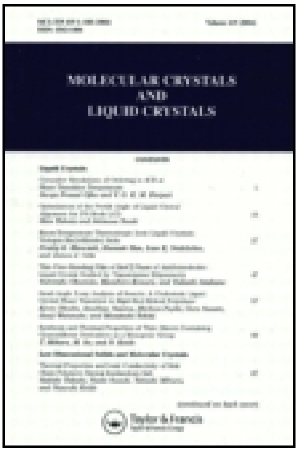

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Mesophases of Alkylammonium Salts. I. First-Order Transitions

A. Xenopoulos [a], J. Cheng [a], M. Yasuniwa [a b c] & B. Wunderlich [a b]
[a] Department of Chemistry, University of Tennessee
[b] Chemistry Division, Oak Ridge National Laboratory
[c] Department of Applied Physics, Faculty of Sciences, Fukuoka University, Nanakuma, Jonan-ku, Fukuoka, 814, Japan

To cite this article: A. Xenopoulos, J. Cheng, M. Yasuniwa & B. Wunderlich (1992): Mesophases of Alkylammonium Salts. I. First-Order Transitions, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 214:1, 63-79

To link to this article: http://dx.doi.org/10.1080/10587259208037282

Mol. Cryst. Liq. Cryst., 1992, Vol. 214, pp. 63–79
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Mesophases of Alkylammonium Salts.
I. First-Order Transitions

A. XENOPOULOS, J. CHENG, M. YASUNIWA† and B. WUNDERLICH

Department of Chemistry, University of Tennessee and Chemistry Division, Oak Ridge National Laboratory

(Received September 22, 1991)

Thermal properties of symmetric tetra-*n*-alkylammonium salts are interpreted based on the concept of conformational motion and disorder (condis crystals). A special effort is made to separate the well-known plastic crystalline states for the lower homologs of this series from the condis state. New transition parameters for $(C_2H_5)_4NBr$, $(C_3H_7)_4NBr$, $(C_8H_{17})_4NBr$, $(C_{10}H_{21})_4NBr$, $(C_{12}H_{25})_4NBr$, $(C_{12}H_{25})_4NI$, $(C_{16}H_{33})_4NBr$, and $(C_{18}H_{37})_4NBr$ are added to data in the literature. Three groups of compounds displaying distinct behavior are found: A) Short-chain tetra-*n*-alkylammonium salts do not melt nor disorder conformationally, they transform to plastic crystals at a single disordering transition, followed by sublimation or decomposition. B) Long-chain tetraalkylammonium salts show conformational disorder and motion before fusion and do not exhibit a plastic crystalline phase. C) In the intermediate alkyl-chain lengths both plastic and condis crystals may exist, not all phases are, however, equilibrium phases.

1. INTRODUCTION

Disordering of a crystal of molecules or ions of suitable structure may involve the loss of three types of orders: positional, orientational, and conformational. One can write, thus, the overall entropy of fusion[1]:

$$\Delta S_f = \Delta S_{\text{pos}} + \Delta S_{\text{orient}} + \Delta S_{\text{conf}}$$

The order can be lost, i.e., fusion can occur, in one or more steps. Multiple-step fusion gives rise to mesophases which are distinct from both the perfect (rigid) crystal and the isotropic melt. It has been recognized that conformationally disordered crystals (condis crystals) do not fit the earlier classification of mesophases, that included only plastic crystals and liquid crystals.[2] A large number of small and macromolecular examples of condis crystals was reviewed recently.[3]

Empirical rules that are useful in accounting for the entropy changes during the transition from the crystal to the melt were developed earlier.[1] Specifically, the

---

†Visiting Professor. Permanent address: Department of Applied Physics, Faculty of Sciences, Fukuoka University, Nanakuma, Jonan-ku, Fukuoka 814, Japan.

change in positional entropy of fusion, ΔS_{pos}, is generally 7–14 JK^{-1} mol^{-1} (Richards' rule).[4] Similarly, the orientational change in entropy of fusion, ΔS_{orient}, is usually in the range 20–50 JK^{-1} mol^{-1} (as first noted by Walden).[5] Finally, the conformational increase in entropy of fusion, ΔS_{conf}, is about 7–12 JK^{-1} mol^{-1} (based on the rotational isomeric model and in agreement with experimental data).[1] The quantities ΔS_{pos} and ΔS_{orient} refer to the whole molecule, i.e. they do not change with size. On the other hand, ΔS_{conf} refers to a single flexible bond and increases as the molecule has more flexible bonds. For flexible, linear macromolecules the gain of conformational disorder dominates fusion.[1] All other contributions to the transition entropies are smaller and are included in the rather large range of values for the contributions.[1,3]

In an earlier series of publications[6–10] the conformationally disordered state of crystals of small molecules was discussed based on calorimetry, thermomechanical analysis, microscopy, X-ray diffraction, and solid-state NMR. Based on data of a typical liquid-crystal-forming material [N,N′-bis(4-*n*-octyloxybenzal)-1,4-phenylenediamine] (OOBPD)[7,10] and typical plastic-crystal-forming cyclosilanes[8,9] it could be shown that in the liquid-crystalline and plastic-crystalline states the conformational motion and disorder is similar to that of the melt. In addition, it was proven that separate condis states of considerable motion and disorder can exist at lower temperatures. In the case of cyclododecamethylhexasilane and OOBPD increasing conformational motion could be observed with increasing temperature even below the disordering transition to the plastic and condis crystalline states, respectively. This large-amplitude conformational motion below T_d can be a jump-like motion to symmetric states so that it does not substantially increase the disorder. This jump-like motion seems common in molecular crystals.[3]

In this paper the discussion of mesophases in small-molecular compounds is extended to tetraalkylammonium halides. These compounds are ionic salts with flexible, linear organic substituents. In order to delineate their transition behavior, a survey of simple and complex salts is presented first. Following this description, the transition behavior of the tetra-*n*-alkylammonium salts is analyzed with an attempt at separating the different types of disorder. This class of compounds provides a unique case study, as one can not only increase the size and symmetry of the alkyl groups, but one can also adjust the balance of ionic and non-ionic character.

