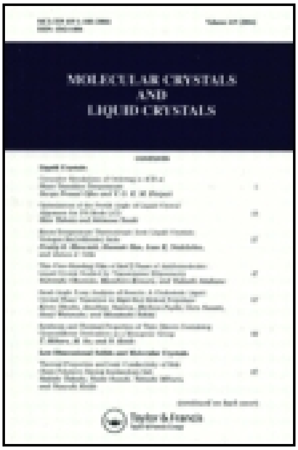

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Mesophases of Alkylammonium Salts. V. Heat Capacities of Symmetric Halides with Alkyl Chains Longer than Ethyl

Alexander Xenopoulos [a] [b] , Jinlong Cheng [a] [b] & Bernhard Wunderlich [a] [b]

[a] Department of Chemistry, University of Tennessee, Knoxville, TN, 37996-1600

[b] Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831-6197

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Mesophases of Alkylammonium Salts. V. Heat Capacities of Symmetric Halides with Alkyl Chains Longer than Ethyl

ALEXANDER XENOPOULOS, JINLONG CHENG and BERNHARD WUNDERLICH

Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600 and Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6197

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The heat capacities of tetra-*n*-alkylammonium bromides and iodides in the solid state have been measured from 130 K through their respective transitions and fitted at low temperatures to two Θ temperatures, using group vibrations computed from the vibrational spectra and the Tarasov analysis, as developed for linear macromolecules. The compounds analyzed were $(C_3H_7)_4NBr$, $(C_4H_9)_4NBr$, $(C_5H_{11})_4NBr$, $(C_6H_{13})_4NBr$, $(C_7H_{15})_4NBr$, $(C_8H_{17})_4NBr$, $(C_{10}H_{21})_4NBr$, $(C_{12}H_{25})_4NBr$, $(C_{16}H_{33})_4NBr$, $(C_{18}H_{37})_4NBr$, $(C_3H_7)_4NI$, $(C_4H_9)_4NI$, $(C_5H_{11})_4NI$, $(C_6H_{13})_4NI$, $(C_7H_{15})_4NI$, and $(C_{12}H_{25})_4NI$. The total vibrational contribution to the heat capacity is thus derived and compared to the experimentally measured heat capacity over the whole temperature range. Positive deviations of the measured heat capacity from the calculation occur already below room temperature, implying the existence of large-amplitude, nonvibrational motion in the solid state, as suggested before by solid-state ^{13}C NMR analysis. Quantitative information on the entropy of disordering generated outside of the transition ranges is derived and agrees with the entropy deficits predicted by the analysis of the first-order transitions. An addition scheme is developed for the heat capacity of the methylene groups in these compounds, that is similar to the paraffins.

Keywords: tetra-n-alkylammonium bromides and iodides, disorder and motion, mesophases, thermal analysis, heat capacity, entropy

1. INTRODUCTION

The thermal transitions of tetra-*n*-alkylammonium salts have been reviewed in the first paper of this series.[1] The discussion of all transition entropies from the literature, combined with new data, has led to the conclusion that empirical rules can give the frame for the discussion of the stages of disordering of the crystals on heating: structurally simple salts are characterized on fusion mainly by positional disordering; if one of the ions is polyatomic (nonspherical), but rigid, orientational contributions are added to the disordering process; in the case of flexible ions, as in alkyl-substituted salts, the conformational contribution to the transition entropy may become large and for sufficiently long alkyl chains, may dominate the transition behavior. For the long-chain alkylammonium salts both the behavior of ionic crystals and that of flexible organic molecules must be understood. A full account of the motion of the alkyl groups, based on solid-state ^{13}C NMR studies was given in papers II to IV of this series.[2]

An observation made during the review of the first-order transitions was that the total changes of state cannot always be accounted for solely by assuming that all the entropy of disordering is gained or lost in the transition regions. Two reasons may cause such a deficit in the total entropy of transition. First, it may be that on initial ordering on cooling, the transition remained incomplete. In this case, the sample structure should be only partially crystalline, as is common in linear macromolecules. The sample properties are then strongly thermal-history dependent. We have studied this thermal-history dependence also for the tetra-*n*-alkylammonium salts, and some problems of such deficit in entropy of ordering could, indeed, be found. A full report of this study will be given at a later date.[3] The second reason may be that motion and disorder can be introduced gradually outside of the temperature region of the transitions.[4] The thermal effect is then an increase in heat capacity beyond that expected from the crystal vibrations. An earlier example of such behavior was shown for a liquid-crystal-forming molecule with flexible end groups, *N,N'*-bis(4-*n*-octyloxybenzal)-1,4-phenylenediamine, OOBPD.[5] For a complete thermal analysis, both the transition parameters and the heat capacities must thus be studied.

In this paper, the heat capacities of a series of tetra-*n*-alkylammonium halides are studied in detail. The salts were chosen so that the linear sections of the cations $CH_3(—CH_2)_{x-1}—N(—CH_2)_{x-1}—CH_3$ have at least seven atoms in the chain. This number of atoms was required in the analysis of *n*-paraffin heat capacities to permit data treatment using the Tarasov function, originally proposed for chain molecules.[6] The measured data are compared to calculations based on approximate vibrational spectra. The deviations are discussed, and the entropy gained gradually through the increase of the heat capacity is evaluated.

