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Fusion Properties of Some Ionic Quaternary Ammonium Compounds

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Abstract: Enthalpy, entropy, and molar volume changes during the fusion process of a wide range of quaternary ammonium compounds are presented. This group of compounds has hitherto been unexplored and is of interest since, as far as melting mechanisms are concerned, it is related to two groups of compounds whose melting phenomena have been studied extensively, *i.e.*, the *n*-paraffins and the alkali metal halides. The data are examined for general trends and comparisons are made with similar data for the paraffins and alkali metal halides. Some regularities in the entropy changes are noted and can be correlated with structural changes within the cation.

While a considerable amount of work has been done on the fusion properties of organic compounds, hydrocarbons and polymers in particular on the one hand, and inorganic ionic compounds on the other, and theories to account for the transition and melting phenomena have been proposed, relatively little has been done on amine or quaternary ammonium compounds. With the exception of the studies of Tsau and Gilson[1] of a series of monoalkylammonium halides and the more recent work on the tetraamylammonium thiocyanate,[2] information on the fusion properties of quaternary ammonium compounds is virtually nonexistent.

In our preceding communication[2] on the melting of tetraamylammonium thiocyanate, it was apparent that a kink-block type of rearrangement of the alkyl groups within the quaternary ammonium cation largely accounted for a solid-state transition just preceding fusion. The present paper reports the results of an investigation of the enthalpy and entropy changes for 34 quaternary compounds and volume changes for a more limited number. These results are examined for trends which give further information on the melting behavior of this interesting class of compounds.

Experimental Section

Materials. $(C_4H_9)(i\text{-}C_5H_{11})_3NBr$, $(C_3H_7)_4NBr$, $(C_4H_9)_4NBr$, $(C_3H_7)_4NI$, $(C_4H_9)_4NI$, and $(i\text{-}C_5H_{11})_4NI$ were samples received from R. L. Kay (Mellon Institute), the preparation and purification of which are described in Kay's paper.[3] Similarly, samples of $(C_3H_7)_4NBF_4$, $(C_4H_9)_4NBF_4$, $(n\text{-}C_6H_{13})_4NBF_4$ $(C_3H_7)_4NBPh_4$, $(C_4H_9)_4NBPh_4$, and $(C_4H_9)_4NPF_6$ were supplied by J. E. Lind, Jr. (Stanford University), and the preparation and purification are given elsewhere.[4,5] J. Gordon (Kent State University) supplied small amounts of the following compounds (grouped according to increasing number of carbon atoms, with subsequent recrystallization indicated in brackets afterward): $(n\text{-}C_7H_{15})(n\text{-}C_6H_{13})_3NI$, $(n\text{-}C_5H_{11})_4NNO_3$, and $(n\text{-}C_6H_{13})_4NNO_3$ [twice from ethyl acetate–ether]; $(n\text{-}C_6H_{13})_4NBr$, $(n\text{-}C_7H_{15})(n\text{-}C_6H_{13})_3NNO_3$, $(n\text{-}C_7H_{15})_2(n\text{-}C_6H_{13})_2NI$, $(n\text{-}C_7H_{15})(n\text{-}C_6H_{13})_3NNO_3$, and $(n\text{-}C_7H_{13})_4NClO_4$ [three times from ethyl acetate–ether]; $(n\text{-}C_7H_{15})(n\text{-}C_6H_{13})_3NClO_4$ and $(n\text{-}C_6H_{13})_2(n\text{-}C_7H_{15})_2NClO_4$ [twice from aqueous ethanol]; and $(n\text{-}C_6H_{13})_4NClO_4$ [twice from ether, once from ethyl acetate–ether]. With the exception of $(n\text{-}C_5H_{11})_4NSCN$, the remaining compounds were from Eastman Organic Chemicals. The preparation of $(n\text{-}C_5H_{11})_4NSCN$ has been described in our preceding communication.[2] The melting points for the above compounds are in Table I.

Apparatus and Techniques. Calorimetry. The heats of fusion and solid–solid transition were investigated with the Perkin-Elmer differential scanning calorimeter (model DSC-1) described else-

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(3) D. F. Evans, C. Zawoyski, and R. L. Kay, *J. Phys. Chem.*, 69, 3878 (1965).

(4) J. E. Lind, Jr., H. A. A. Abdel-Rehim, and S. W. Rudich, *ibid.*, 70, 3610 (1966).