The discussion will be based on new thermal analyses of the transition region of $(C_2H_5)_4NBr$, $(C_3H_7)_4NBr$, $(C_8H_{17})_4NBr$, $(C_{10}H_{21})_4NBr$, $(C_{12}H_{25})_4NBr$, $(C_{12}H_{25})_4NI$, $(C_{16}H_{33})_4NBr$, and $(C_{18}H_{37})_4NBr$ and data available in the literature. In this first paper of the series, the first-order transitions will be discussed by analyzing well-crystallized samples. The effects of thermal history, observable by fast cooling, will be treated later, together with an analysis of heat capacities. Some preliminary results have been presented earlier at the *International conference on relaxations in complex systems* (Heraklion, Greece, June 1990).[11] Later publications will focus on the details of motion and disorder in specific salts, as derived from the appropriate experimental methods (DSC, solid-state NMR, X-ray diffraction, neutron scattering, and microscopy).

2. MELTING OF IONIC SALTS

2.1 Simple Salts

Melting of salts, consisting of two or more monoatomic ions, can be interpreted to a considerable degree in terms of positional disordering. The case of alkali halides is particularly illustrative, as can be seen from the data in Table I.[12] The average value of the entropy of fusion for all 20 salts is 24.2 ± 1.7 JK^{-1} mol^{-1}, well within the range specified by Richards' rule for two ions.

Data were also inspected for all other simple salts easily accessible in the literature[12] (76 salts). These were the fluorides of Ca^{2+}, Sr^{2+}, Ba^{2+}, Be^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+} and As^{3+}; the chlorides of Cu^{+}, Ag^{+}, Tl^{+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Be^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Sn^{2+}, Al^{3+}, Bi^{3+}, Fe^{3+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Gd^{3+}, Ho^{3+}, Er^{3+}, Pu^{3+}, As^{3+} and Sb^{3+}; the bromides of Cu^{+}, Ag^{+}, Tl^{+}, Sr^{2+}, Ba^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ca^{2+}, Sb^{3+}, Al^{3+}, La^{3+}, Pr^{3+}, Nd^{3+}, As^{3+}, Gd^{3+} and Bi^{3+}; the iodides of Cu^{+}, Ag^{+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Al^{3+}, Ce^{3+}, Pr^{3+} and Nd^{3+}; the oxides of Mg^{2+}, Ca^{2+}, Ba^{2+} and Pb^{2+}, and the sulfides of Fe^{2+}, Mn^{2+} and Pb^{2+}. The majority of the salts have, again, values of entropy of fusion close to those predicted by Richards' rule. Some of the salts show low-temperature solid-solid transitions and it is necessary to include their entropy changes in the total entropy gain.

There are, however, exceptions in which one finds either a smaller or a larger ΔS_f than $n \times \Delta S_{pos}$, where n is the number of ions. These deviations illustrate the possible complications.[13] Lower entropies of fusion can be observed when the melt is more ordered because it contains partially covalently bonded dimers, complexes, or networks. In case the aggregates in the melt gain additional orientational degrees of freedom because the dimers, complexes, and networks have lost their spherical symmetry, ΔS_f can also be higher. A lowering of ΔS_f can also arise from a disorder in the crystal caused by a dissimilarity in ion radii, charges, or polarizabilities. The sublattices of the different ions may then disorder at different temperatures and introduce positional disorder of one of the ions in the crystal. Some type of orientational disordering, or crystal-structure changes can also be observed before fusion. As the disordering in the crystal may be gradual, the corresponding entropy may be hidden within the common increase in heat capacity,[3] again decreasing the transition entropy. For older measurements these gradual entropy changes, and

TABLE I

Entropies of fushion in JK^{-1} mol^{-1} of alkali halides (data in parentheses indicate the melting temperatures)

ION	F^-	Cl^-	Br^-	I^-
Li^+	24.1 (1121 K)	22.6 (883 K)	21.5 (823 K)	19.7 (742 K)
Na^+	25.9 (1268 K)	26.1 (1073 K)	25.6 (1020 K)	25.3 (933 K)
K^+	25.0 (1131 K)	25.4 (1043 K)	25.4 (1007 K)	25.2 (954 K)
Rb^+	24.1 (1068 K)	23.8 (995 K)	24.1 (965 K)	24.0 (920 K)
Cs^+	22.3 (986 K)	22.6 (918 K)	25.9 (909 K)	26.2 (899 K)

even low-temperature transitions, are usually not considered and may account for some otherwise hard-to-explain low entropies of fusion.

Excluding such possible special cases, the other salts seem to follow Richards' rule exceptionally well. The average obtained for 82 salts is 10.9 ± 2.0 JK^{-1} mol^{-1} for each ion of the salts (this average includes the 20 alkali halides from Table I and all but 14 of the above listed 76 salts).

2.2 Salts of Rigid, Nonspherical Ions

If the salt molecules consist of polyatomic molecular ions, the possibility of orientational disorder arises. A critical collection of relevant entropies of fusion from Table 6.2 of Ubbelohde's monograph[13] (also reproduced in Reference 1) give an average of 36.2 ± 9.6 JK^{-1} mol^{-1} for a total of 26 nonionic compounds, a value that includes positional disordering. It will be shown in this paper that for large, rigid, asymmetric ions this value is also reached, but that more symmetric ions have much smaller orientational contributions to the entropy of fusion.

The fusion of symmetrical tetrahedral compounds with carbon at their center offers a first step in the discussions of orientational disorder in salts with nonspherical ions.[14] Their high symmetry permits the molecule to reorient among several equivalent positions. Data on the total entropies of transition exist (in JK^{-1} mol^{-1}) for CH_4 (16.5), CD_4 (18.6), CF_4 (30.5), CCl_4 (30.5), CBr_4 (31.8), $C(CH_3)_4$ (31.1) and $C(CH_2F)_4$ (67.0) (see §9.7 and §10.1 of Reference 14). All compounds exhibit a disordering and an isotropization transition. The value of ΔS_i is for all of these compounds in the range required for positional disordering (7–14 JK^{-1} mol^{-1}). This implies that the high-temperature crystals (phases I) are orientationally disordered and represent, as expected, plastic crystals.[15] In fact, CH_4 and CD_4 are known to be in the plastic crystalline state for most of the crystalline existence temperature.[14,15] Orientational motion still persists at 1.8 K by virtue of spin-isomer conversion and tunneling, thus explaining the low disordering entropy. In most of the other cases, a disordering transition exists at low temperature with a transition entropy of about 20 JK^{-1} mol^{-1}, which is at the lower end of the typical range for ΔS_{orient}. Studies of the motion in the solid state of the listed compounds have revealed the possibility of orientational disorder even at temperatures lower than the disordering transition. This effect satisfactorily accounts for the otherwise low overall entropy of fusion. The case of $C(CH_2F)_4$ is instructive for our later discussion. The difference of $\Delta S_{\text{tr}}^{\text{tot}}$ between $C(CH_2F)_4$ and CF_4 or $C(CH_3)_4$ is about 36 JK^{-1} mol^{-1}, and gives an additional entropy contribution of 9 JK^{-1} mol^{-1} for each C—F bond of the substituent to acquire conformational flexibility. This is close to the expected ΔS_{conf} required for three rotational isomers becoming available on conformational disordering for the —CH_2F group.