2. EXPERIMENTAL

All commercially available symmetrical tetra-*n*-alkylammonium halides were purchased for a systematic investigation of the transition behavior. The samples of $(C_4H_9))_4NI$, $(C_6H_{13})_4NBr$, $(C_7H_{15}))_4NBr$, $(C_8H_{17})_4NBr$, $(C_{10}H_{21})_4NBr$, $(C_{12}H_{25})_4NBr$, $(C_{16}H_{33})_4NBr$, and $(C_{18}H_{37})_4NBr$ were purchased from Fluka Chemical Corp. (980 South Second Street, Ronkonkoma, NY 11779); $(C_3H_7)_4NI$, $(C_5H_{11})_4NBr$, $(C_5H_{11})_4NI$, $(C_6H_{13})_4NI$, 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); $(C_3H_7)_4NBr$ 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

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*Note the abbreviation used in the following for the alkylammonium halides: *nX* indicates a side chain with *n* carbon atoms, and *X* as the anion.

aluminum pans for measurement and all other sample handling was done in a glove bag under an atmosphere of dry nitrogen.

For the measurement of heat capacity (C_p) the TA Instruments TA-2100 DSC was used in order to measure from 130 K. A single-run heat capacity measurement technique was used for the measurements. The details of the measurements of heat capacities have been discussed in previous publications of this laboratory.[7] All samples were cooled at 5 K/min to 120 K, to assure good crystallization. A Liquid Nitrogen Cooling Accessory was specially modified for more cooling efficiency. It was found that cooling at faster rates did not have a systematic effect on the heat capacities. The samples were subsequently heated at 10 K/min up to room temperature. The measured data represent an average of three to five runs performed on two samples. The standard deviation was smaller than 2% in all cases. A single run was then performed above room temperature, using the same samples and instrument. All data were spliced together and fitted to third-order polynomial functions over the whole temperature region up to the first transitions. The standard deviation of the raw and fitted data sets was smaller than 0.5% in all cases, excluding the transition regions. Heat capacities were calibrated with a sapphire standard. Temperature was calibrated using the disordering and melting transitions of cyclopentane, cyclohexane, acetone, *n*-octane, naphthalene, indium, and tin.

3. RESULTS

3.1 Vibrational Spectra

The theory of heat capacity and the methods used to calculate it are well known.[8] With our Advanced THermal Analysis System (ATHAS) a method was developed that permits the computation of the heat capacity of linear macromolecules in the solid state from limited experimental data. In this paper it is shown that this method can be applied also to alkyl-substituted ionic salts of sufficient chain length. Similarly, the applicability was recently tested on a large number of paraffins.[6] In the present work we discuss heat capacities of tetra-*n*-alkylammonium salts with alkyl chains larger than ethyl groups. In summary, the vibrational spectrum of a molecule is separated into skeletal and group vibrations. The latter are known from spectroscopic studies, and their heat capacity contribution can be calculated and subtracted from the experimental heat capacity. The remaining skeletal heat capacity can then be fitted to two parameters Θ_1 and Θ_3, that characterize the skeletal vibrational frequency spectrum. Once an approximate frequency spectrum is known, it can be inverted to heat capacity using for each vibration the Einstein function:

$$C_v/NR = E(\Theta_E/T) = \frac{(\Theta_E/T)^2 \exp(\Theta_E/T)}{[\exp(\Theta_E/T) - 1]^2} \qquad (1)$$

Following the successful analysis of the heat capacities of *n*-paraffins,[6] it seems feasible to treat tetra-*n*-alkylammonium halides with propyl or longer chains in the same way. The group vibrations of the alkyl chains are taken from studies of polyethylene and polypropylene.[9] The analysis of the paraffins[6] showed that this is a good approximation for heptane and larger paraffins.

The number of group vibrations for a CH_2-group is 7 (one C—C or C—N stretching, two C—H stretching and four C—H bending vibrations), for a CH_3-group it is 9 (one C—CH_3 stretching, three C—H stretching and five C—H bending vibrations). In the case of a CH_2-group vicinal to the nitrogen atom, the C—C stretch is substituted by the nitrogen C—N stretch. The C—N stretch is more difficult to identify because of the high symmetry of the central part of the cation. This vibration is active in the Raman and not in the infrared. For the longer alkyl chains a constant frequency distribution was used from 1177 to 1517 K (box term), based on data on tertiary amines.[10]

After choosing the group vibrations, the number of the remaining skeletal vibrations is two and three for the CH_2- and CH_3-groups, respectively. The skeletal vibrations represent the bending and torsional vibrations, both inter- and intramolecularly. For the nitrogen atom there are three skeletal vibrations chosen, representing the three vibrational modes of the center of the cation.

To account for the vibrations of the ionic lattice, one must assume that the 6 lattice vibrations (three for the cation and three for the anion) may be similar to those found in analogous simple bromides and iodides. For RbBr, for example, the heat capacity can be represented by a Debye function with a characteristic temperature of 130 K.[8] This frequency limit is sufficiently low, that the detailed distribution function is of little influence in the temperature range of measurements (above 130 K). For this reason, the six ionic lattice modes are added to the skeletal vibrations of the cation chains and fitted to the experimental skeletal heat capacities. A more detailed accounting will be made for the short-chain salts at a future time. In the short-chain salts proper accounting for the ionic lattice vibrations and chain vibrations is necessary to give a correct heat capacity representation even at higher temperatures, since the lower cation mass increases the frequency limit and shows thus a sizeable temperature-dependent contribution at higher temperatures.

