Molecular Motion in Solid Tetraethyl- and Tetrapropylammonium Tetrafluoroborates

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Proton and fluorine NMR second moments and spin-lattice relaxation times for polycrystalline tetraethyl- and tetrapropylammonium tetrafluoroborates have been measured over a wide range of temperatures. Solid-solid phase transitions were found for both compounds and confirmed by DSC. Methyl group C_3 reorientation followed by more complex cation motions was evidenced in the low temperature phases. Overall cation reorientation characterises the high temperature phases of both compounds. Isotropic anion reorientation was found in both salts in both phases.

Key words: NMR, Molecular motions, Phase transitions

Introduction

Our NMR studies of the molecular motion in symmetrical tetraalkylammonium compounds revealed the existence of various types of reorientations of cations and anions [1–6]. The solid-solid phase transitions appear to be connected with changes in molecular dynamics. For all salts we have discovered C_3 reorientation of the methyl groups with very similar activation parameters determined mainly by intraionic interactions. At higher temperatures we have found additional motions inside the alkyl chains in spite of existing strong structural hindrances, and tumbling of the whole cations.

In this work we have examined the molecular reorientations of the cations and anions in tetraethyl- and tetrapropylammonium tetrafluoroborates. The aim of this study was to compare the motions of smaller and larger cations embedded in the same anion sublattice.

Experimental

The polycrystalline samples of tetraethyl- and tetrapropylammonium tetrafluoroborate ($TEABF_4$ and $TPABF_4$) 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 28 MHz for protons or 26.3 MHz for fluorine nuclei, NMR spectra were recorded over a wide range of temperatures. The second moments were calculated by numerical integration of the spectra and corrected for the finite modulated field [7]. The accuracy was of about 10%. Proton and fluorine spin-lattice relaxation times T_1 were measured for $TEABF_4$ at 25 MHz as functions of temperature using our spectrometer with a saturation recovery pulse sequence. The temperature of the sample 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 (DSC 605M).

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Results

a) Second Moment

The temperature dependences of the second moment of magnetic resonance lines are shown in Figure 1. For $TEABF_4$ (Fig. 1 a) the proton second moment between 110 and 270 K is about 14.5 G^2, and then it decreases to 2.2 G^2 at 333 K. Above this temperature it jumps to 0.6 G^2 and decreases further very slowly to 0.4 G^2 at about 530 K (the compound melts above 570 K). The fluorine second moment of 2.4 G^2 between 110 and 270 K diminishes slowly to 0.8 G^2 at higher temperatures.

For TPABF (Fig. 1 b) the proton second moment of about 20.0 G^2 at 130 K diminishes to 7.0 G^2 at 390 K. Above this temperature it jumps to 1.0 G^2. At about 340 K one can scarcely distinguish a plateau value of 11.0 G^2. The fluorine second moment of 2.4 G^2 at 110 K diminishes slowly to 1.0 G^2 at 380 K and jumps to 0.6 G^2 above 390 K.

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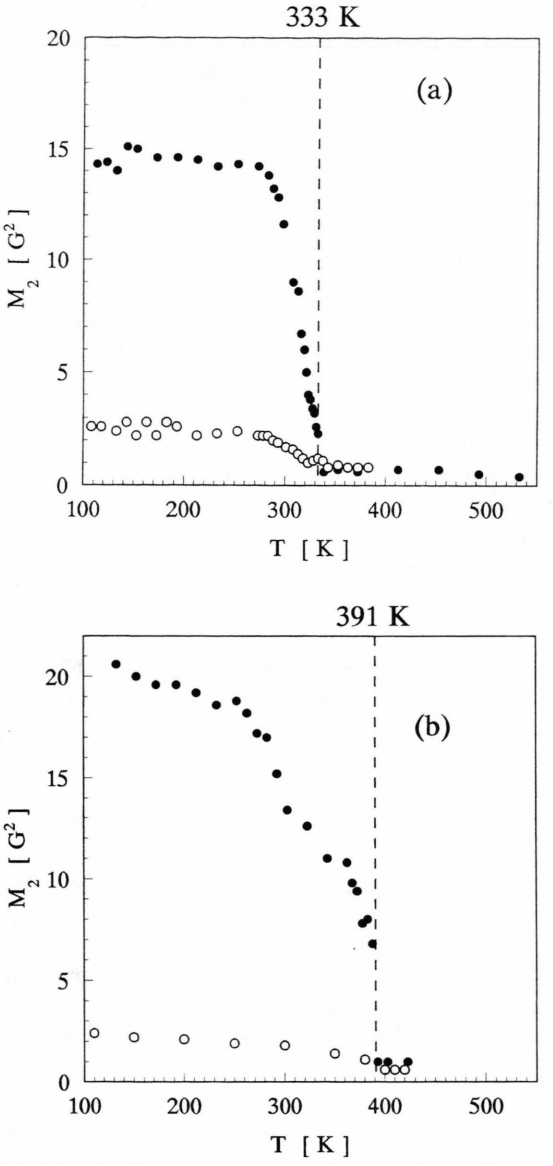

Fig. 1. Temperature dependences of proton (●) and fluorine (○) second moments for $TEABF_4$ (a) and $TPABF_4$ (b).

