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ON THE THERMAL PROPERTIES OF SOME DI- AND TRI-ALKYLAMMONIUM TETRAFLUOROBORATES

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ABSTRACT

The phase relationships in eight di- and tri-alkylammonium tetrafluoroborates ($R_2NH_2BF_4$, where R = CH_3 [16970-97-1], C_2H_5 [170185-33-5], *n*-C_3H_7 [73159-65-6], *n*-C_4H_9 [676-13-1]; and R_3NHBF_4, where R = CH_3 [16970-98-2], C_2H_5 [16962-50-8], *n*-C_3H_7, *n*-C_4H_9 [41584-11-6]), were investigated by means of DSC and thermogravimetric analysis: several solid-solid phase transitions were disclosed; fusion and transition temperatures and enthalpies were measured. The di- and tri-*n*-propyl- and *n*-butyl- substituted salts proved to be non-hygroscopic and stable within a wide temperature range. Their use as molten electrolytes near ambient temperature can therefore be suggested.

INTRODUCTION

Of the supporting electrolytes used in electrochemistry in non-aqueous solvent systems, salts containing alkylammonium ions, fluoroborates in particular, are of great theoretical interest as well as of practical importance [1], but the literature on their physico-chemical properties is surprisingly poor.

As a part of a research we have undertaken on fluoroborates, our first paper investigated the thermal behaviour of four tetraalkylammonium salts (from methyl- to *n*-butyl-) [2].

In the present work, the thermal phenomena occurring in the $R_{(4-n)}NH_nBF_4$ salt family, where n=1 and 2, and the R group, being the same in one molecule, is methyl, ethyl, *n*-propyl and *n*-butyl, are reported. The goal of this work is to

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provide information on the phase transitions of these materials in the solid state, thus contributing to a deeper knowledge of their melting mechanism. The thermal stability and the hygroscopicity of the salts were also examined, in view of their possible use as molten electrolytes.

The only previous investigation is that of Gatner, who, in a series of papers on the properties of several fused alkylammonium fluoroborates [3], provided measurements on the di- and tri-methyl- and -ethyl- substituted salts and discussed the trend of transport properties, such as viscosity and electrical conductivity, as a function of temperature within a T range of 50+80 degrees above fusion. Apart from this, only the preparation and melting point of some of these salts are found in the organic chemistry literature [4-7].

EXPERIMENTAL

Materials

The following amines were employed: dimethylamine 40% in water (Ferak-Berlin, purum), diethylamine (Fluka, puriss. p.a.>99.5%), dipropylamine (Fluka, puriss. p.a.>99.5%), dibutylamine (International Enzymes, Ltd., pure), trimethylamine (Fluka, purum, 45+50% in water), triethylamine (Fluka, puriss. p.a.>99.5%), tripropylamine (Fluka, purum, >98%), and tributylamine (Fluka, purum, >98%). The fluoroboric acid was usually 40% in water (P.O.[Polish Organic] Ch., pure).

The salts were prepared as in [3] by slowly dropping the tetrafluoroboric acid into an excess of the free base. The aqueous solution was evaporated and the salts, except for the dimethylammonium one (see below) were recrystallized at least twice from *n*-butanol (Hungary, a.g.).

After this general preparation, further purification cycles were carried out as follows. The diethyl-, dipropyl-, and dibutylammonium fluoroborates were dissolved at room temperature in absolute methanol (Fluka, puriss. p.a.>99.5%), then precipitated with diethylether (Fluka puriss. p.a.>99.8%); the triethyl- and the tributyl- substituted salts were either used as such, or purified as above, except for the latter, which was precipitated with diethylether from acetone (C. Erba RPE 99.7%). The trimethylammonium salt was recrystallized from hot methanol, the tripropylammonium salt either from deionized water or from a mixture (1:5 by volume) of methanol and *n*-butanol (Aldrich, 99.5%).