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Table I. Calorimetric Data for Quaternary Ammonium Salts

Cation	t_{tr}, °C	ΔH_{tr}, kcal mol^{-1}	ΔS_{tr}, eu	t_f, °C	ΔH_f, kcal mol^{-1}	ΔS_f, eu	ΔH_{tot}, kcal mol^{-1}	ΔS_{tot}, eu
(a) Chlorides								
$(n\text{-}C_4H_9)_4N$				41	4.9	15.6	4.9	15.6
$(n\text{-}C_5H_{11})_4N$	8	0.66	2.3	22	0.31	1.1	0.97	3.4
$(n\text{-}C_7H_{15})_4N$	−58	exothermic		−9		not investigated		
(b) Bromides								
	94							
$(n\text{-}C_4H_9)_4N$	99	3.4	9.2	122	3.7	9.3	7.2	18.8
	108	0.1	0.3					
$(i\text{-}C_5H_{11})_3(n\text{-}C_4H_9)N$	69	0.96	2.8	122	3.8	9.6	4.6	12.4
$(n\text{-}C_5H_{11})_4N$				103	9.9	26.4	9.9	26.4
$(n\text{-}C_6H_{13})_4N$	32	1.6	5.3	104	3.8	10.1	8.3	24.5
	42	2.9	9.1					
$(n\text{-}C_7H_{15})(n\text{-}C_6H_{13})_3N$	62	7.0	20.9	108	1.8	4.6	10.6	30.6
	83	1.8	5.1					
$(n\text{-}C_7H_{15})_4N$	70	1.3	3.7	96	8.6	23.3	9.9	27.0
$(n\text{-}C_8H_{17})_3(n\text{-}C_3H_7)N$				78	10.6	30.1	10.6	30.1
(c) Iodides								
$(n\text{-}C_3H_7)_4N$	146	7.8	18.7			Dec		
$(n\text{-}C_4H_9)_3(n\text{-}C_3H_7)N$				195	3.3	7.0	3.3	7.0
$(n\text{-}C_4H_9)_4N$	119	6.7	17.1	146	2.3	5.5	9.0	22.6
$(n\text{-}C_5H_{11})_4N$	132	4.1	10.2	139	9.4	22.9	13.5	33.1
$(i\text{-}C_5H_{11})_4N$	72	6.9	14.8	149	3.8	8.9	9.7	23.7
	79	1.4	4.1					
$(n\text{-}C_7H_{15})(n\text{-}C_6H_{13})_3N$	92	5.1	14.0	98	4.9	13.1	10.0	27.1
$(n\text{-}C_7H_{15})_2(n\text{-}C_6H_{13})_2N$	89	3.1	8.5	100	6.4	17.1	9.5	25.6
$(n\text{-}C_7H_{15})_4N$	83	2.3	6.4	123	8.9	22.5	11.9	30.8
	118	0.74	1.9					
(d) Nitrates								
$(n\text{-}C_4H_9)_4N$	93	0.05	0.1	119	3.5	9.0	3.6	9.1
$(n\text{-}C_5H_{11})_4N$	93	3.0	8.2	114	6.8	17.7	9.8	25.9
$(n\text{-}C_6H_{13})_4N$	50	5.3	16.5	72	4.2	12.3	9.5	28.8
$(n\text{-}C_7H_{15})(n\text{-}C_6H_{13})_3N$				72	8.0	23.1	8.0	23.1
(e) Perchlorates								
$(n\text{-}C_6H_{13})_4N$	62	5.5	16.5	110	4.4	11.4	11.9	33.3
	85	1.4	3.9					
	96	0.6	1.5					
$(n\text{-}C_7H_{15})(n\text{-}C_6H_{13})_3N$	89	3.9	10.9	103	5.8	15.3	9.7	26.2
$(n\text{-}C_7H_{15})_2(n\text{-}C_6H_{13})_2N$	92	3.4	9.3	105	6.2	16.3	9.6	25.6
$(n\text{-}C_7H_{15})_4N$	83	1.1	3.1	126	7.6	19.0	10.8	27.9
	92	1.1	3.1					
	115	1.0	2.7					
(f) Miscellaneous								
Salt								
$(n\text{-}C_5H_{11})_4NSCN$	42	5.4	17.3	49.5	4.7	14.3	10.1	31.6
$(n\text{-}C_3H_7)_4NBF_4$	124	3.5	8.8	239	3.4	6.7	6.9	15.5
$(n\text{-}C_4H_9)_4NBF_4$	68	1.6	4.7	166	2.5	5.8	4.1	10.5
$(n\text{-}C_6H_{13})_4NBF_4$	61	4.7	14.0	94	4.6	12.6	9.3	26.6
$(n\text{-}C_3H_7)_4NBPh_4$	195	5.4	11.6	207	2.9	6.1	8.3	17.7
$(n\text{-}C_4H_9)_4NBPh_4$	185	1.6	3.4	229	9.2	18.4	10.8	21.8
$(n\text{-}C_4H_9)_4NPF_6$	93	2.5	6.7	244	4.1	7.8	6.6	14.5

where.[6,7] The operating procedure was described previously,[2] and up to 20 mg of each sample was used for measurement. The samples were generally cycled three or four times through fusion and freezing at a heating rate of 5°/min and a cooling rate of 1.25°/min. For most compounds the temperature range studied was from room temperature to a few degrees above the melting point, while for those with low melting points the range was extended to lower temperatures with a liquid nitrogen well. With the exception of these compounds, transitions below room temperature were not investigated.