For $(C_3H_7)_4NX$, as an example, the number of skeletal vibrations is 16 for the CH_2-groups, 12 for the CH_3-groups, and 6 for the ionic lattice, to give a total of 34. The group vibrations are 56 for the CH_2-groups, 36 for the CH_3-groups, a total of 92. On lengthening the alkyl chains by one CH_2-group, 28 group and 8 skeletal vibrations must be added to the whole molecule. Table I shows the group vibrations frequencies used in our calculations. Note that the frequencies are expressed in kelvins (1 Hz = 8.40×10^{-11} K).

3.2 Heat Capacities

Tables IIa and IIb show the smoothed experimental data for all measured heat capacities of iodides and bromides, respectively. Gaps in the table reflect the first-order transitions. Their temperatures and heats have been described in Reference 1. Table III shows the parameters used in the calculation of the heat capacities, and the average and RMS errors relative to the experimental data. The average error is defined by $C_p^{meas} - C_p^{calc}$. Note that literature data do not exist for any of these heat capacities. Since data could only be measured above 130 K, only a Θ_1 value could be determined, and is included in Table III. The value of Θ_3 is not

TABLE I

Group vibration frequencies for $[CH_3(C_nH_{2n})]_4NX$*

Assignment	Frequency (K)	N of vibrators
CH_2 group (4*n*)		
asymmetric stretching	4148	1.00
symmetric stretching	4098	1.00
bending	2075	1.00
wagging	1977	0.35
	1698-1977	0.65
twisting	1874	0.52
	1690-1874	0.48
rocking	1494	0.04
	1038-1494	0.59
	1079	0.37
C-C stretching	1375-1638	0.34
	1525	0.31
	1378-1525	0.35
C-N stretch	1177 - 1517	1.00
CH_3 group (4)		
asymmetric stretching	4262	1.00
asymmetric stretching	4259	1.00
symmetric stretching	4147	1.00
C-CH_3 stretching	1568-1614	0.44
	1534-1614	0.56
asymmetric bending	2107	1.00
asymmetric bending	2101	1.00
symmetric bending	1987	0.25
	1973-1987	0.38
	1973	0.37
rocking	1453-1521	0.55
	1453	0.45
rocking	1361-1393	0.65
	1333-1361	0.21
	1336	0.14

* The CH_2- and CH_3- data are taken from Ref. 9, the C-N stretch frequency from Ref. 10.

significant in this temperature range, since one expects the intermolecular vibrations to be largely excited by 130 K, i.e. give a constant contribution to the heat capacity. For the purpose of getting also reasonable heat capacity estimates at low temperatures, Θ_3 was estimated to be 100 K for 5I, 7Br, and 18Br, 170 K for 7I, 12I, 8Br, and 12Br, and 130 K for all other salts.

TABLE IIa

Experimental heat capacities of solid tetra-*n*-alkylammonium iodides

T(K)	3I	4I	5I	6I	7I	12I
130	176.9	224.5	280.0	298.4	319.9	545.2
140	195.6	237.1	292.3	329.4	343.4	585.4
150	210.1	249.5	304.9	357.7	366.7	624.3
160	221.8	261.6	317.7	383.7	390.1	662.0
170	231.6	273.4	330.8	407.6	413.7	699.1
180	240.9	285.1	344.0	429.9	437.5	735.9
190	250.7	296.5	357.5	450.9	461.7	772.7
200	262.4	307.8	371.1	471.0	486.5	809.8
210	276.9	319.0	385.0	490.4	512.0	847.5
220		330.2	399.0	509.6	538.3	886.4
230	273.4	341.2	413.2	529.0	565.4	926.6
240	280.7	352.3	427.5	548.8	593.7	968.5
250	288.9	363.4	441.9	569.4	623.1	1012.4
260	297.8	374.6	456.5	591.2	653.9	1058.8
270	307.4	385.8	471.3	614.5	686.1	1107.9
280	317.4	397.2	486.1	639.7	719.8	1160.2
290	327.7	408.7	501.0	667.2	755.3	1215.8
300	338.3	420.4	516.0	697.3	792.5	1275.2
310	349.0	432.3	531.1	730.3	831.8	1338.8
320	359.7	444.5	546.3	766.6	873.1	1406.8
330	370.2	457.0	561.5	806.5	916.6	
340	380.5	469.7	576.8		962.5	
350	390.3	482.9	592.1		1010.8	
360	399.6	496.4	607.5			
370	408.3		622.9			
380	416.1		638.3		903.3	
390	423.1		653.6		972.5	
400	429.0					
410	433.8					
420						
430	463.1					
440	473.0					
450	485.8					
460	507.1					

For the conversion of C_p to C_v a Nernst-Lindemann type calculation was used, since compressibility and expansivity data are not available[11]:

$$C_p - C_v = 3RA_0C_pT/T_m^\circ \qquad (2)$$

The universal A_0 parameter [3.9×10^{-3} (K mol)/J] was found to represent the data best for 12Br and 18Br, while for the rest we took the value chosen earlier