Dimethylammonium fluoroborate, which looks very sticky at room temperature, was prepared in two independent ways, the first starting from the

Ferak-Berlin amine and the P.O. Ch. acid, the second from both Fluka products (dimethylamine, purum, 40% in water, and fluoroboric acid 50% in water). The reaction flask was kept in an ice bath, and the rate of addition of the acid was controlled so that the temperature did not rise above 25 °C. After evaporation, the products were dried under vacuum at room temperature for 48 hours. Both salts were recrystallized from anhydrous *iso*-propanol (Fluka, puriss. p.a.>99.5%). They behaved in a similar way, except that the second had a remarkably higher melting point. The latter product only was used for thermal measurements, after having been fused twice under vacuum at ~110 °C.

Finally, before measurements, the products were dried under vacuum at least 48 h at 100 °C, except for the low melting salts, which were kept under vacuum at ~20 °C below their melting points.

Methods

A Perkin-Elmer Mod. DSC-2 differential scanning calorimeter was employed to determine phase transition temperatures and enthalpies in the T range between ~100 K and a few degrees above the melting point. Details on the calibration and operating procedure have already been reported [2]. Typical heating and cooling rates were 5, 10, and 20 K min^{-1}. Above room temperature, pans with a hole were always used, in order to ensure the elimination of oxygen by the flowing dry pure nitrogen.

A Du Pont Mod. 951 Thermogravimetric Analyzer with a 1090 Thermal Analyzer was used to perform thermogravimetric analysis (TG), on samples held in DSC pans with a hole, as above indicated, at a heating rate of 10 K min^{-1} in a dry nitrogen flow.

RESULTS AND DISCUSSION

Thermal data

The transition and fusion temperatures and enthalpies of the studied di- and trialkyl- substituted ammonium salts are listed in Table 1a and 1b, respectively; all quantities, with their mean deviations, are reported as the average of at least two runs on five or more samples. As far as the transition peaks are concerned, it was observed that transition peaks recorded on previously fused samples were usually much sharper than those recorded in first heating scans, the corresponding thermal effect remaining practically constant. This increase in the sharpness of the transition peaks was more evident for the diethyl-, trimethyl- and triethylammonium fluoroborates. In the following, the thermal

TABLE 1

Thermal data for di- and tri-alkylammonium fluoroborates.

R	Transition(s) T/K	Transition(s) ΔH/kJ mol^{-1}	Fusion T/K	Fusion ΔH/kJ mol^{-1}
		a) $R_2NH_2BF_4$		
CH_3	275-283	6.7 ± 0.4		
	309 ± 3	0.6 ± 0.2	368 ± 1	3.6 ± 0.2
C_2H_5	180 ± 1	2.1 ± 0.2		
	336 ± 1	3.8 ± 0.2	438 ± 1	12.6 ± 0.4
n-C_3H_7	230 ± 1	~0.4		
	303 ± 1	~0.4		
	347 ± 1	7.1 ± 0.4	516 ± 1	18.4 ± 0.4
n-C_4H_9	268 ± 2	11.7 ± 0.8		
	284 ± 2	2.7 ± 0.4	539 ± 1	18.8 ± 0.4
		b) R_3NHBF_4		
CH_3	378 ± 1	1.3 ± 0.2		
	446 ± 1	4.0 ± 0.2	481 ± 1	10.9 ± 0.2
C_2H_5	217 ± 3	7.5 ± 0.8		
	368 ± 4	5.0 ± 0.4	385 ± 1	6.7 ± 0.4
n-C_3H_7	298 ± 1	0.4 ± 0.1	517 ± 1	20.9 ± 0.8
n-C_4H_9			349 ± 3	17.2 ± 0.4

phenomena occurring in each of these salts, usually reversible and well reproducible in subsequent thermal cycles, are presented in detail, together with the pertinent literature data.