The instrument was calibrated with a sample of pure succinonitrile (U.S. Department of Commerce, National Bureau of Standards), the values of the phase transitions being those reported by Wulff and Westrum:[8] ΔH_f = 885 cal/mol, ΔS_f = 2.68 eu. The melting points and solid–solid transition points were taken from the peak maxima and are accurate to ±0.5°. No special thermal pretreatment was applied to the samples before the DSC measurements, and since recycling of the measurements generally gave reproducible results, the "frozen-in" disorder was probably small. Enthalpy changes were calculated from peak areas and are accurate to ±3%.

Molar Volume Studies. Densities from 25° to fusion were determined by a modification of the confining volume dilatometer of Bekkedahl and Marker.[9,10] The confining liquid was mercury, which was also used for calibration. All measurements were made with a Gaertner Scientific cathetometer. The dilatometer was kept

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Table II. Dilatometric Measurements for some Quaternary Ammonium Salts

Cation	Density 25°, g cm^{-3}	$\Delta \bar{V}_f$, cm^3 mol^{-1}	$\left(\frac{\Delta \bar{V}_f}{V_{25}}\right)$, %	Expansivity, deg^{-1} × 10^4	
				at 25°	at mp
		(a) Bromides			
(n-C_4H_9)$_4$N	1.0350	26.4	8.5	0.93	5.9
(n-C_5H_{11})$_4$N	1.0662	34.2	9.5	1.8	4.5
(n-C_6H_{13})$_4$N	1.0036	21.3	4.9	15	4.4
		(b) Iodides			
(n-C_4H_9)$_4$N	1.0027	37.6	10.2	0.98	
(n-C_5H_{11})$_4$N	1.1800	39.0	10.9	0.34	
(i-C_5H_{11})$_4$N	1.1205	22.9	6.0		
(n-C_6H_{13})$_4$N	1.0922	33.6	7.6	0.79	1.05
(n-C_7H_{15})$_4$N	1.0660	36.9	7.3	0.26	1.84
		(c) Other Salts			
(n-C_5H_{11})$_4$NSCN	0.9431	17.2	4.5	0.32	6.3
(n-C_5H_{11})$_4$NNO$_3$	0.9329	11.7	3.0	0.125	
(n-C_6H_{13})$_4$NClO$_4$	0.9129	59.2	11.9	4.0	15.2
(n-C_6H_{13})$_4$NBF$_4$	1.0482	48.4	11.3		

in a silicone oil bath, the temperature of which could be controlled to ±0.03°. The estimated error in the determination of the density was about ±0.2%. The dilatometric measurements are also affected by the thermal histories of the samples, as was shown in the case of tetra-n-amylammonium thiocyanate.[2]

Results

Transition temperatures, melting points, and ΔH_{tr}, ΔH_f, ΔS_{tr}, and ΔS_f values are in Table I; the dilatometry results are in Table II. The melting points are in general accord with literature values.[4,11]

Many of the quaternary ammonium salts are low melting (*i.e.*, below 120°); it has been shown[12] that such salts may be used for short periods at temperatures just above their melting points without decomposition. This was confirmed in the present work; the compounds with complex anions similarly were found to give quite reproducible results at their melting points. The compounds were generally cycled three or four times through fusion to establish reproducibility. For a few compounds, irreproducible behavior was thus detected, and some general observations are as follows.

The transition at 94–99° of (C_4H_9)$_4$NBr was absent on a second cycle, and the transition and fusion peaks of (n-C_5H_{11})$_4$NI and (i-C_5H_{11})$_4$NI coalesced on reheating (without affecting the magnitude of ΔH_{tot}). While two peaks are reported for (n-C_6H_{13})$_3$(n-C_7H_{15})NI, only one peak with a large shoulder was observed in the first heating. Such dependence on thermal history has also been observed in earlier studies with quaternary ammonium compounds. Thus, for monosubstituted ammonium salts[1] and with tetra-n-amylammonium thiocyanate,[2] it has been shown that such irreproducibility is not due to decompositions or impurities, but rather may be ascribed to the thermal properties of the quaternary alkylammonium cation, *i.e.*, the freezing in of disorder.[2,13] Gordon, Stenhagen, and Vand[14] have shown that the crystal structure of the monosubstituted ammonium salts depends on their thermal histories.

