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ON THE THERMAL BEHAVIOUR OF SOME TETRAALKYLAMMONIUM TETRAFLUOROBORATES

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SUMMARY

The phase relationships in four tetraalkylammonium tetrafluoroborates (R_4NBF_4, where R = CH_3 [661-36-9], C_2H_5[429-06-1], n.C_3H_7[338-38-5], and n.C_4H_9 [429-42-5]) were investigated by means of dsc analysis: some solid-solid phase transitions were brought out; fusion and transition temperatures and enthalpies were measured. The results obtained are compared with the previous literature data.

INTRODUCTION

Alkylammonium salts, especially tetraalkylammonium tetrafluoroborates, have been successfully and widely applied in electrochemistry over the last thirty years, not only as supporting electrolytes in non-aqueous solvent systems, but also in several electrochemical methods of both analytical and industrial interest (1). The physico-chemical information for most of these compounds, however, is still fragmentary (see, e.g., a recent review[2]).

As far as the tetraalkylammonium tetrafluoroborates are concerned, preparation of the first four members of the series was described by Wheeler and Sandstedt (3), and the fusion properties of three salts (with number of carbon atoms in the alkyl chain n_C = 3, 4, and 6) were reported by Coker et al. (4); on the same three salts in the molten state Lind et al. (5) provided density, conductance and viscosity data, and on the salts with n_C = 4-7 conductance and volume measurements in the molten state were carried out by Barton and Speedy (6). Thus, the thermal behaviour of this salt class in the solid state is still unknown to a large extent.

We therefore decided to investigate the thermal phenomena occurring in the R_4NBF_4 salt family, where the R group, being the same in one molecule, is methyl, ethyl, n.propyl, and n.butyl, to contribute to a better understanding of the melting mechanisms in these materials, and to assess their thermal stability.

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EXPERIMENTAL

Materials

The following products were employed: Aldrich (97%) and Fluka (purum) tetramethylammonium tetrafluoroborate; Aldrich (99%) and Fluka (puriss.) tetraethylammonium tetrafluoroborate; Fluka (purum) tetrapropylammonium tetrafluoroborate; Aldrich (99%) and Fluka (puriss.) tetrabutylammonium tetrafluoroborate. The tetramethyl- and tetraethylammonium salts were kept 24 h in a vacuum oven at IOO °C before use; tetrapropylammonium fluoroborate was recrystallized twice, either from methyl alcohol (Fluka puriss. p.a. >99.5 mole%) or from deionized water. The tetrabutylammonium salts were recrystallized twice, either from acetone (Fluka puriss. p.a.>99.5%) or from sec.butyl alcohol (Fluka puriss. p. a.>99%); however, dsc analysis did not reveal any significant difference between the recrystallized materials and the commercial products.

Methods

Phase transition temperatures and enthalpies were determined by means of a Perkin-Elmer Mod. DSC-2 differential scanning calorimeter in the T range between IOO K and a few degrees above the melting point. Pure nitrogen and pure helium were used as purge gases above and below 320 K, respectively.

The instrument was calibrated at heating rates of 5, IO, and 20 K min^{-I} with the following substances: gallium (Fluka, puriss. 99.999%), indium, tin, lead, and zinc (supplied by Perkin-Elmer), for use with nitrogen as the flow gas; and with cyclopentane (Fluka, puriss. 99.5%), mercury (C. Erba RP-ACS) and gallium (as above) for use with flowing helium.

For every salt at least five samples of different origin, weighing 3-IO mg, tightly sealed in volatile sample pans, were cycled at least twice between IOO and 320 K, usually at heating rates IO-20, and cooling rate 20 K min^{-I}; at least five more samples were generally cycled twice from 320 K through fusion at the above scan rates.

A small hole was drilled in the aluminum pans for the measurements above room temperature, to ensure a good contact between the samples and the flowing dry nitrogen atmosphere, thus preventing or delaying thermal decomposition. Reproducible results were usually obtained, and hysteresis on cooling was negligible; the pan weight was checked after every thermal cycle.

The thermal stability of the salts was checked by means of a Du Pont 95I Thermogravimetric Analyzer with a I090 Thermal Analyzer, on samples held in dsc pans with a similar hole, at heating rate IO K min^{-I} in a dry pure nitrogen flow.