Dimethylammonium fluoroborate. In Fig. 1a and 1a', an example of a DSC record illustrates the thermal behaviour of this salt. The tabulated melting temperature is higher than that reported in [3a], and some 30-40 degrees higher than those in [5] and [7] respectively; the datum of 465 K reported by Spitsyn *et al.* [4] seems to be erroneous. The fusion peak is rather diffuse, and seems to be formed by at least two associated peaks, i.e. a premelting phenomenon and fusion; on cooling, a peak with a tail was usually seen, and sometimes, owing to hysteresis, two distinct peaks could be recorded, the sum of their areas being comparable, as expected, with the area of the fusion peak from which the tabulated enthalpy was calculated.

The group of transitions at 275-283 K seems to behave in a similar way. It was not possible to separate the associated peaks on heating, even at a scan rate

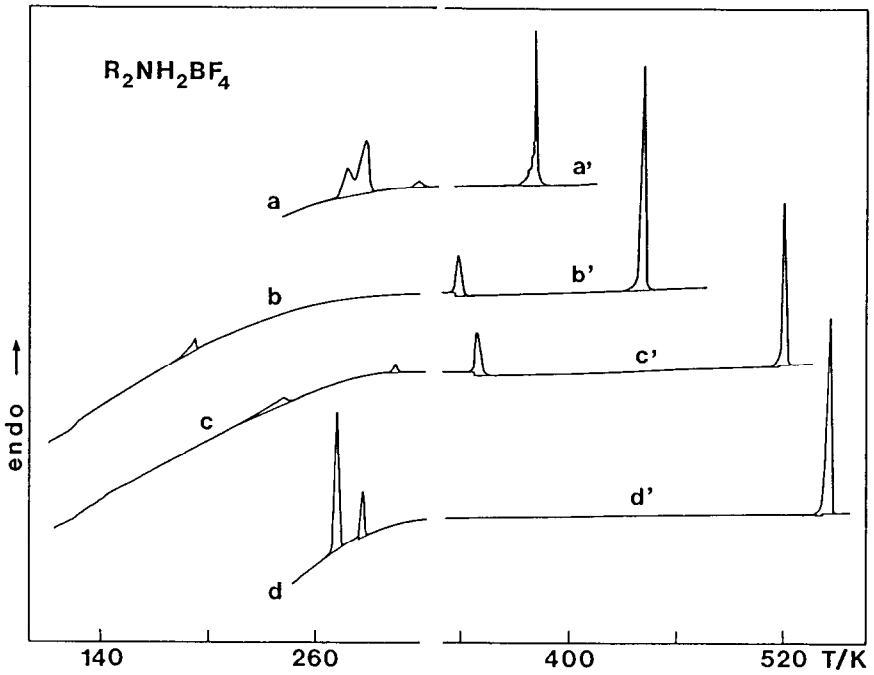

Fig. 1. DSC heating traces of dialkylammonium fluoroborates. R = CH_3 (a, a'), C_2H_5 (b, b'), n-C_3H_7 (c, c'), and n-C_4H_9 (d, d'). The records below room temperature were taken with a sensitivity range 1.6 times higher than that programmed in the higher temperature scans.

of 1.25 K min^{-1}, whereas on cooling a better distinction was obtained, and three or more peaks were usually observed; the total transition enthalpy has been given in Table 1, because the relations among them were not clear enough.

Qualitative information on the behaviour and appearance of this salt was provided by Stammler *et al.* in a paper devoted to an X-ray and thermal study of alkylammonium perchlorates [8]. According to this work, dimethylammonium perchlorate is isomorphous with the fluoroborate and behaves in a similar manner, undergoing a rather rapid "transition form the brittle state to the tacky state", the reverse reaction being slower. Comparable properties were found by the same Authors in the 1,1-dimethylhydrazine fluoroborate [9]. The present peaks at 309 and/or at 275-283 K should be considered as due to analogous transitions.

Diethylammonium fluoroborate. In Fig. 1b and 1b' a typical DSC trace is shown. In [3.a] a melting temperature of 444.7 K was observed, somewhat

higher than the present one, whereas the datum of 408-409 K [4] seems too low.