TABLE IIb

Experimental heat capacities of solid tetra-*n*-alkylammonium bromides*

T(K)	3Br	4Br	5Br	6Br	7Br	8Br	10Br	12Br	16Br	18Br
130	185.8	246.8	287.6	291.3	398.9	395.5	489.9	520.8	667.5	1008.0
140	196.4	253.1	300.4	309.0	402.9	420.9	513.3	565.9	740.5	1024.9
150	206.8	259.8	313.4	325.3	409.6	446.3	538.8	611.1	810.4	1045.4
160	216.9	267.0	326.4	340.2	419.0	471.7	566.2	656.2	877.4	1069.4
170	226.7	274.7	339.7	353.7	431.1	497.4	595.1	701.4	941.6	1097.0
180	236.3	283.0	353.1	365.8	445.8	523.6	625.4	746.6	1003.4	1128.0
190	245.7	291.9	366.8	376.6	463.2	550.4	656.8	791.7	1063.0	1162.5
200	254.9	301.4	380.7	386.0	483.1	578.1	689.1	836.9	1120.5	1200.6
210	263.9	311.5	394.9	394.1	505.6	606.7	722.1	882.0	1176.1	1242.1
220	272.8	322.3	409.4	400.8	530.7	636.5	755.4		1230.1	1287.2
230	281.4	333.8	424.3	406.1	558.2	667.6	789.0	919.6	1282.7	1335.7
240	290.0	346.1	439.6	410.0	588.2	700.3	822.5	953.2	1334.1	1387.8
250	298.3	359.1	455.2		620.7	734.7	855.6	991.2	1384.5	1443.4
260	306.6	372.9	471.3		655.6	770.9	888.3	1033.7	1434.1	1502.5
270	314.8	387.5	487.8		692.9	809.3	920.1	1080.6	1483.1	1565.1
280	322.8	402.9	504.9		732.5	849.8	951.0	1131.9	1531.8	1631.3
290	330.8	419.3	522.5		774.6	892.8	980.5	1187.7	1580.4	1700.9
300	338.7	436.5	540.6		818.9	938.4	1008.6	1247.9	1629.1	1774.1
310	346.6	454.7	559.3		865.5	986.8	1035.0	1312.5	1678.0	1850.7
320	354.4	473.9	578.6		914.3		1059.4	1381.6	1727.4	1930.9
330	362.3	494.0	598.5		965.4		1081.6	1455.1	1777.6	2014.6
340	370.1	515.2	619.1		1018.7			1533.0	1828.7	2101.7
350	377.9	537.4	640.4						1880.9	2192.4
360	385.7									
370	393.6									
380										
390										
400										
410	479.0									
420	489.4									
430	507.1									

* In both Tables 2a and 2b, empty spaces correspond to transition regions.

for the paraffin analysis [3.18 × 10^{-3} (K mol)/J].[11] The isotropization temperature was used in the C_p to C_v conversion instead of the melting temperature in these crystals. As a measure of comparison, note that the analysis of more than 100 polymers calculated in the past, showed an average deviation of about 3%.

The comparison between the calculated and the experimental data is shown in Figures 1 and 2, for the iodides and the bromides, respectively. The fit is usually satisfactory at low temperatures. The larger negative deviations of the calculated from the experimental data, seen at higher temperatures, will be interpreted as the

TABLE III

Parameters for R4NX heat capacity calculation*

Salt	#skeletal	T_m^* (K)	θ_1 (K)	avg ± rms error (T range)
3Br	34	553	596	0.0 ± 2.2 (130-370)
3I	34	554	630	0.3 ± 0.8 (230-400)
4Br	42	394	633	-0.1 ± 2.6 (140-320)
4I	42	421	623	1.4 ± 1.5 (130-360)
5Br	50	374	567	-1.0 ± 1.0 (130-280)
5I	50	412	604	-0.3 ± 0.8 (130-390)
6Br	58	375	(689)	1.1 ± 1.2 (130-170)
6I	58	379	(589)	—
7Br	66	367	615	-0.2 ± 2.6 (140-240)
7I	66	399	644	1.8 ± 2.9 (140-210)
8Br	74	374	595	0.3 ± 1.9 (130-190)
10Br	90	363	597	0.6 ± 1.9 (130-220)
12Br	106	363	602	0.3 ± 2.9 (150-270)
12I	106	389	647	-1.0 ± 1.3 (130-170)
16Br	138	378	(588)	—
18Br	154	380	551	-0.3 ± 1.8 (150-300)

* The last column represents the percent average difference of calculated minus experimental heat capacity, over the temperature range indicated, with its RMS deviation. For the special cases of 6Br, 6I, and 16Br, see text.

additional entropy gain due to initiation of large-amplitude motion outside of a first-order transition. For the salts 6I and 16Br, an increase of the experimental heat capacity was noted below room temperature, of the magnitude expected for one or two CH_2-groups in the side chain obtaining mobility. To make sure that these discrepancies are not due to some systematic experimental error, the measurements were repeated, but without change in the results. For clarity for these two salts only experimental data are shown in Figures 1 and 2.

3.3 Addition Scheme

An empirical addition scheme was developed for the measured heat capacities of the tetra-*n*-alkylammonium salts. The raw (unsmoothed) data below room temperature were used, and iodides and bromides were treated together (the data for 6Br were not included in the fit, because of the intervening exotherm, discussed in Reference 1). In the procedure we assumed that the heat capacity of each compound is an additive contribution from methylene groups and the rest of the