A number of salts with polyatomic anions have been studied and transition entropies are available in the literature.[12] Such anions should introduce an orientational contribution of ΔS_f, i.e, exceed the Richards' rule value by about 30 JK^{-1} mol^{-1}. Instead of such large positive deviations, only small, and sometimes even negative, deviations from Richards' rule are observed. The average total entropy of fusion per anion for 49 salts of Reference 12 is 16.0 ± 5.7 JK^{-1} mol^{-1} (using 10 JK^{-1} mol^{-1} for the entropy of fusion of the cation). The average value is higher than typical positional entropy of fusion, but not sufficiently high to account for full orientational disordering at the transition. In six sulfates the average per ion is only 7.6 ± 3.5 JK^{-1} mol^{-1}, a value sufficiently low to point towards retention of the order in the melt. For seven nitrates, the average per ion is 11.8 ± 6.3 JK^{-1} mol^{-1}, leaving also only barely recognizable orientational contribution. The low ΔS_{orient} is probably linked to the high symmetry of most of the analyzed anions, which permits many equivalent positions among which they can exchange without gain in entropy. This argument is corroborated by salts that have large asymmetric anions (e.g., $Ca_2P_2O_7$, $\Delta S_f = 62\ JK^{-1}\ mol^{-1}$ and $K_2Cr_2O_7$, $\Delta S_f = 55\ JK^{-1}\ mol^{-1}$).

Ammonium halides are the lowest homologs of alkylammonium salts; they have been studied with both thermodynamic and spectroscopic methods. Some information relating to transitions of the ammonium halides is summarized in Table II. All data, as well as the following discussion in this section, are based on Chapter 7 of Reference 14 and individual papers of the extensive literature are cited there.

The average total transition entropy for the halides is 15.4 ± 2.3 JK^{-1} mol^{-1}. Above the highest-temperature transition, all have the *fcc* (NaCl-like) crystal structure. Ultimately the crystals sublime, without ever reaching the liquid state. Of the other salts of Table II, the ones that also reach a cubic structure of high temper-

TABLE II

Thermodynamic parameters of ammonium salt transitions[a]

Salt	T_{tr} (K)	ΔS_{tr} ($JK^{-1}mol^{-1}$)	ΔS_{tr}^{tot}
Cl^-	242.5, 457.6	5.7, 9.8	15.5
d–Cl^-	249.7, 442	(not given), 9.7	(9.7)
Br^-	107.5, 235.1, 411.2	1.1, 3.0, 9.0	13.1
d–Br^-	166.7, 215.05, 391	3.4, 1.9, 9.1	14.4
I^-	231.0, 257	4.6, 13.1	17.7
SO_4^{2-}	223.1	17.5	17.5
d–SO_4^{2-}	223.6	17.5	17.5
BeF_4^{2-}	176	7.9	7.9
d–BeF_4^{2-}	179	9.6	9.6
HSO_4^-	154, 270	8.7, 2.1	10.8
ClO_4^-	511.2	19.5	19.5
BF_4^-	461.9	19.1	19.1
PF_6^-	131.3, 191.8	10.3, 9.3	19.6
SiF_6^{2-}	38.6	5.8	5.8
$SnBr_6^{2-}$	144.8	18.7	18.7
$SbBr_6^{2-}$	212, 236	2.8, 2.9	5.7
NO_3^-	256.2, 305.38, 357.2, 399.0	1.7, 5.6, 3.8, 11.1	22.2

[a] Only the anion is shown; *d* indicates a perdeuterated ammonium ion; multiple transitions are listed in respective sequence; all salts remain crystalline at the highest transitions listed and ultimately sublime.

atures, also have higher entropies of transition. The generally low values of the transition entropy indicate that the NH_4^+ cations are disordered already below the first transition. Critical in terms of the ammonium cation motion is the barrier to reorientation, which is largely determined by the anion. In halides, for example, the barrier to reorientation changes with the size of the halide ion, decreasing in the order $Cl^- > Br^- > I^-$. For the polyatomic anions, the negative charge is distributed among several atoms and the barriers are thus lower than for the halides. For ClO_4^-, BF_4^-, and PF_6^- the barrier is so low, that reorientation is facile down to the lowest temperatures.

In the case of NH_4Cl the ammonium ions gain some orientational disorder at the low-temperature transition (III → II), with an entropy of 5.7 JK^{-1} mol^{-1}.[14] The disorder involves two different orientations of the N—H bonds with respect to the chloride ions towards which they are directed ($\Delta S \approx R\ln 2$). In phase II there is a gradual further change in disorder, as evidenced by a gradual increase in heat capacity, due to the ions making use of orientations other than the two mentioned above. The bromides have an additional phase at low temperatures, phase IV. It corresponds to phase III of NH_4Cl and changes only little on going to phase III. The III → II transition involves a 90° flipping of the ammonium ions, coupled to displacements of the bromide ions. In both phases I and II of the halides the motion of the ammonium ion is a large-amplitude libration about the N—H—X axis, with a rate of reorientation increasing with temperature.[14]

The motion in ammonium salts other than halides also involves reorientation of the anions. For the nitrate there are at least five stable crystal forms and the cations have some orientational freedom even in the lowest-temperature phases, IV and V, while in phase I they can also diffuse in the crystal. The orientational disordering of the nitrate ions begins probably in phase III and it reorients among 2 and 4 positions in phases III and II, respectively.

To summarize, the orientational entropy gained in disordering transitions of small, symmetric, rigid ions may be smaller than deduced from large, nonspherical, rigid molecules. The reason for this small entropy may be attainment of disorder outside of a sharp transition or smaller values of ΔS due to limited disorder. It will be shown in the course of this research that the additional conformational motion possible in flexible, large, asymmetric ions is easier to interpret.