Dipropylammonium fluoroborate. This salt exhibits three thermal phenomena in the solid state: a sharp transition at 347 K, similar to that found in the preceding salt; and two very small and diffuse solid-solid transitions, the existence of which was proved on samples heavier than the usual ones (pellets weighing from 13 to 25 mg). A typical DSC run is illustrated in Fig. 1c and 1c'. The tabulated melting point is close to the only datum (517-518 K) found in the literature [6].

Dibutylammonium fluoroborate. Two well-defined and reversible solid-solid transitions very close to each other were found in the T range 260-290 K, as shown, for example, by the heating trace in Fig. 1d; the melting point is the highest for this group of salts.

Trimethylammonium fluoroborate. No phase transitions were found below room temperature in this salt, which undergoes two solid-solid transitions between 373 and 450 K, as illustrated, e.g., in Fig. 2a, and at higher temperatures shows a definite tendency to sublimate. Its melting point as measured by DSC was somewhat lower than that observed by Gatner [3a] at 489.2 K.

Triethylammonium fluoroborate. The thermal events occurring in this salt can be seen, e.g., in Fig. 2b. Here again the melting point turned out to be lower than that observed in [3a] at 389.5 K. The remarkable fluctuations in the tabulated transition temperatures are probably due to the fact that both phenomena are not so simple as one might believe at first glance. At 368 K, in fact, a diffuse peak associated with the enthalpy of a rather slow transition (demonstrated at slow scan speed) seemed to coincide with a step in heat capacity; and at ~217 K the reported peak seemed to be due to a double phenomenon, which in the present operational conditions could not be clearly split into two independent contributions.

Tripropylammonium fluoroborate. The DSC trace in Fig. 2c shows the highest melting point among the trialkyl- substituted salts, and only one solid-solid transition, associated with a very small heat effect, although well reversible and reproducible. In the temperature range 460-480 K, sublimation slowly begins, as seen also by means of hot-stage microscopy, and confirmed by thermogravimetry (see below).

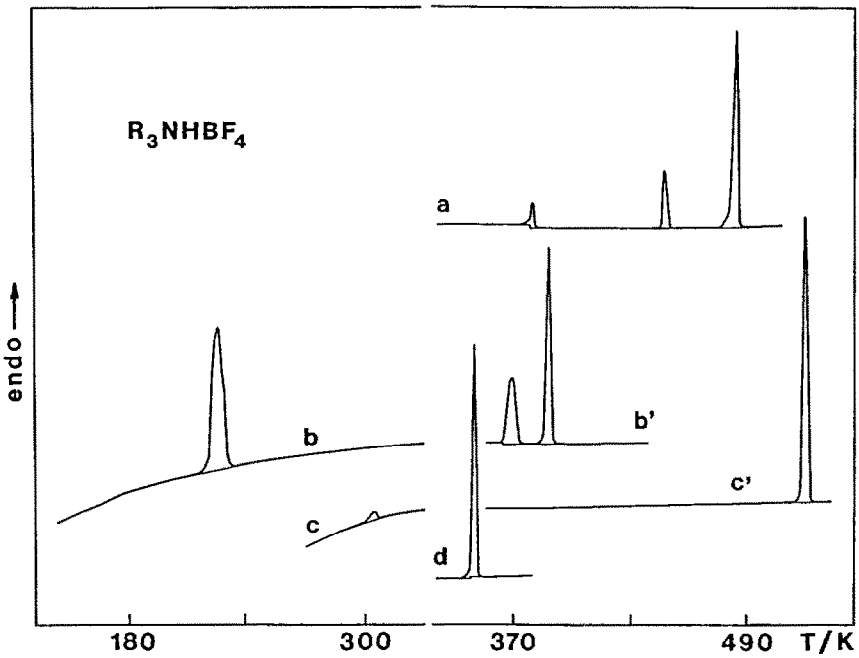

Fig. 2. DSC traces of trialkylammonium fluoroborates. R = CH_3 (a), C_2H_5 (b, b'), n-C_3H_7 (c, c'), and n-C_4H_9 (d). The records in (b) and (c) were taken with a sensitivity range four times higher than that programmed in the scans above room temperature.