DTA studies show a heat capacity anomaly at 333 K for $TEABF_4$ and at 391 K for $TPABF_4$.

b) Relaxation Time

The temperature dependences of ^1H and ^{19}F spin-lattice relaxation times for $TEABF_4$ are shown in Figure 2. For protons a distinct minimum of $T_1 = 25$ ms appears at 133 K. In the temperature region of the minimum the ^1H magnetisation decay due to H–F interaction is two-exponential. In the figure only the long component of T_1 corresponding to a magnetisation amplitude higher than 80% is presented. At 286 K the relaxation time starts to decrease, above 333 K a sudden jump to higher T_1 values is observed, and then the relaxation time increases in the log T_1 vs. $1/T$ plot. For the fluorines T_1 diminishes, with temperature then tending to a minimum expected at lower temperatures. Above 270 K the relaxation time starts to decrease, and at 333 K it jumps to much higher values.

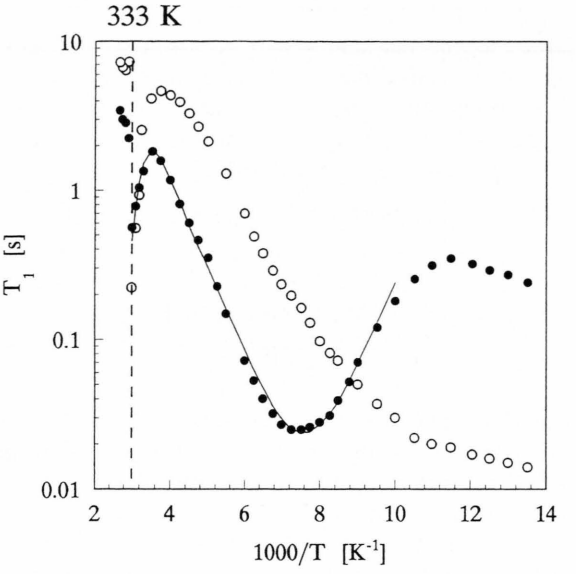

Fig. 2. Temperature dependences of proton (●) and fluorine (○) spin-lattice relaxation times for $TEABF_4$.

The temperature dependences of T_1 for $TPABF_4$ have been measured by Lewicki [8], and will be commented in the discussion.

Discussion

a) Second Moment

A theoretical value of the second moment for a rigid lattice structure can be calculated by Van Vleck's formula [9]. For a polycrystalline sample one obtains

$$M_2 = \frac{3\gamma_I^2 \hbar^2 I(I+1)}{5N} \sum_{j,k} r_{jk}^{-6} + \sum_s \frac{4\gamma_s^2 \hbar^2 S(S+1)}{15N} \sum_{j,m} r_{jm}^{-6}. \quad (1)$$

All symbols have their usual meaning [10]. The rigid lattice second moment values can be calculated as a sum of respective intra- and interionic contributions. The intracationic homonuclear part of M_2 for protons in the TEA or TPA cation comprising different functional groups is determined as [11]

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

and

$$M_{2\text{intra}}^{\text{TPA}} = (2 * 4/28)\,[M_2^{\text{I}}(\text{CH}_2) + M_2^{\text{II}}(\text{CH}_2)] + (3 * 4/28)\, M_2(\text{CH}_3). \quad (3)$$

where $M_2^{\text{I}}(\text{CH}_2)$ includes the interaction of protons of the four CH_2 groups nearest to the nitrogen atom; $M_2^{\text{II}}(\text{CH}_2)$ describes the interaction of protons attached to the second carbon atom in the propyl chain, and $M_2(\text{CH}_3)$ includes the interaction of protons of the four CH_3 groups. The intracationic heteronuclear contribution from nitrogen atom $M_2(\text{H–N})$ is 0.03 G^2 and can be neglected. In the calculations the nitrogen atom is assumed to be in the centre of a regular tetrahedron with an 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 intracationic parts (equal 25.2 G^2) were found to be the same for the TEA and TPA cation. Since no structural data of both substances are known, the homonuclear intercationic parts of the second moment $M_2(\text{H–H})$ were estimated to be 1.0 G^2 for both compounds [1, 2, 4]. By comparison with the literature data [12], taking into account the number of protons in the respective cation, the heteronuclear interionic contributions $M_2(\text{H–F})$ were estimated to be 1.0 G^2 for $TEABF_4$ and 0.7 G^2 for $TPABF_4$. Thus, the total rigid lattice values of the second moments determined for protons equal 27.2 G^2 for the TEA and 26.9 G^2 for the TPA cation sublattices.