3. EXPERIMENTAL

3.1 Samples

All commercially available symmetrical tetra-*n*-alkylammonium halides were purchased for a systematic investigation of the transition behavior. In this report the bromides and iodides are treated. The analysis of the chlorides is more involved and is still in progress. $(CH_3)_4NBr$, $(C_4H_9)_4NI$, $(C_6H_{13})_4NBr$, $(C_7H_{15})_4NBr$, $(C_8H_{17})_4NBr$, $(C_{10}H_{21})_4NBr$, $(C_{12}H_{25})_4NBr$, $(C_{16}H_{33})_4NBr$, and $(C_{18}H_{37})_4NBr$ were purchased from Fluka Chemical Corp. (980 South Second Street, Ronkonkoma, NY 11779); $(C_2H_5)_4NI$, $(C_3H_7)_4NI$, $(C_5H_{11})_4NBr$, $(C_5H_{11})_4NI$, $(C_6H_{13})_4NI$, and $(C_7H_{15})_4NI$ from Eastman Kodak Company (Rochester, NY 14650); $(C_{12}H_{25})_4NI$

from Lancaster Synthesis Ltd. (P.O. Box 1000, Windham, NH 03087); $(CH_3)_4NI$, $(C_2H_5)_4NBr$, $(C_3H_7)_4NBr$, and $(C_4H_9)_4NBr$ existed already in our laboratory, kindly provided by Professor G. Janz of Rensselaer Polytechnic Institute. The purities were approximately 99% in all cases. All samples were used as received, but kept in a desiccator filled with $CaSO_4$. Transfer of samples to the DSC aluminum pans for measurement and all other sample handling was done in a glove bag under an atmosphere of dry nitrogen.

We chose to still use the older samples that existed in our laboratory, as storage for a long time (in dark vials) results in improvement rather than deterioration of the samples. We also decided not to recrystallize our samples from solution, as it was shown that this does not always produce better crystals.[16]

3.2 Calorimetry

For preliminary measurements, including sublimation and decomposition, the Mettler FP-800 DSC system was used. All samples were run from room temperature to 670 K with a check of mass loss after completion of the run. The Mettler instrument was calibrated for temperature and heat of fusion using indium.

The samples were subsequently run in a Perkin-Elmer DSC-7 for a quantitative study of the transitions outside of the decomposition or sublimation range. The instrument had been calibrated for temperature with naphthalene and indium, and for heat of fusion with indium. The lowest achievable temperature was 230 K.

In addition, the temperature range from 140–230 K was checked for additional transitions using the TA Instruments (previously DuPont) single-run DSC-2100.[17] The samples were cooled at 5 K/min to 140 K, and left there for 30 min to equilibrate. For all three instruments, the experiments were done in a dry nitrogen gas atmosphere at a heating rate of 10 K/min. In all cases, sample weights ranged from 5–25 mg. In order to verify whether fusion had indeed occurred at the highest-temperature transition, a digital melting point apparatus with capillary sample containers (model MFB-595 from Gallencamp company) was also used for visual verification.

4. RESULTS

All measured thermodynamic data relevant to the current discussion are listed in Table III. Two additional transitions of $(C_6H_{13})_4NBr$ from the literature are also included in the Table, for reasons explained in the Discussion. Some characteristic DSC traces are reproduced in Figure 1. They represent different types of behavior, as elaborated in the Discussion.

No transitions are observed for the methyl compounds before sublimation. The ethyl and propyl salts do not melt at the highest transition included in Table III, as was seen in the melting point apparatus. Melting occurs in these compounds along with sublimation and possible decomposition at higher temperatures. In the low-temperature range from 140–230 K only minor transition peaks were found for $(C_3H_7)_4NI$, $(C_6H_{13})_4NBr$, and $(C_{12}H_{25})_4NBr$. Their transition parameters changed significantly after thermal cycling. The parameters included in Table III were the

TABLE III

Thermodynamic parameters of symmetric tetra-*n*-alkylammonium halide first-order transitions[a]

Salt	T_{tr} (K)	ΔS_{tr} ($JK^{-1}mol^{-1}$)	ΔS_{tr}^{tot}
Bromides			
(C_2H_5)	448.3, 462.6	44.6, 3.2	47.8
(C_3H_7)	382.2, 395.8	44.4, 0.9	45.3
(C_4H_9)	367.0, 379.2, 393.9	41.2, 1.4, 37.6	80.2
(C_5H_{11})	374.0	97.9	97.9
(C_6H_{13})	148, 167, 196, 305, 315, 374.9	8.1, 1.2, 17.5, 22, 38, 42.6	129.4
(C_7H_{15})	339.5, 366.5	13.5, 99.3	112.8
(C_8H_{17})	323.2, 374.1	11.0, 118.0	129.0
$(C_{10}H_{21})$	348.6, 363.4	160.8, 102.6	263.4
$(C_{12}H_{25})$	225.4, (346.5, 362.6)	6.4, (128.1, 206.7)	341.2
$(C_{16}H_{33})$	(370.9, 377.7)	(237.7, 251.9)	489.6
$(C_{18}H_{37})$	(375.1, 379.9)	(226.7, 328.6)	555.3
Iodides			
(C_2H_5)	471.3	44.3	44.3
(C_3H_7)	225.4, 418.9	6.4, 35.8	42.2
(C_4H_9)	394.0, 420.6	71.2, 21.3	92.5
(C_5H_{11})	(404.6, 412.1)	(41.2, 94.0)	135.2
(C_6H_{13})	(345.1, 352.3), 378.7	(83.3, 16.2), 43.9	143.4
(C_7H_{15})	355.4, (391.0, 398.7)	26.1, (6.2, 97.9)	130.2
$(C_{12}H_{25})$	284.1, (343.4, 351.2, 364.6), 388.7	12.3, (12.6, 109.1, 15.1), 122.2	271.3

[a] Parentheses indicate a multiple, overlapping transition; for assignment of the transitions see text.

largest ones determined. The special case of $(C_6H_{13})_4NBr$ is described in the Discussion.

Considerable work on alkylammonium salt transitions has been reported before. In particular, the methyl-substituted ammonium halides have been studied in detail. The first thermal analysis study was reported in 1940.[18] The heat capacity of $(CH_3)_4NI$ was measured and no transitions were seen from 10 K to room temperature. Heat capacities of $(CH_3)_4NCl$ and $(CH_3)_4NBr$ were also measured.[19] Two transitions at 75.8 and 184.8 K with a total of 2.1 JK^{-1} mol^{-1} were seen for the chloride, and none for the bromide. Above room temperature, an additional transition occurs at 536 K for $(CH_3)_4NCl$[20] and its transition entropy was measured[21] to be 23.4 JK^{-1} mol^{-1}. No transitions were seen for the iodide and the bromide from 293 K to 593 K,[19] as also observed in the present work. Above 600 K all salts sublime and decompose.

