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# A DIFFERENTIAL SCANNING CALORIMETRIC STUDY OF PHASE TRANSITIONS IN POLYSUBSTITUTED *n*-ALKYLAMMONIUM HALIDES

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A DSC investigation of several *n*-alkylammonium salts is reported. The results of this investigation can be used to help decide which of several crystalline forms should be studied by X-ray diffraction for the best correlation between the liquid and solid states.

The *n*-alkylammonium halide compounds are currently under intensive investigation for a number of reasons. For example, the quaternary salts are excellent cationic detergents when dissolved in hydrocarbons; their concentrated solutions are known as liquid membranes (and are believed to control a large number of biological processes, with their bioactivity being a function of the structure of the solute); and they are pharmacologically active substances [1]. The secondary salts are widely used in solvent extraction processes in general and in the extraction of fused salts in particular [2].

During the course of these investigations, attempts have been made to correlate the properties of these materials in solution and in the molten state with the structure in the solid state [2, 3]. However, the existence of several solid-solid transitions in these compounds have been previously established [4—7]. It would seem that the crystal and molecular structure of the solid phase existing closest to the melting points (Phase I) should be used as the basis for any comparisons between the solid and molten or solution phases. However, if the structural differences between Phase I and the room-temperature phase are minor, then a reasonable and more practical approach would be to base the comparison on the room-temperature phase.

As a first step in making this decision, the temperatures of the phase transitions and several thermodynamic parameters should be obtained. This information will be helpful in selecting proper temperature ranges for the crystal structure analyses and in predicting the degree of disorder to be expected in the high-temperature phases.

Enthalpies and entropies of transition and of fusion, as well as the transition and fusion temperatures, have been reported for a number of substituted *n*-alkyl-

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ammonium halides [4]. However, no data have been reported for disubstituted compounds.

This communication reports the results of a study of several representative compounds using differential scanning calorimetry (DSC). The DSC curves were obtained using a Perkin-Elmer DSC-1B differential scanning calorimeter with a scanning rate of 5°/minute. Peak areas were measured with a planimeter. Calibration standards and the error analysis have been described previously [8]. Several samples of each compound (weighing between 5 and 0.4 mg) were investigated.

Two examples of disubstituted compounds were selected for study: di-*n*-decylammonium bromide and di-*n*-dodecylammonium bromide. In addition, tetra-*n*-heptylammonium nitrate was investigated to confirm the rather unusual results reported for several other tetrasubstituted salts [5]. The results are listed in the Table.

Table 1

| Compound | Transition | | | Fusion | | | M.W. |
|---|---|---|---|---|---|---|---|
| | $T$, K | $\Delta H$ $\frac{\text{Kcal}}{\text{Mole}}$ | $\Delta S$ e.u. | $T$, K | $\Delta H$ $\frac{\text{Kcal}}{\text{Mole}}$ | $\Delta S$, e.u. | |
| $(C_7H_{15})_4N(NO_3)$ | 335.2 | 1.11 | 3.31 | 370.5 | 8.56 | 23.1 | 472.80 |
| $(C_{10}H_{21})_2NH_2Br$ | 318.2 | 9.42 | 29.6 | 519.8 | 4.59 | 8.83 | 378.49 |
| $(C_{12}H_{25})_2NH_2Br$ | 317.5 | 8.13 | 25.6 | 516.8 | 4.07 | 7.88 | 437.60 |

A previous investigation of monosubstituted *n*-alkylammonium halides showed that the entropies of fusion were less than 5 e.u. The (total) entropy of transition, although greater than the entropy of fusion, was 10 e.u. or less. Thus, it might be concluded that the structures in the several solid phases are not significantly different and the configurational and/or positional disorder occur in the solid while some degree of ordering exists in the liquid state (the latter being due to the effects of the polar end of the molecule) [4]. From our data it is clear that the high- and low-temperature solid phases of the disubstituted compounds are significantly different. Also, the effect of the polar end of the molecule is somewhat muted by the relatively large non-polar portion of the molecule. Therefore, it can be concluded that, in these cases, any comparison of the molten or solute form of these molecules is best made with Phase I. On the other hand, the extremely large entropy of fusion of the tetrasubstituted compound (and the low entropy of transition) indicate that little significant information would be obtained by using the high temperature phase as a basis for further studies of the molten or solute state.

The value obtained for the entropy of fusion of tetra-*n*-heptylammonium nitrate is in excellent agreement with the values reported for the bromide, iodide and perchlorate salts of this cation: 23.3, 22.5 and 19.0 e.u., respectively [5].

As a result of this survey, a detailed single-crystal X-ray investigation of the di-*n*-decylammonium halides has been initiated.

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Résumé — On communique les résultats d'une étude par analyse calorimétrique différentielle (DSC) de divers sels de *n*-alkylammonium. Les résultats de cette étude donnent des indications pour le choix des formes cristallines qui nécessitent d'être étudiées par diffraction des rayons X afin d'obtenir la meilleure corrélation entre les états liquides et solides.

Zusammenfassung — Es wird über eine DSC-Untersuchung verschiedener *n*-Alkylammoniumsalze berichtet. Die Ergebnisse dieser Untersuchung können zur Entscheidung beitragen, welche von mehreren Kristallformen durch Röntgendiffraktion untersucht werden sollten um die beste Korrelation zwischen den flüssigen und festen Zuständen zu erzielen.

Резюме — С помощью дифференциальной сканирующей калориметрии проведено исследование некоторых N-алкиламмониевых солей. Результаты исследования могут быть использованы при решении вопроса какие кристаллические формы должны быть изучены посредством дифракции рентгеновых лучей для наилучшей корреляции между жидким и твердым состоянием.