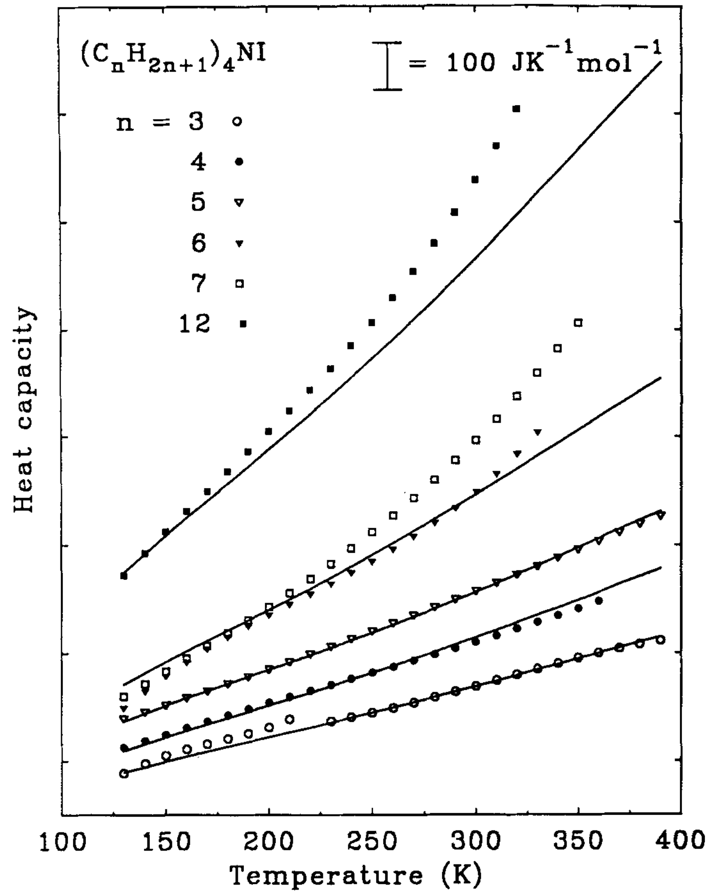

FIGURE 1 Experimental (symbols) and calculated (lines) heat capacities for tetra-*n*-alkylammonium iodides with alkyl chains longer than ethyl. Note the omission of calculated data for 6I.

molecule. A linear fit of all data was performed at each temperature. Given the large variation of the number of methylene groups, it is possible to obtain a heat capacity contribution for the methylene group as a function of temperature. Table IV shows the heat capacity contributions of the methylene group, and of the rest of the molecule (the latter with its standard deviation). Also listed is the deviation of the addition-scheme CH_2-group heat capacity from the polyethylene heat capacity.[6] The heat capacity contribution of four methyl groups taken from even paraffins is listed in the last column of Table IV.[6] The average and RMS deviation for the calculation of the methylene group heat capacity was 1.9 ± 0.6% between 140 and 290 K. The results of the addition scheme fit are also shown graphically in Figure 3.

4. DISCUSSION

There are no prior heat capacity measurements for the salts described in this work, and the data in Tables IIa and IIb can only be discussed in comparison with

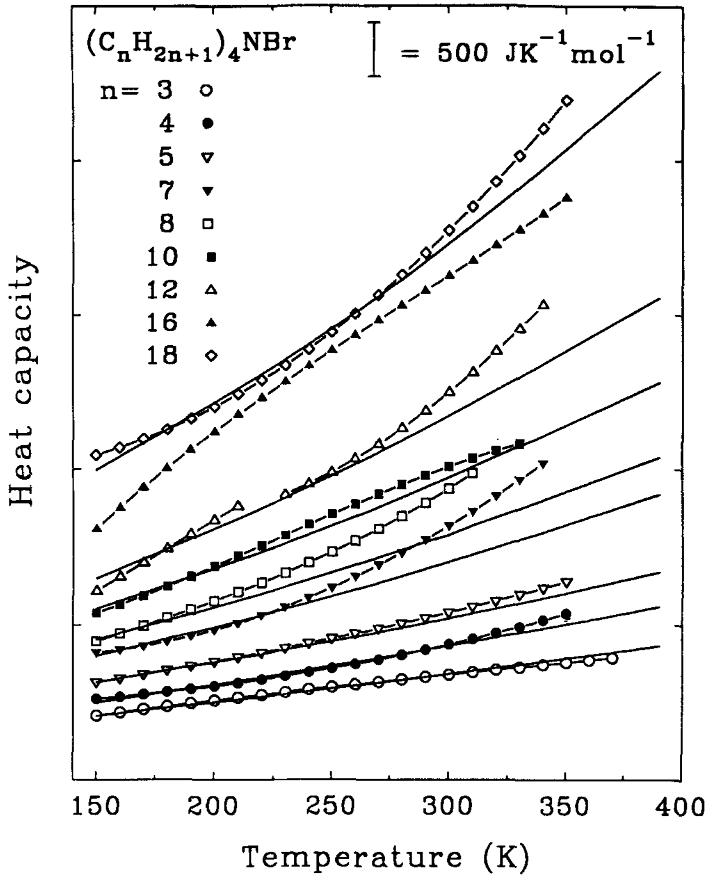

FIGURE 2 Experimental (symbols) and calculated (lines) heat capacities for tetra-*n*-alkylammonium bromides with alkyl chains longer than ethyl. Note the omission of calculated data for 16Br.

computed data and data of similar compounds. The heat capacity calculations based on the approximate vibrational spectra give satisfactory results for tetra-*n*-alkylammonium halides with side chains longer than ethyl. The average and RMS deviations seen in Table III for various temperature ranges are typical of this type of calculation of heat capacities for linear macromolecules[9] and paraffins.[6] An example of one of the larger temperature-range fits is shown in Figure 4 for 5I. Up to the disordering transition [T_d = 405 K, ΔS_d = 41.2 JK^{-1} mol^{-1}], followed by isotropization [T_i = 412 K, ΔS_i = 94.0 JK^{-1} mol^{-1}], the computed vibration-only heat capacity fits the experiment. The reason for the success of this analysis for ionic compounds is the relative insensitivity of the heat capacity in this temperature range to the details of the ionic lattice vibrations. The major contribution to the heat capacity comes from the methylene groups, and can be represented quite well by their well-known vibrational modes. The interpretation of practically no additional heat capacity increase due to disordering of the alkyl chains agrees well with the earlier ^{13}C NMR analysis of this compound in paper III of this series.[2]