The second moment for the anion was calculated assuming its structure as in lithium tetrafluoroborate [12]. This intraanionic value amounts to 14.4 G^2. The interionic cation-anion contribution $M_2(\text{F–H})$ was estimated to be 5.5 G^2 [13]. The interanionic contribution $M_2(\text{F–F})$ could be ignored because neighbouring anions are separated by the large tetraalkylammonium cations. Thus the fluorine total rigid-lattice second moment should be about 20.0 G^2 in both substances.

At low temperatures the experimental values of the ^1H and ^{19}F second moments for both salts are much lower than the total rigid-lattice values determined. This means that the anion and cation in both salts undergo simultaneously reorientations which significantly reduce the second moment. When molecular reorientation occurs, the second moment is reduced by a factor

$$\varrho = \tfrac{1}{4}(1 - 3\cos^2\Theta)^2, \quad (4)$$

where Θ is the angle between the respective internuclear vector and the axis of reorientation. It must be concluded that the reorientations, reducing the rigid lattice values of the ^1H and ^{19}F second moments, are taking place already below the measured temperature. There are several motions which can be discussed for alkyl chains of the cations. In the Dreiding model the freedom to reorient due to increasing strong steric hindrances declines sharply when going from CH_3 groups to CH_2 groups closer and closer to the central nitrogen atom. Therefore the end methyl groups in both substances will have the highest mobility about their symmetry C_3 axes. The calculations of the reduced ^1H second moments were performed for models with consecutive onsets of: the methyl groups reorientation about their C_3 symmetry axes, ethyl groups reorientation, and the whole cation reorientation around its centre of gravity. The obtained values of proton M_2 are listed in Table 1. For $TEABF_4$ the

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

Type of motion	$TEABF_4$				$TPABF_4$			
	$M_{2\text{intra}}^{(\text{H-H})}$	$M_{2\text{inter}}^{(\text{H-H})}$	$M_{2\text{inter}}^{(\text{H-F})}$	$M_{2\text{total}}$	$M_{2\text{intra}}^{(\text{H-H})}$	$M_{2\text{inter}}^{(\text{H-H})}$	$M_{2\text{inter}}^{(\text{H-F})}$	$M_{2\text{total}}$
Rigid structure	25.2	1.0	1.0	27.2	25.2	1.0	0.7	26.9
CH_3 groups	14.2	0.8	0.5	15.5	18.1	0.8	0.3	19.2
Ethyl groups	4.5	0.6	0.4	5.5	10.2	0.6	0.2	11.0
Cation tumbling	0	0.4	0.1	0.5	0	0.6	0.1	0.7

experimentally observed constant value of about 14.5 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 the NMR line observed above 270 K can be interpreted as due to the reorientation of all ethyl groups, superposed by the starting of whole cation reorientation. The abrupt decrease of the protons second moment at 333 K to about 0.6 G^2 and next to 0.4 G^2 can be interpreted as a result of a phase transition leading to the whole cation reorientation around its centre of gravity. The fully reduced value of the ^1H second moment for an overall motion determined only by cation-cation interaction should be about 0.4 G^2 [1], in accordance with the experimentally observed value between 339 and 530 K.

The model of reorientation of the smaller TEA cation becomes more complicated for the larger TPA cation. The experimentally observed proton M_2 of about 20.0 G^2 at 130 K is in good agreement with that calculated for the structure with reorienting four methyl groups. The diminishing of the proton second moment to 7.0 G^2 at 390 K means that not only all methyl groups reorient with a frequency greater than 10^5 Hz, but that additional motions reduce the second moment. One can assume that the onset of successive reorientations of the methylene groups takes place with increasing temperature. For the case of superposed reorientations of the methyl and ethyl groups, calculations give an M_2 reduced to about 11.0 G^2. In our experiment a slightly marked plateau of this value can be noticed between 340 and 360 K. A whole propyl chain motion may further reduce M_2 to 7.0 G^2 at higher temperatures. However, the Dreiding model shows that the steric hindrances prevent the reorientation of the more internal groups. Therefore it seems reasonable to explain this controversy by assuming that the motions of the internal CH_2 groups in the propyl chains are to a certain extent correlated. Similar situations were observed in solid hexamethylene [14], solid tetraethylammonium halides [1] and solid tetrabutylammonium perchlorate [6]. The abrupt narrowing of ^1H NMR line, observed above 390 K, can be interpreted as a result of the phase transition leading to whole cation reorientations.