Tributylammonium fluoroborate. In the temperature range explored, fusion was the only phenomenon observed (see, e.g., Fig. 2d), and the melting point was the lowest one of all the salts studied. The absence of solid-solid transitions in this T range leads one to suppose that one or more transitions may occur at very low temperature, i.e. at $T \leq 100$ K.

Thermal stability

Information on the thermal stability of these salts is needed to assess their possible use as molten electrolytes, either as pure salts or as components of binary, ternary or more complicated systems formed with different tetrafluoroborates, or with other salts.

Examples of thermogravimetric analysis for the studied di- and tri-alkylammonium fluoroborates are illustrated in Figs. 3 and 4 respectively. Near 550 K, all the salts began to undergo significant weight loss, followed by decomposition, which was complete for $T > 670$ K.

However, if the ordinate scale is magnified enough, one can see that the

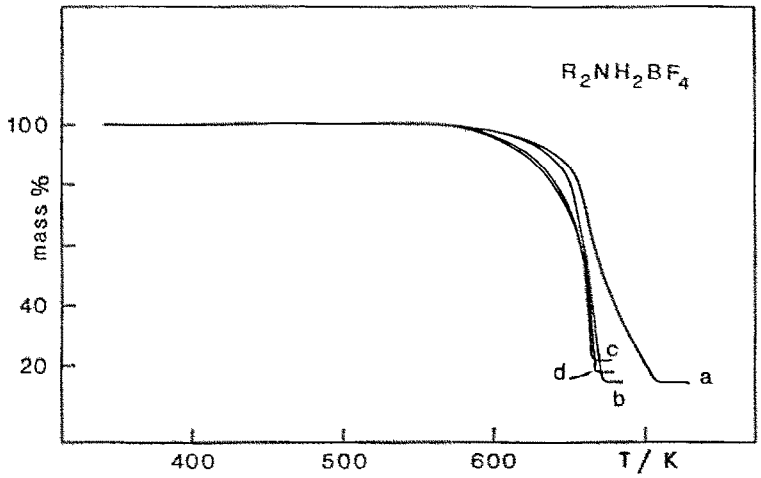

Fig. 3. TG records of dialkylammonium fluoroborates. R = CH_3 (a), C_2H_5 (b), n-C_3H_7 (c), and n-C_4H_9 (d).

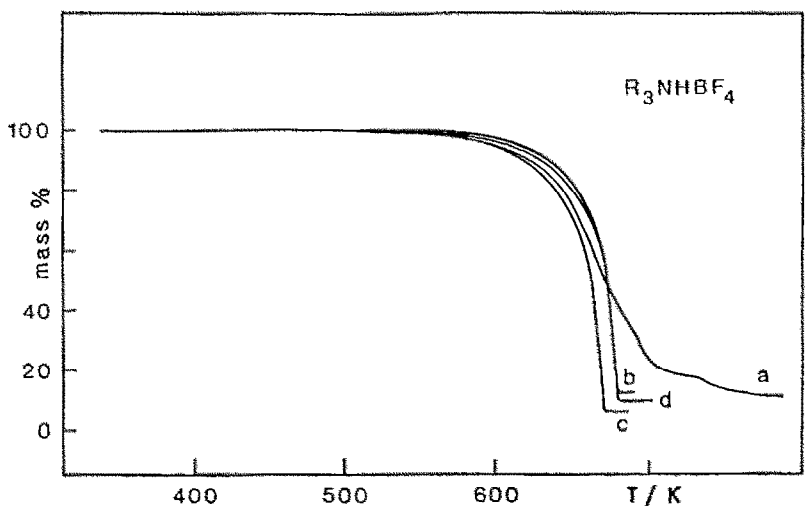

Fig. 4. TG records of trialkylammonium fluoroborates. R = CH_3 (a), C_2H_5 (b), n-C_3H_7 (c), and n-C_4H_9 (d).

trimethyl- and tripropyl- substituted ammonium salts slowly start losing mass near 490-520 K, owing to sublimation, which was detected visually by hot-stage microscopy. In these cases, DSC analysis still provides reproducible data for

enthalpies of fusion if one weighs the sample pan carefully after every scan, keeping thus into account the corresponding mass loss in the enthalpy calculations.