Janz and coworkers have investigated thermodynamically 34 tetraalkylammonium salts from 250 K to a few kelvins above melting.[16,22] The studied compounds

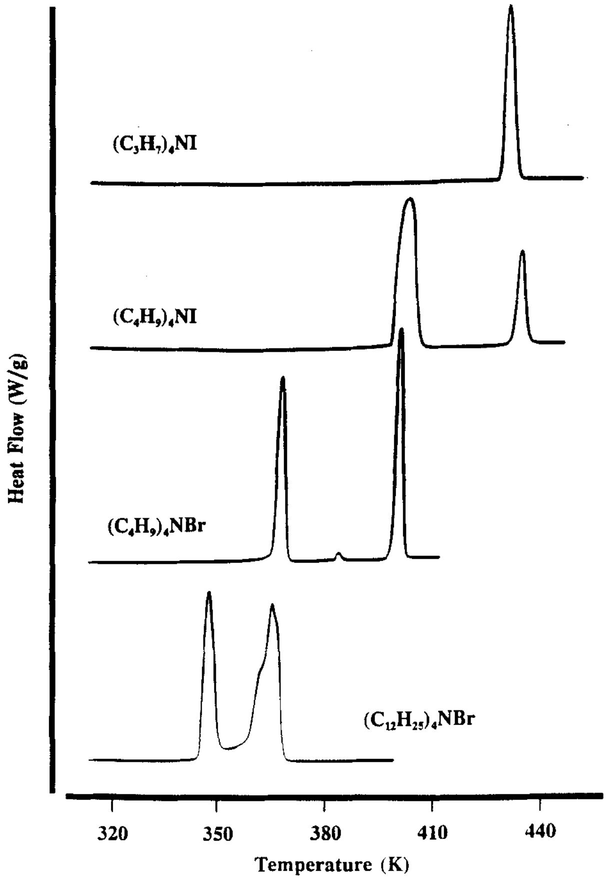

FIGURE 1 Typical DSC traces for tetra-*n*-alkylammonium halides: $(C_3H_7)_4NI$ has a single disordering transition to a plastic crystal; $(C_4H_9)_4NI$ has a disordering transition to a plastic crystal and an isotropization transition; $(C_4H_9)_4NBr$ has a disordering transition to a condis crystal, a minor transition probably related to some crystal readjustment, and an isotropization; $(C_{12}H_{25})_4NBr$ has a double transition, the first peak representing conformational disordering and the second peak representing isotropization.

included both halides and other miscellaneous anions, as well as symmetrical and asymmetrical cations. The agreement with our data is substantial, except for $(C_3H_7)_4NI$ and $(C_6H_{13})_4NBr$; this disagreement is resolved in the Discussion. All symmetrical salts other than halides are listed in Table IV. For all the salts of the large collection studied,[22] the volume change on melting is much smaller than for comparable paraffins and alkali metal halides.

Gordon and coworkers have also studied alkylammonium salts, focusing their research on the properties of the melt. Their results on $(C_6H_{13})_4NClO_4$ from Reference 23, and on $(C_5H_{11})_4NClO_4$ and $(C_5H_{11})_4NBPh_4$ from Reference 24 are also included in Table IV. Finally, Levkov *et al.* studied iodides by DSC and infrared spectroscopy above 200 K.[25] The agreement with our data is very good.

Finally, some melting points are reported in the literature,[26] as follows: $(C_8H_{17})_4NI$ (400.6 K), $(C_{10}H_{21})_4NI$ (392.2 K), $(C_{14}H_{29})_4NI$ (387.9 K), $(C_3H_7)_4NClO_4$ (511.2

TABLE IV

Thermodynamic parameters of tetra-*n*-alkylammonium salts obtained from the literature[a]

Salt	T_{tr} (K)	ΔS_{tr} ($JK^{-1}mol-1$)	ΔS_{tr}^{tot}
$(C_3H_7)_4NBF_4$	397, 512	36.8, 28.0	64.8
$(C_3H_7)_4NBPh_4$	468, 480	48.5, 25.5	74.0
$(C_4H_9)_4NNO_3$	366, 392	0.4, 37.7	38.1
$(C_4H_9)_4NBF_4$	341, 439	19.7, 24.3	44.0
$(C_4H_9)_4NBPh_4$	458, 502	14.2, 77.0	91.2
$(C_4H_9)_4NPF_6$	366, 517	28.0, 32.6	60.6
$(C_5H_{11})_4NNO_3$	366, 387	34.3, 74.1	108.4
$(C_5H_{11})_4NSCN$	315, 322	72.4, 59.8	132.2
$(C_5H_{11})_4NClO_4$	364, 391	92.0, 50.2	142.2
$(C_5H_{11})_4NBPh_4$	477	33.5	33.5
$(C_6H_{13})_4NNO_3$	323, 345	69.0, 51.5	120.5
$(C_6H_{13})_4NClO_4$	334, 356, 368, 379	68.9, 16.4, 7.2, 43.1	135.6
$(C_6H_{13})_4NBF_4$	334, 367	58.6, 52.7	111.3
$(C_7H_{15})_4NClO_4$	356, 365, 388, 399	13.0, 13.0, 11.3, 79.5	116.8

[a]See text for references

K), $(C_4H_9)_4NClO_4$ (486.6 K), $(C_3H_7)_4NNO_3$ (533.2 K), $(C_4H_9)_4NSCN$ (399.8 K), $(C_3H_7)_4NPic$‡ (392.7 K), $(C_4H_9)_4NPic$ (363.4 K), and $(C_5H_{11})_4NPic$ (347.1). No heats or entropies of fusion were given in this publication.

5. DISCUSSION

5.1 Comparison of the New Measurements with Literature Data

The agreement of the new data with the two publications reporting on tetra-*n*-alkylammonium halides[22,25] is good. Table III contains 45 transition temperatures and corresponding entropies. In Reference 22 we find 17 of these and most agree within typical DSC error limits (1% in temperature, 5% in entropy). Similarly, most of the 13 transitions of Reference 25 are within these limits. Besides $(C_3H_7)_4NI$ and $(C_6H_{13})_4NBr$, that will be discussed below, there are two transition entropies of larger error [$(C_5H_{11})_4NBr$, + 12%[22]; $(C_5H_{11})_4NI$, − 17%[25]], and two transition temperatures that were outside the present error limits [$(C_4H_9)_4NBr$, + 5 K[22]; $(C_3H_7)_4NI$, − 6 K[25]]. These disagreements cannot be easily explained, but the prior measurements were done on the older Perkin-Elmer DSC-1B instrument, furthermore the instrument used in Reference 25 was uncalibrated. We expect that these discrepancies are due to systematic errors. Given the fact that the present

---

‡Pic means picrate. Picric acid is 2,4,6-trinitrophenol.

experiments cover a much wider temperature range, were repeated several times on separate samples, and that a well-calibrated and optimized instrument was used, and in order to keep the consistency between all reported data, we discuss only the new data even for those samples where somewhat different older data exist.