The experimental value of the fluorine M_2 for $TEABF_4$ between 110 and 270 K can be interpreted as due to the isotropic reorientation of the anion around its center of gravity. The value 2.4 G^2 is in agreement with our calculations (Table 2). The experimental value of 0.8 G^2 above 300 K may reflect an additional diminishing of the F–H anion-cation interaction averaged due to the cation motions. The experimental fluorine value $M_2 = 2.4$ G^2 for TPA BF_4 at 110 K can be also interpreted as due to the isotropic reorientation of the anion around its center of gravity (Table 2). The additional diminishing of M_2 to 0.6 G^2 reflects F–H anion-cation interaction averaged due to the cation motions observed at lower temperatures than in the case of TEA BF_4. Taking into account our results concerning the anion motion in TBA BF_4 [3] it seems fully justified to assume that the same model of isotropic reorientation is valid for all three tetraalkylammonium salts investigated.

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

Type of motion	$M_{2\text{intra}}^{(F-F)}$	$M_{2\text{intra}}^{(F-B)}$	$M_{2\text{inter}}^{(F-H)}$	$M_{2\text{total}}$
Rigid structure	6.2	8.2	5.5	19.9
Anion tumbling	0	0	2.0	2.0

b) Relaxation Time

The relaxation rate of the nuclei from the different molecular groups CH_3 and CH_2 of the tetraethylammonium ion is given [15] as

$$\frac{1}{T_1} = \left(\frac{n}{N}\right)(1/T_1)^{CH_3} + \left(\frac{1-n}{N}\right)\left(\frac{1}{T_1}\right)^{CH_2}, \qquad (5)$$

where n is the number of relaxing nuclei in the methyl group and N is the number of all relaxing nuclei in the ion. The relaxation rates $(1/T_1)^{CH_3}$ and $(1/T_1)^{CH_2}$ were calculated similarly as in [1, 4], using the formula of Dunn and McDowell [16].

The second moments for $TEABF_4$ indicate that the minimum of T_1 may be associated with the methyl group reorientation. The diminishing of T_1 above 286 K could be explained as due to the onset of reorientation of all ethyl groups and the superposed whole cation reorientation around its center of gravity. The best fitted activation parameters for all four methyl groups are $E_a = 11.3$ kJ/mol and $\tau_0 = 1.5 \cdot 10^{-13}$ s, while the activation energy for the complex motion is about 49 kJ/mol.

The phase transition at 333 K revealed by DSC and M_2, leads to a distinct jump of T_1 to higher values. It was hard to define the activation parameters for the motions responsible for T_1 values in the high temperature phase. Perhaps the phase transition accelerates only the motions defined already below 333 K.

The distinct diminishing of T_1 observed below 87 K seems to reflect the minimum of the fluorine T_1 expected at about 71 K, via H–F interaction.

The relaxation rate of the nuclei from the different CH_3 and CH_2 molecular groups of the tetrapropylammonium ion were analysed similarly by Lewicki [8]. However, the more complicated cation demonstrates a dynamical nonequivalence of one methyl group, as was already observed in tetrabutylammonium perchlorate [6]. The molecular dynamics of the compound at higher temperatures described above is in agreement with earlier T_1 experiments [8].

Our fluorine M_2 data for TEA · BF_4 indicate an isotropic reorientation of the anion in the whole temperature range. The expected minimum of fluorine T_1 for this motion is about 14 ms, and this value was observe at about 74 K. The diminishing of T_1 above 267 K seems to reflect only the high temperature behaviour of the cation. A similar T_1 behaviour we have observed for tetrabutylammonium tetrafluoroborate [3].

The temperature dependence of the fluorine T_1 for TPA · BF_4 [8] corroborates the similar molecular dynamics of the anion in tetraethyl-, tetrapropyl, and tetrabutylammonium tetrafluoroborates.

It is interesting to note that the molecular dynamics of the highly symmetrical anion studied for various tetrafluoroborates is quite similar [17–23]. Independently of the cation, the onset of the isotropic reorientation is observed already at low temperatures. The anion activation energy, ranging between about 2 and 8 kcal/mol, was reported to diminish with increasing cation radius [18]. This conclusion seems to be valid also for tetraalkylammonium tetrafluoroborates which we have studied.

Conclusions

1) Two solid phases are evidenced for tetraethyl- and tetrapropylammonium tetrafluoroborates. The phase transitions found at 333 K for TEA · BF_4 and 391 K for TPA · BF_4 are confirmed by DSC.

2) In the low temperature phases of both compounds, all methyl groups reorient with typical activation energies. Below the solid-solid phase transitions one observes the onset of the simultaneous, additional reorientations of the alkyl chains.

3) In the high temperature phases, both compounds show overall reorientation of the cation.

4) Isotropic reorientation of the anion characterises both phases of both compounds.

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