole cation around its centre of gravity is evidently manifested for both salts. The onset of successive CH_2 group reorientations takes place at temperatures far below the phase transition for the bigger TBA cation, while for the smaller TEA cation it is obscured by the close phase transition. These reorientations overcome strong steric hindrances assuming a kind of geared motions of the alkyl chains. The activation energies determined for the aforesaid reorientations are close to those determined for other tetraalkylammonium salts. The existence of solid-solid phase transitions found in both substances is confirmed by DSC.

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