The Θ_1 values in Table III do not change significantly with alkyl chain length,

TABLE IV

Addition scheme results*

T (K)	**C_p of CH_2**	**C_p of rest**	**%DEV from PE**	**4xC_p of CH_3**
140	10.8	115.7 ± 20.9	-11.6	99.9
150	12.3	113.0 ± 19.6	-4.4	104.6
160	13.3	103.9 ± 22.7	-1.1	109.8
170	14.0	106.2 ± 17.4	0.3	115.4
180	14.9	106.8 ± 15.8	2.5	121.7
190	15.2	118.3 ± 12.9	1.0	128.5
200	16.2	118.0 ± 17.8	3.9	136.0
210	17.0	119.3 ± 19.6	5.3	144.2
220	17.6	123.9 ± 23.0	5.5	153.2
230	18.4	127.9 ± 22.6	6.5	162.8
240	19.1	132.9 ± 25.8	6.7	173.2
250	19.7	141.4 ± 31.5	6.2	184.2
260	20.4	148.6 ± 33.1	6.4	195.9
270	21.6	149.8 ± 30.0	8.5	208.3
280	22.8	152.0 ± 31.8	10.6	221.2
290	23.9	158.3 ± 39.2	12.8	234.6

* The column "%DEV from PE" represents the difference of the herein calculated C_p of the methylene group minus the C_p calculated from polyethylene.

or the type of anion. They appear to fluctuate about 600 K, with perhaps an eventual decrease for 18Br. Eventually one expects for very long chains an approach to the value of polyethylene (519 K). It is obvious that heat capacity data at much lower temperatures are needed in order to obtain Θ_3 values for a discussion of the intermolecular vibrations and their changes with chain length.

All of the salts, besides the just discussed 5I of Figure 4, show some systematic deviation from the computed heat capacities at higher temperatures. A small deviation from the computed vibration-only heat capacity due to smaller experimental data in the high temperature range is seen in the case of 3I, 4I, and 3Br. This positive deviation reaches 4–5% just below the disordering transition, and is too close to the experimental error to be interpreted with certainty (see Figures 1 and 2). A possible explanation for such positive deviation could be in the relatively large number of CH_3 groups, which are known to start rotating already at low temperatures. If a vibration is changed to a rotation, its heat capacity would decrease from R to ultimately $R/2$. For four such vibrations, representing the cation, the total decrease could be as much as 16 JK^{-1} mol^{-1}. At room temperature this

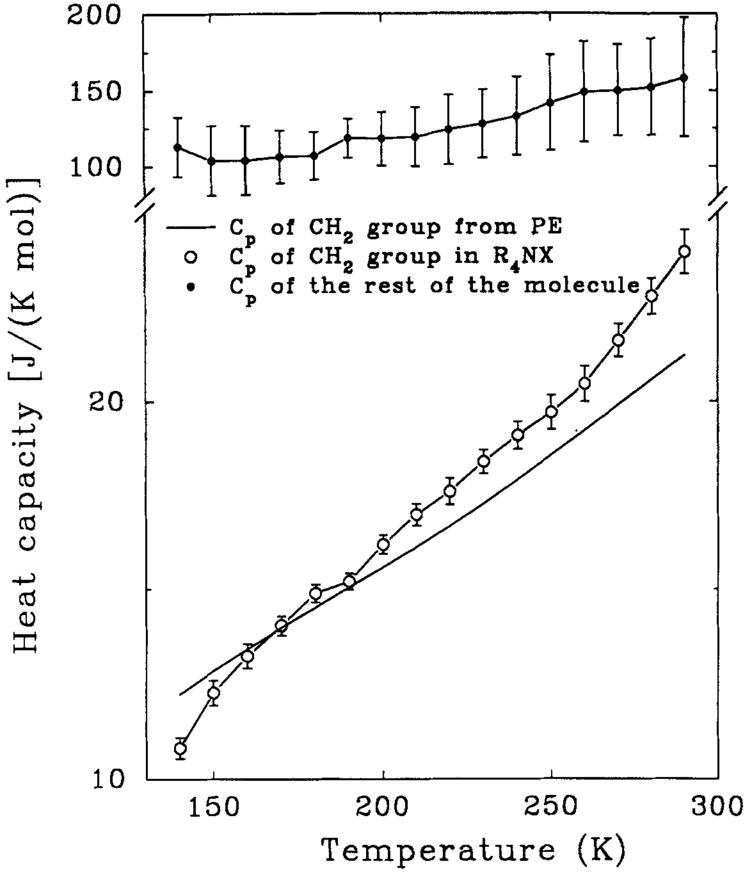

FIGURE 3 Results of the linear addition scheme fit of the heat capacities of tetra-*n*-alkylammonium halides.

could amount to as much as 5 and 4% of the heat capacity, for the propyl and the butyl salts, respectively. The deviations observed are indeed of that order of magnitude. Note, however, that the disordering transition for these three compounds, and only these three, causes a transformation to an orientationally disordered plastic crystal [T_d = 419, 394, 382 K, and ΔS_d = 35.8, 71.2, 44.4 $\mathrm{JK^{-1}\,mol^{-1}}$, respectively]. The use of identical constants to convert C_p to C_v [Equation (2)] may in these cases not be justified. A smaller value of A_0 could easily shift the deviation into the common error limit. A smaller A_0 would arise if these plastic-crystal-forming salts have a higher compressibility already below T_d.