RESULTS and DISCUSSION

The transition and fusion temperatures and enthalpies of the studied salts are listed in Table I; the fusion enthalpies of the tetramethyl- and tetraethylammonium salts, which undergo remarkable decomposition in the melting temperature range, were evaluated with a large approximation, and are indicated in parentheses; all other quantities , with their mean deviations, are reported as the average of several runs.

TABLE I

Thermal data for R_4NBF_4

	transition(s)		fusion	
R	T/K	ΔH/kJ mole^{-I}	T/K	ΔH/kJ mole^{-I}
CH_3	I54 ± I	0.5 ± 0.I		
	60I ± 4	I.7 ± 0.3	7I6 ± 3	(I7.2)
C_2H_5	336 ± I	II.7 ± 0.4	642 ± 3	(I3.8)
$n.C_3H_7$	289 ± I	I.5 ± 0.3		
	392 ± I	I6.3 ± 0.2	5II ± I	I9.2 ± 0.4
$n.C_4H_9$	335 ± I	7.9 ± 0.I	429 ± I	I2.I ± 0.4

The thermal phenomena occurring in the listed compounds will now be presented in detail, together with the pertinent literature data.

Tetramethylammonium fluoroborate

An example of a dsc trace obtained on heating is shown in Fig. I,a and a'; two rather flat and small, but reversible and reproducible peaks were found. They were apparently associated with phase transitions in the solid state preceding the fusion peak, which was always interrupted by sharp and more or less large exothermal effects due to decomposition; this behaviour confirms previous DTA results by Stammler et al. (7). Then, if the sample was suddenly cooled, an exothermal peak due to crystallization could be observed (at about 698 K), the heat effect of which could be roughly estimated in relation to the sample mass, as weighed after the end of the thermal cycle. Of course, after fusion and partial decomposition of a given sample, the solid-solid transition peaks were no longer so evident and reproducible as in samples never heated to fusion.

The fusion temperature was higher than in the literature (69I and 708 K, given in Refs. 3 and 7, respectively); the temperature of the higher solid-solid transition is comparable with the value (606 K) of Stammler et al. (7), who did

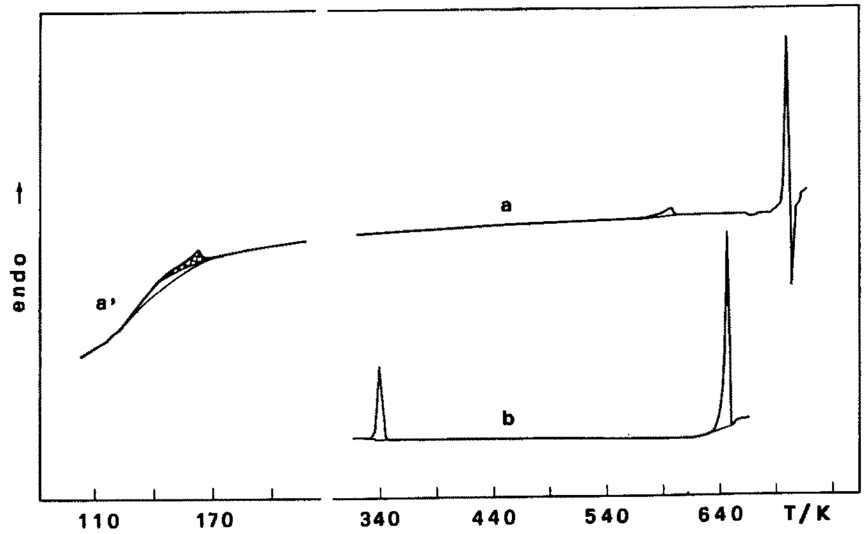

Fig. I. Dsc traces for tetramethyl- (a and a') and tetraethyl- (b) ammonium fluoroborates. The record in (a') was taken with a sensitivity range ten times higher than that programmed in (a) and (b).

not report any datum for the heat effect, but indicated that "very little energy is required for this transition".