In all cases where transitions were observed below room temperature, their entropies were small. These transitions are often indicative of minor adjustments in the crystal structure. The transition parameters and the appearance of these transitions depend significantly on thermal history (cooling rate and waiting time at the low temperature). It is therefore quite difficult to give close-to-equilibrium values for these. We give the largest values that we could obtain. For example, $(C_3H_7)_4NI$ has a transition at 225 K, and our determined entropy is almost half that quoted in Reference 25. The absolute error, however, only amounts to about 6 JK^{-1} mol^{-1}. We therefore also include our value for that compound in Table III. Fortunately all samples show their major transitions at higher temperatures, where equilibrium is more easily attained.

The entropy for the major transition of $(C_3H_7)_4NI$ (Table III) is in agreement with the value determined in Reference 25, but is less than half the value given in Reference 22. Provided the fact that we performed five measurements using three different instruments, the high value cannot be substantiated and is disregarded in the present discussion.

The case of $(C_6H_{13})_4NBr$ of Table III is more puzzling. Compared to Reference 22, the new standard DSC traces are missing two transitions (at 305 K and 315 K totalling 60.3 JK^{-1} mol^{-1}). The sample that we used gave erratic results in the temperature range of these two transitions, when using different thermal histories. Slow cooling of the as-received sample from room temperature to 230 K with subsequent heating gave only the high-temperature transition peak (374.9 K, 42.6 JK^{-1} mol^{-1}). Heating directly from room temperature gave an additional small peak at 360.7 K, but the total entropy was only about 31.2 JK^{-1} mol^{-1}, a clear sign of incomplete crystallization. Reheating after quick cooling to 230 K gave an exotherm at 282 K, followed by an endotherm at 304.7 K with the same area as the exotherm (16 JK^{-1} mol^{-1}), but less transition entropy than reported in Reference 22. This close to room temperature transition could not be reproduced in other runs, even after careful cycling performed specifically for the purpose of producing the special crystal structure. The second transition of Reference 22 was never observed by us. A related observation was the high hygroscopicity of this sample,[27] as opposed to other similar alkylammonium salts. Water usually diffuses into amorphous or disordered samples, rather than into perfect rigid crystals. Metastability of the high-temperature crystal form of $(C_6H_{13})_4NBr$ can perhaps explain all these different observations. We suggest that the two additional transitions found in Reference 22 result from a sample with a more stable low-temperature crystal form. We therefore included the additional two transitions in Table III (305 K, 315 K). Our new data on the other transitions of this salt were in agreement with Reference 22.

Melting points for $(C_3H_7)_4NBr$ and $(C_3H_7)_4NI$ are quoted in the literature[26] as 525 and 553 K, respectively. The present thermal analyses showed sharp transitions with onsets around 500 and 515 K, and peaks at 553 and 554 K, respectively. The entropies of these transitions are, however, extremely high. In addition, there was about 99% weight loss of the samples after the transition. This indicates that, even if melting begins at these temperatures, it is within the sublimation range of these salts. Neither the peak temperatures nor the transition entropies were very reproducible and are not included in the present discussion.

5.2 Conformational Disorder

The halide compounds were chosen for this research because the halide anion, naturally, does not contribute to the $\Delta S_{\mathrm{orient}}$, and its melting entropy can easily be separated from the entropy changes of the cation. In this way, the different types of disorder in the alkyl segments can be discussed. The discussion of the entropy of fusion of simple ionic salts, above, has provided a value for ΔS_{pos} of about 10 JK^{-1} mol^{-1} per ion. Furthermore it was suggested that an average value of about 25 JK^{-1} mol^{-1} is expected for $\Delta S_{\mathrm{orient}}$. Subtracting these values from the total entropy of fusion should give ΔS_{conf} gained within the transition ranges. The number of bonds that gain conformational mobility can furthermore be obtained by dividing ΔS_{conf} by 9 JK^{-1} mol^{-1}, the average conformational entropy of fusion per bond becoming flexible.

Observation of molecular models indicates that, for alkyl chains longer than ethyl, the first two bonds adjacent to the nitrogen atom do not have rotational freedom due to steric repulsions, an observation already made by Janz.[22] The methyl-group rotation at the end of alkyl chains is facile already at very low temperatures and has been studied in detail.[28,29] The methyl-group rotation can therefore not contribute to conformational entropy changes of the cation in the transitions regions. In other words, only a maximum of $n - 3$ bonds (per alkyl chain with n carbons) are able to acquire conformational freedom.

These simple considerations point to three different groups of compounds. (1) The low homologs (methyl, ethyl, and propyl) may have orientational and positional contributions, but are not expected to have conformational entropy contribution to fusion. (2) The salts that have long alkyl chains (octyl and higher) are dominated by conformational entropies of transition. The orientational and positional entropies are only found at the ultimate isotropization. (3) The intermediate homologs may exhibit a combination of the two types of behavior and need detailed analysis.

5.3 Short-Chain Tetra-*n*-Alkylammonium Halides

Of the methyl salts, only the chloride has a disordering transition (23.4 JK^{-1} mol^{-1}). This entropy is comparable to the transition entropies found for the ammonium salts (Table II) and should represent orientational disordering of the cation. The lower density of the chloride salt, determined from the known crystal structures of the methyl salts,[30] is in accord with a reorientation of the cation starting at this first-order transition. For the denser iodide and bromide, only librations or jump motions are possible, leading to a higher heat capacity, but showing no first-order transition.[29]

For the ethyl and propyl salts of Table III, only $\Delta S_{\mathrm{orient}}$ is seen experimentally at a disordering transition, leading to a plastic crystal state stable up to the sublimation or decomposition. The average value for the transition entropy is 44.9 ± 2.3 JK^{-1} mol^{-1}, within the range given by Walden's rule for $\Delta S_{\mathrm{orient}}$ only. It is, however, higher than the value found for the ammonium and tetramethylammonium halides. The larger value is most likely linked to the higher asymmetry of the cations. Even if one were to accept the lower $\Delta S_{\mathrm{orient}}$ of the more symmetric cations of Table II, there would not be enough ΔS_{conf} to account for the conformational disordering of more than 0.25 bonds per alkyl chain.