Inspection of the results for the remaining salts in Figures 1 and 2 shows that, at higher temperatures, the experimental data are increasingly higher than the calculated data. A similar observation was made in 1962 for polyethylene,[12] and more recently for the paraffins.[6] In these cases it has been linked to conformational disorder and mobility introduced in the crystals without a first-order transition. The deviations first occur below room temperature for most compounds in our series. The excess (i.e. experimental minus calculated vibration-only) heat capacity,

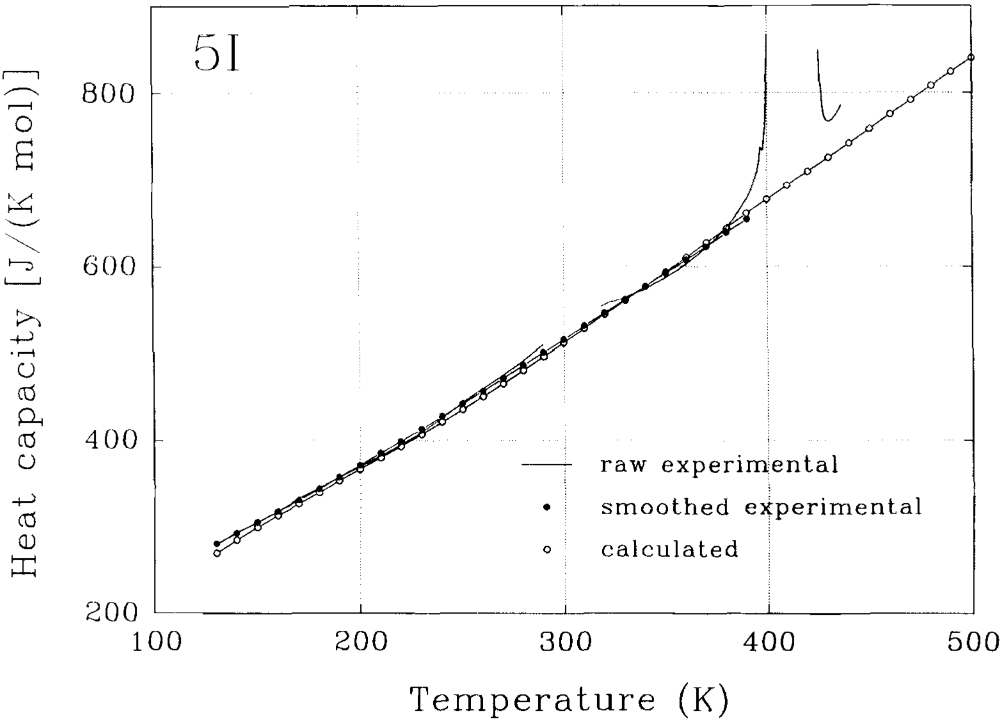

FIGURE 4 Raw experimental, smoothed experimental, and calculated heat capacities of 5I. Note the good agreement of calculation and experiment.

C_p^{excess}, should be proportional to the conformational disorder that is introduced gradually. The integral C_p^{excess}/T over the temperature range of the deviations yields the excess entropy ($\Delta\Delta S$). The results of such integrations are shown in Table V. An example of this procedure is given for 8Br in Figure 5, where the integrated area is shaded. Note that the transition data reported previously[1] were obtained by taking the transition area above the baseline indicated by the filled circles in Figure 5, leading to a considerable deficit in entropy.

In Part I of this series,[1] the various mesophase transitions were assigned, and the respective mesophases classified, based only on the entropies of the first-order transitions. An entropy deficit compared to the empirical transition entropy rules ($\Delta\Delta S$) was often noted. It is included in Table V and should be compared with the experimental, integrated entropy [$\int(C_p/T)dT$]. Given the large uncertainty involved in the empirical rules (estimated to be ±30%), the overall agreement with $\Delta\Delta S$ can be considered good. The always lower experimental excess entropy could reflect some residual entropy of incompletely ordered methylene groups at absolute zero, as was also suggested for OOBPD.[5] For comparison, the entropy of one CH_2-group in glassy polyethylene is 3 JK^{-1} mol^{-1}.[13] It should, finally, be noted that the excess entropies are much larger than those determined for the paraffins. In the paraffins it is known that only a few percent of the bonds assume a gauche conformation at any one time, as most gauche defects are accommodated at the chain ends.

TABLE V

Entropy obtained from the integration of excess heat capacity*

Salt	ΔS^{meas}	ΔS^{pred}	$\Delta\Delta S$	$\int(C_p^{excess}/T)dT$	NMR observations
5Br	98	127	29	15 (190-390)	Gradual disordering about $NCH_2CH_2CH_2$-CH_2CH_3 below T_i, stepwise for other bonds at T_i
5I	135	127	(-8)	0	Stepwise disordering at T_d and T_i
7Br	113	199	86	47 (230-380)	Similar to 7I
7I	130	199	69	40 (200-360)	Gradual disordering of 3 bonds (per chain) between T_{d1} and T_{d2}, stepwise disordering of C2-C3 bonds at T_i
8Br	129	235	106	62 (170-390)	Gradual disordering of 3 bonds below T_i, stepwise disordering of 2 bonds at T_i
10Br	263	307	44	27 (190-380)	Stepwise disordering of 4 bonds at T_d, 4 bonds at T_i
12Br	341	379	38	33 (230-370)	Gradual disordering of 2 bonds below T_d, and stepwise disordering at T_d and T_i for other 7 bonds
12I	271	379	108	79 (140-400)	Same as-for 12Br
18Br	555	595	40	21 (270-390)	Mainly stepwise

* The value of ΔS^{pred} is obtained by adding 20 $JK^{-1}mol^{-1}$ for positional, 35 $JK^{-1}mol^{-1}$ for orientational, and 9 $JK^{-1}mol^{-1}$ for conformational entropy per bond becoming flexible, assuming n - 3 bonds can become flexible for a side chain with n carbon atoms. The integration of the excess heat capacity is made over the temperature range indicated, ranging approximately up to the isotropization peak temperature.