The $\Delta_{trs}H_m$ for the low temperature phase transition has been evaluated by taking into account the area of the small peak only (hatched area in Fig. I.a'), for which drawing of the base line is less subject to uncertainties due to the C_p increase at low temperature. If one takes the whole area limited by the base line drawn in the figure in the range I20-I70 K, a $\Delta_{trs}H_m = 1.8 \pm 0.2$ kJ mole^{-1} can be approximately estimated, i.e. about 4 times larger than that tabulated. From nuclear magnetic relaxation results, Jurga et al. (8) suggested that in the same T range "isotropic rotation of the tetramethylammonium ion as a whole" takes place.

Tetraethylammonium fluoroborate

In Fig. I, b an example of a dsc heating trace is illustrated. A solid state transition was brought out; the fusion peak was usually followed by decomposition phenomena. Like for the tetramethylammonium salt, on immediately cooling a molten sample a crystallization peak was seen (at about 635 K). The tabulated fusion temperature is slightly higher than those indicated in Refs. 3 and 9 (638-640 K).

Tetrapropylammonium fluoroborate

The thermal behaviour of this salt on heating is illustrated by the dsc trace of Fig. 2, a and a', where an example of the two solid state transitions and of fusion is shown. The fusion temperature of Table I is lower than the data from Refs. 3 and 5 (522-523 and 52I K, respectively), but is comparable with the dsc value by Coker et al. (4) (5I2 K); whereas the present enthalpy datum is higher (Ref. 4 reports I4.2 kJ mole^{-I}). Similarly, the tabulated temperature for the higher solid state transition can be compared with that reported in (4) (397 K), the pertinent enthalpy value being, however, slightly higher (in Ref. 4: I4.6 kJ mole^{-I}).

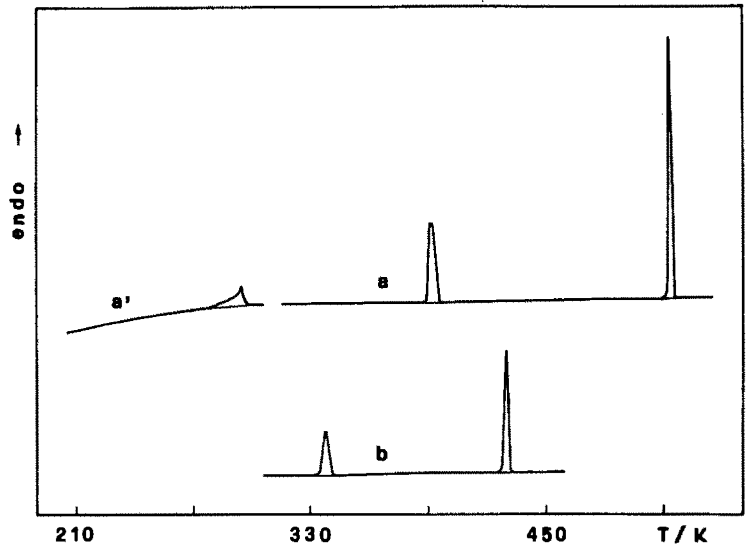

Fig. 2. Dsc traces for tetrapropyl- (a and a') and tetrabutyl- (b) ammonium fluoroborates. The record in (a') was taken with a sensitivity range four times higher than that programmed in (a) and (b).

Tetrabutylammonium fluoroborate

A dsc trace obtained on heating is shown as an example in Fig. 2, b. The fusion temperature, although comparable with the datum of Ref. 3 (426-428 K), is lower than those reported by other Authors (4, 6, 9, IO) ranging between 433.5 and 439 K. The solid state transition temperature is also about 6 degrees lower than that of (4) (34I K); the transition and fusion enthalpies of Ref. 4 (6.7 and I0.5 kJ mole^{-I}) are significantly lower than the present ones, as in the case of the tetrapropylammonium salt.

Thermal stability

A comprehensive picture of the thermal stability of these fluoroborates can be sketched from the thermogravimetric analysis curves shown in Fig. 3.