5.4 Intermediate-Chain Tetra-*n*-Alkylammonium Halides

The next group of tetra-*n*-alkylammonium salts contains butyl through heptyl side chains. The total entropies of fusion of these salts are 10–20% higher for the iodides than for the bromides, while the isotropization temperatures of the iodides are also higher than for the bromides. This may well be related to the higher volume change of the iodides on transition,[22] that must be coupled to a higher enthalpy change ($T_{tr} = \Delta H_{tr}/\Delta S_{tr}$). The isotropization temperatures are the highest for the short-chain compounds, decrease for the intermediate cases, and start to increase again for the long-chain compounds. This trend reflects the transition between two largely different crystal structures, an almost purely ionic one for the low alkyl chain lengths, to an essentially paraffinic one for long alkyl chains. A distinct minimum for $(C_6H_{13})_4NI$ is therefore not unexpected, and needs to find its explanation in its still not explored crystal structure.

The $(C_4H_9)_4NI$ has an entropy of isotropization at 420.6 K that can account only for positional disordering, i.e. the mesophase, stable between 394.0 and 420.6 K, must be a plastic crystal with maximum conformational disorder. At the low-temperature transition, orientational disordering of the cation and conformational disordering for about one bond per alkyl chain occur, as is expected from the number of bonds able to gain mobility discussed above ($n - 3$). For the bromide, in contrast, orientational and positional disordering seem to occur both at the isotropization temperature, i.e. the mesophase, stable between 367.0 and 393.9 K, should be a condis crystal and not a plastic crystal.

Both hexyl salts have about an entropy of transition of 43 JK^{-1} mol^{-1} at their isotropization temperature and are therefore also only condis crystals in the mesophase. The entropy of the combined disordering transitions is enough to account for approximately three bonds per alkyl chain to become flexible, as expected. Multiple transitions between different condis crystals have also been observed for other paraffinic condis materials and are an indication of stepwise attainment of conformational disorder.[3]

The four pentyl and heptyl salts have an entropy change of about 100 JK^{-1} mol^{-1} at their isotropization temperature. This value is high enough to contain conformational entropy for one to two bonds becoming flexible per alkyl chain, in addition to the positional and orientational entropy. For $(C_5H_{11})_4NBr$, within the limits of our approximations, all order is lost in one step. For $(C_5H_{11})_4NI$, on the other hand, one bond per alkyl chain becomes mobile slightly below the isotropization temperature, giving for a temperature range of 7.5 K a condis crystal with half of the total possible conformational disorder.

The two heptyl salts have total entropies of transition lower than their hexyl counterparts. The low-temperature transitions have enough entropy for disordering of only one bond or less per alkyl chain. There are two possible explanations for this observation. The first is that the equivalent of one to two bonds of the alkyl segments can be already disordered below the transitions observed (i.e. did not crystallize). The second explanation may be the existence of a gradual transitionless disordering, as found, for example, for the alkyl chains in OOBPD.[10] X-ray diffraction and heat capacity measurements together with solid-state NMR, planned in our laboratory, should be able to resolve this question.

The odd-even effect in the ΔS_i of this group (the even-n salts have a low ΔS_i compared to the odd-n ones) has been already noted in the past.[25] Based on a swastika-like structure that $(C_2H_5)_4NI$ is known to have,[31] the authors suggested that the higher even-n salts also have this structure before their isotropization transition. This would result in a more coiled-up cation, requiring a smaller entropy for melting. The same reasons were put forth to explain the similarity of entropies for the ethyl and propyl salts. Using the concepts that we propose here, these arguments say that all disordering occurs at the fusion transition for odd-n salts. Detailed crystal structure determinations are needed to elucidate this point.

5.5 Long-Chain Tetra-*n*-Alkylammonium Halides

With increasing alkyl chain length $\Delta S_{\mathrm{orient}}$ becomes gradually less important in comparison to ΔS_{conf}, as is also typically seen for linear macromolecules.[1] The cation is too large to reorient below isotropization and most of the entropy of transition into the mesophases is accounted for by conformational disordering.

Of the higher halide homologs, the bromides with 10, 12, 16, and 18 carbon atoms in their alkyl chains behave as expected, with enough entropy for $n - 3$ bonds to become flexible. Conformational disordering occurs in a step with a large entropy gain, but the condis phase goes to an isotropic melt only 5 to 15 K higher. This short range of stability is more evident with increasing alkyl chain length. A lower entropy of transition is noted for $(C_8H_{17})_4NBr$ and for $(C_{12}H_{25})_4NI$, indicating an additional entropy deficit for two bonds per alkyl chain. Alternatively, the average entropy per bond becoming flexible might be less than the typical value of 9 JK^{-1} mol^{-1}, due to difficulties in crystallization or due to disordering outside of the transition region, again to be studied by X-ray diffraction, heat capacity, and solid-state NMR.

5.6 Tetra-*n*-Alkylammonium Salts with Polyatomic Anions

Salts other than halides can be discussed based on the literature data of Table IV. They demonstrate a more complicated transition behavior. The BF_4^- and BPh_4^- tetra-n-propyl ammonium salts have a similar entropy of disordering to the plastic crystalline phase as the bromides and iodides, but these salts undergo as the last transition an isotropization to the melt. One finds, thus, an additional 20 and 30 JK^{-1} mol^{-1} that accounts for the remaining positional disordering of the plastic crystals.

Of the tetra-n-butyl ammonium salts, only the tetraphenylborate, and perhaps the hexafluorophosphate, behave similar to the iodide and bromide, with enough conformational entropy to account for one bond per alkyl chain. The tetra-*n*-pentyl ammonium salts generally behave also analogous to the iodide and bromide, except for the tetraphenylborate, that shows only enough transition entropy for the positional and orientational entropy in its single transition. The melting mechanism of $(C_5H_{11})_4NSCN$, that has a rod-like anion, was investigated by calorimetry, dilatometry, and electric conductance measurements.[16] Two transitions were observed above room temperature. The high-temperature transition has a reasonable amount of entropy for positional and orientational disordering. In addition, electrical conductance measurements indicate all the increase of conductivity occurring at this transition, thus confirming it is the isotropization. The low-temperature transition has a large ΔS and practically all of the total ΔV measured. It was attributed by the authors to the introduction of one mobile 2*g*1 kink defect[32] (i.e., two gauche bonds separated by a trans bond) in each pentyl group. A related observation was the low volume observed on melting for most of the alkylammonium salts, that do melt.[22] The major structural and packing changes thus occur below melting, and specifically on conformational disordering. The perchlorate and thiocyanate are thus both condis crystals in their mesophase, while the nitrate salt loses conformational order in two steps.