The earlier NMR observations,[2] are also summarized in Table V. They are generally in agreement with the just discussed excess entropy. Gradual changes of the ^{13}C chemical shift as a function of temperature were linked to the increasing disordering of CH_2-groups from all-*trans* conformations (via the γ-gauche effect) in the cases of 5Br, 7I, 8Br, 10Br, 12Br, and 12I. These observations correlate well with the gradual increase of the heat capacity linked to the increase in entropy noted in this work. It was further noted in the NMR study that the C—C bonds at the end of an alkyl chain are the ones that become conformationally disordered gradually, while those close to the cation center lose their conformational order only on isotropization. Thus, a combination of sharp transition (arising from the

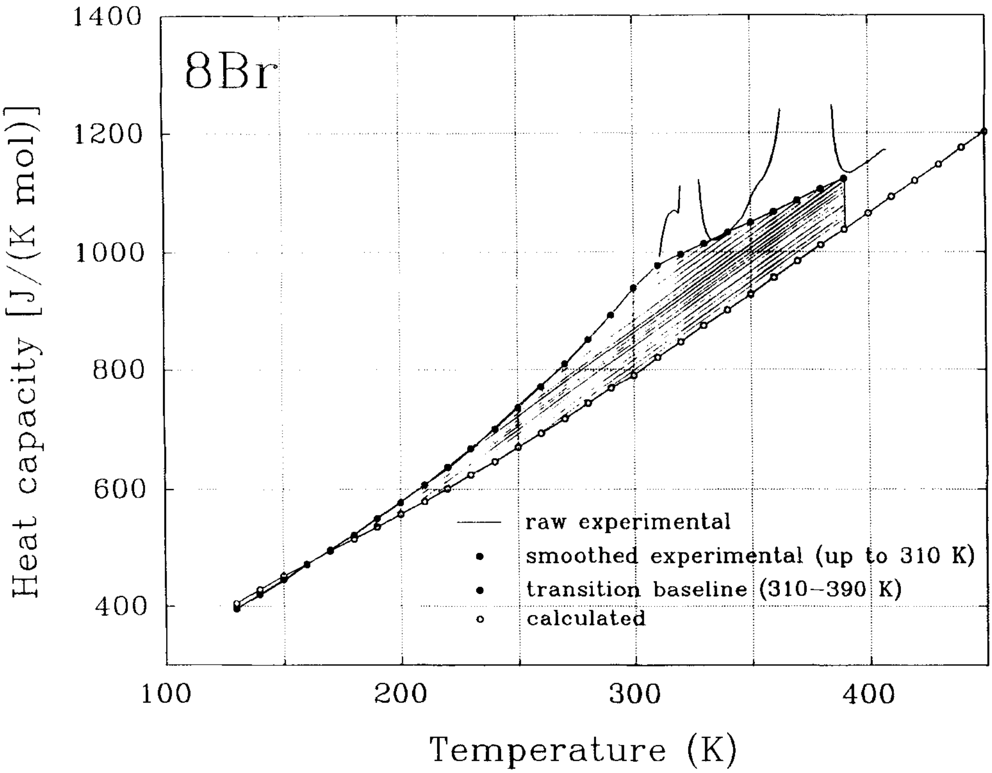

FIGURE 5 Raw experimental, smoothed experimental, and calculated heat capacities of 8Br. Note the increasingly negative deviation of the calculated from the experimental data. The shaded area was integrated to give the entropy obtained gradually.

inner part of the cation) and gradual transition (from the chain ends) is a common characteristic of the transition behavior in this class of materials. The heat capacities of 6I and 16Br in Figures 1 and 2, respectively, seem also to indicate an additional entropy increase outside the transition region. The NMR data do not support such interpretation. As was indicated in the description of the experiments it is also unlikely that experimental error is the cause of this discrepancy. At present no satisfactory answer is offered.

Empirical addition schemes have been used in our laboratory for the heat capacities of both the liquid and the solid states.[14] They are more successful for the liquids, as their heat capacities are often found to be linear with temperature. This is not usually the case for the solids. Table IV shows that the addition scheme works reasonably well for the methylene group in the solid state, giving a value comparable to that determined for polyethylene and paraffins. The deviation found, less than 2%, is comparable to the experimental error. The increasingly positive deviation of the C_p of the CH_2-groups of the salts compared to polyethylene seen in column 4 of Table IV is similar to that seen for odd paraffins (see Table V of Reference 6). The comparison with odd paraffins is natural, as our salts can be thought of as two crossing chains, each consisting of an odd number of atoms in the chain. An increasingly larger heat capacity is also expected to account for the excess entropy in some of the salts.

A C_p contribution for the rest of the molecule is also listed in Table IV (column 3). This quantity contains contributions from the anion, four methyl groups, and the central nitrogen atom, and it is also plotted in Figure 3. As the left-over contribution it, of course, contains all the errors of the linear fit. Surprisingly, it is smaller than what would be expected for the four methyl groups alone (a value taken from even paraffins and included in Table V).

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