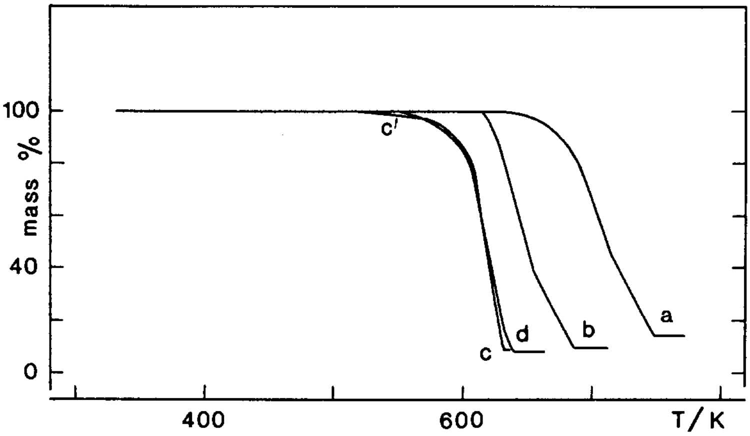

Fig. 3. Thermogravimetric analysis of R_4NBF_4. R = CH_3 (a), C_2H_5 (b), n.C_3H_7 (c), and n.C_4H_9 (d).

Decomposition of the tetramethylammonium salt (Fig. 3,a) begins at ~635 K, i.e. some 80 degrees below the fusion temperature; tetraethylammonium fluoroborate starts decomposing at ~ 613 K (Fig. 3,b), whereas the salts containing the tetrapropyl- and tetrabutyl- substituted cations decompose above ~ 550 and ~ 518 K, respectively, i.e. some 40 and 90 degrees above their melting point (Fig. 3, c and d). It seems therefore that the latter can safely remain some time in the molten state (under a pure nitrogen flow) without suffering thermal degradation, and it may be stressed that these two salts are very stable in the temperature range covered by dsc experiments, their thermal phenomena being reproducible in subsequent cycles.

As for reactivity with ambient moisture, only tetraethylammonium fluoroborate seemed to be very slightly hygroscopic after a two days exposure to the room atmosphere; the other three salts were insensitive to humidity.

Concluding remarks

It is worth mentioning that in the T range 120-180 K all four salts displayed rather sluggish thermal phenomena, that could not be clearly evidenced by dsc analysis in the quoted experimental conditions, except for tetramethylammonium fluoroborate, as mentioned above. The associated heat effects were very small,

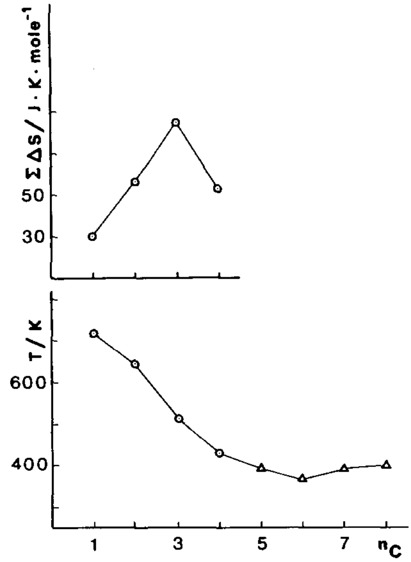

Fig. 4. Melting points (lower part) and total entropies ($\Sigma\Delta S = \Delta_{trs}S_m + \Delta_{fus}S_m$, upper part) vs. the R chain length in R_4NBF_4. Circles: this work; triangles: Ref. 6.

and could barely be revealed; moreover, these phenomena seemed to be rather dependent on the thermal history of the sample. More information might be obtained by different experimental techniques (e.g. adiabatic calorimetry, N.M.R., etc.). For the time being, the lack of structural information, in particular, makes it impossible to provide a clearer description of the phase relations in this salt class.

Finally, the trend of the melting temperatures vs. n_C is shown in the lower part of Fig. 4, where the literature data (6) for longer chain terms up to $n_C = 8$ are also reported; in the upper part of the figure, the sum of the transition entropies is presented, also as a function of n_C.

A marked decrease in the melting point is observed, and our data are in good agreement with those of Barton and Speedy (6) showing a minimum at $n_C = 6$, which is followed by a slight increase up to about 400 K for the tetra-n.octylammonium salt. The total entropies of transition and melting display a sharp maximum at $n_C = 3$, the interpretation of which, however, needs a full knowledge of the thermal behaviour at low temperature.

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