All three tetra-*n*-hexyl ammonium salts behave as the iodides and bromides, with positional and orientational order being lost at the final transition. A conformational disordering of about two bonds per alkyl chain occurs at a lower-temperature transition, giving condis crystals. In the case of $(C_6H_{13})_4NClO_4$ a total of four transitions was observed.[23] The two intermediate transitions involve successive excitation of reorientational modes of the perchlorate anion as was suggested by the authors based on entropic considerations. The transitions of $(C_7H_{15})_4NClO_4$ total to less entropy than expected, similar to the iodide and bromide. The two intermediate transitions observed may be associated with disordering of the perchlorate ion, as was also the case for the hexyl perchlorate.[23] One bond per alkyl chain disorders during isotropization, and one more, at the most, at lower temperatures. For hexyl and heptyl salts, one and two bonds, respectively, are already disordered at room temperature, or disorder without a transition.

The transitions of the non-halide tetra-*n*-alkylammonium salts can, naturally, not be easily discussed ignoring the anion. Surprisingly, the data from Table II on ammonium nitrate, perchlorate, hexafluorophosphate, and tetrafluoroborate do not show any entropy changes larger than for the ammonium halides. These low values cannot be explained by assuming that the anion is not disordering orientationally, as the contrary has been proven experimentally.[14] The explanation for the different behavior of the alkyl-substituted salts might be in different crystal structures caused by the polyatomic anions, or by anion contributions not encountered in the simple ammonium salts.

6. CONCLUSIONS AND FUTURE WORK

Using exclusively entropy data, it is found that the tetra-*n*-alkylammonium halides studied can be separated in three groups, each showing a different type of disordering behavior. Methyl, ethyl, and propyl salts can only have orientational disordering transitions, giving plastic crystals. Salts with four to seven carbon atoms may show a combination of orientational and conformational disordering, giving both the possibility of plastic and condis crystals. Salts with longer alkyl chains can only display conformational disordering. The condis mesophases produced, however, have only a short temperature range of stability.

Work is in progress to address the details of the behaviors found. Heat capacity measurements and calculations might explain entropy deficits noted in some of the cases studied. X-ray diffraction studies will search for possible structure changes that might explain some of the transitions observed. Finally, solid-state NMR will directly address the microscopic details of the motion.

Acknowledgments

Supported by the Division of Materials Sciences, Office of Basic Energy Science, DOE under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. and National Science Foundation, Polymers Program DMR-88-18412. The TA Instruments and the Mettler Corporation are both thanked for support with the instrumentation. Generous help by Professor G. Janz (Rensselaer Polytechnic Institute) is acknowledged for providing some of the samples and for useful discussions on the subject.

References

1. B. Wunderlich, *Macromolecular Physics*, Vol. 3, Academic Press, New York (1980).
2. B. Wunderlich and J. Grebowicz, *Adv. Polym. Sci.*, **60/61**, 1 (1984).
3. B. Wunderlich, M. Möller, J. Grebowicz and H. Baur, *Adv. Polym. Sci.*, **87**, 1 (1988).
4. J. W. Richards, *Chem. News*, **75**, 278 (1897).
5. P. Walden, *Z. Elektrochem.*, **14**, 713 (1908).
6. B. Wunderlich, M. Möller and H. G. Wiedemann, *Mol. Cryst. Liq. Cryst.*, **140**, 211 (1986).
7. H. G. Wiedemann, J. Grebowicz and B. Wunderlich, *Mol. Cryst. Liq. Cryst.*, **140**, 219 (1986).
8. M. Cao, J. Wesson, K. Loufakis and B. Wunderlich, *Mol. Cryst. Liq. Cryst.*, **140**, 231 (1986).
9. M. Möller, D. Oelfin and B. Wunderlich, *Mol. Cryst. Liq. Cryst.*, **173**, 101 (1989).
10. J. Cheng, Y. Jin, G. Liang, B. Wunderlich and H. G. Wiedemann, *Mol. Cryst. Liq. Cryst.* (in press).
11. A. Xenopoulos, A. H. Narten, J. Cheng and B. Wunderlich, *J. Non-Cryst. Solids*, **131–133**, 113 (1991).
12. G. J. Janz, *Molten Salts Handbook*, Academic Press, New York (1967).
13. A. R. Ubbelohde, *The Molten State of Matter*, Wiley-Interscience, Chichester (1978).
14. N. G. Parsonage and L. A. K. Staveley, *Disorder in Crystals*, Clarendon Press, London (1978).
15. J. N. Sherwood (ed.), *The Plastically Crystalline State*, Wiley-Interscience, Chichester (1979).
16. T. G. Coker, B. Wunderlich and G. J. Janz, *Trans. Faraday Soc.*, **73**, 3361 (1969).
17. Y. Jin and B. Wunderlich, *J. Therm. Anal.*, **36**, 765, 1519 (1990).
18. L. V. Coulter, K. S. Pitzer and W. M. Latimer, *J. Am. Chem. Soc.*, **62**, 2845 (1940).
19. S.-S. Chang and E. F. Westrum, Jr., *J. Chem. Phys.*, **36**, 2420 (1962).
20. M. Stammler, *J. Inorg. Nucl. Chem.*, **29**, 2203 (1967).
21. J. Dufourcq, Y. Haget-Bouilland, N. B. Chanh and B. Lemanceau, *Acta Cryst.*, **B28**, 1305 (1972).
22. T. G. Coker, J. Ambrose and G. J. Janz, *J. Amer. Chem. Soc.*, **92**, 5293 (1970).
23. J. T. S. Andrews and J. E. Gordon, *J. Chem. Soc., Faraday Trans. I*, **69**, 546 (1973).
24. J. E. Gordon and G. N. SubbaRao, *J. Am. Chem. Soc.*, **100**, 7445 (1978).
25. J. Levkov, W. Kohr and R. A. Mackay, *J. Phys. Chem.*, **75**, 2066 (1971).
26. J. E. Gordon, *J. Am. Chem. Soc.*, **87**, 4347 (1965).
27. H. Nakayama, *Bull. Chem. Soc. Jpn.*, **54**, 3717 (1981).

28. See, for example: J. E. Anderson and W. P. Slichter, *J. Phys. Chem.*, **69**, 3099 (1965).
29. J. Cheng, A. Xenopoulos and B. Wunderlich, *Mol. Cryst. Liq. Cryst.*, second paper in this series.
30. R. W. G. Wyckoff, *Z. Krist.*, **67**, 91 (1928).
31. E. Wait and H. M. Powell, *J. Chem. Soc.*, 1872 (1958).
32. W. Pechhold, *Kolloid Z.Z. Polymere*, **228**, 1 (1968).