Moreover, DSC scans of all the salts in tightly sealed pans gave somewhat different traces, displaying smooth exothermal effects before fusion, with a decrease of both melting point and enthalpy of fusion. Such findings can be due to the fact that air, viz. oxygen, present inside the pan, reacts with the salt, even at a moderately high temperature.

Hygroscopicity

For the di- and tri-methyl- and ethyl-substituted ammonium salts, hygroscopicity was mentioned in references 4 and 5. Therefore, it seemed useful to collect information about the sensitivity to room moisture of all the tetrafluoroborates considered. For each salt, a given amount of powder (60÷100 mg) in a small glass cylinder was exposed to the ambient atmosphere at room temperature for a long time, while the mass was measured from time to time. In these conditions, it was found that only the dimethylammonium fluoroborate was very hygroscopic, absorbing a remarkable amount of water within one day; the remaining salts did not change their mass significantly after several months.

Nevertheless, previously fused samples of diethyl- and trimethyl- and triethyl-substituted ammonium salts stored in aluminum pans with a hole were sensitive to ambient moisture. DSC analysis of these samples, stored after fusion in the laboratory atmosphere for about seven months, showed that only the di- and tri-*n*-propyl- and *n*-butylammonium salts gave reproducible DSC traces (as those shown in Figs. 1 and 2), whereas the samples of the remaining salts were found to have higher mass and displayed phenomena such as dehydration peaks and fusion peaks with tails. The melting points and enthalpies of fusion, much lower than those of dry, freshly prepared samples, proved that hydration and subsequent decomposition reactions had taken place.

CONCLUDING REMARKS

The fusion temperatures and entropies of the studied salts vs. n_C (number of carbon atoms in R) are shown in Fig. 5. Two main features are apparent: i) the regular trend of both the melting point and the entropy of fusion of the disubstituted salts, and ii) the absence of such regularities in the trisubstituted ones.

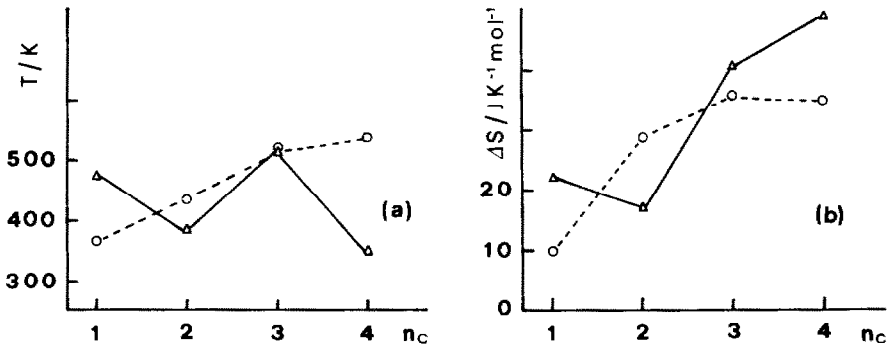

Fig. 5. Melting points (a) and entropies of fusion (b) as a function of the R chain length in $R_2NH_2BF_4$ (circles) and in R_3NHBF_4 (triangles).

In the latter case, however, a distinct odd-even effect is shown by the melting points, whereas the entropies of fusion show a minimum for $n_C=2$. A further insight into the meaning of these facts probably requires a more extensive investigation of the alkylammonium fluoroborates family. Work is in progress in this laboratory, in particular on the monosubstituted terms.

Finally, in the light of the observed thermal stability and hygroscopicity of these compounds, one can suggest the use of the di- and tri-*n*-propyl- and *n*-butyl-substituted ammonium salts, either pure or in mixtures, as molten electrolytes near room temperature.

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