For (n-C_6H_{13})$_3$(n-C_7H_{15})NNO$_3$, decomposition was indicated in the DSC experiments (*i.e.*, broadening of the fusion peak on successive heating–cooling cycles). Broad peaks in the DSC traces were observed for (C_4H_9)$_4$NCl and (C_4H_9)(i-C_5H_{11})$_3$NBr; this suggests the presence of small amounts of impurities; for (n-C_7H_{15})$_4$NCl, water in trace amounts was detected by infrared spectroscopy.

Discussion

The compositions of tetraalkylammonium compounds are such that their behavior on melting would be expected to be related to two important classes of compounds whose melting properties have been examined quite thoroughly: the alkali halides and the paraffins. The conclusions drawn from studies of these two groups of compounds are informative when applied to the data for quaternary ammonium salts. Thus it was found, in our investigation of tetra-n-amylammonium thiocyanate,[2] that the values of ΔH_{tr}, ΔS_{tr}, and ΔH_f, ΔS_f are qualitatively consistent with the melting of polymers (the kink-block theory of Blasenbrey and Pechhold[15]) and the normal melting of ionic compounds (*e.g.*, alkali halides), respectively.

The influence of the alkyl chains in the cation on the melting behavior of the 33 other quaternary ammonium salts is clearly shown by the results from Table I. For some compounds, the values of ΔH_{tot} and ΔS_{tot} appear low relative to the general range of values for most compounds (*e.g.*, Table I, ΔS = 3.4 for (C_5H_{11})$_4$NCl). As already noted, the temperature range embraced in the calorimetry extended from room temperature to the melting temperatures, but for the preceding cases, the measurements were extended to the lower temperature limit of our unit (*i.e.*, −25°). For such compounds, additional work at still lower temperatures appears necessary to search for contributions resulting from further solid-state transitions. They, accordingly, fall outside the discussion that follows.

The total entropy change on fusion, ΔS_{tot}, of alkali metal halides lies between 5 and 7 eu;[16] for NH$_4$NO$_3$,

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[16] G. J. Janz, "Molten Salts Handbook," Academic Press, New York, N. Y., 1967.

ΔS_{tot} is 7.6 eu, while the values for the quaternary compounds are often several times larger than this. By comparison, the straight-chain hydrocarbons (with the same number of carbon atoms as the quaternary salt cation) have much higher ΔS_{tot} values: n-$C_{12}H_{26}$, $\Delta S_{tot} = 33.4$; n-$C_{16}H_{34}$, $\Delta S_{tot} = 43.8$; n-$C_{20}H_{42}$, $\Delta S_{tot} = 54.12$.[17] Unfortunately, no data appear to be available for tetraalkylmethanes with larger alkyl groups than ethyl (*i.e.*, 3,3-diethylpentane); comparison of paraffins with similar configurations to the quaternary salt cations is thus not possible. Estimates can, however, be made for larger alkyl groups. If one takes $\Delta S_{tot} = 10.6$ eu for tetraethylmethane[17] and assumes that each CH_2 involves an increase in ΔS_{tot} of $1.2R$ (see below), then ΔS_{tot} for $C_{17}H_{36} = 29.8$, for $C_{21}H_{44} = 39.4$, and for $C_{25}H_{52} = 49$; these results are still higher than the corresponding quaternary ammonium salts.

To extend the Blasenbrey and Pechhold theory to the present series of quaternary ammonium salts, the transition and melting steps must be considered as separate processes,[2] even though overlap of the transition and melting peaks occurred in the calorimetric studies. In cases where overlap does not occur, the ΔS_f of several of the quaternary ammonium salts is found to be in the region of 9 eu, a value which is of the same order as that for alkali metal halides. If this value is taken to represent the "normal melting" of quaternary ammonium compounds in general, then the entropy change due to configurational changes within the cation

$$\Delta S_{config} = \Delta S_{tot} - \Delta S_{normal\ melting} \qquad (1)$$

can be extracted. Here "normal melting" is considered as that occurring in ionic solids such as the alkali halides, in which configurational rearrangements within the spherical monatomic anions and cations are not possible. These values can be compared with those obtained by calculations based on $R \ln \Omega$, where Ω is the number of conformations that may be attained through *gauche–trans*-type "kinking." The results for the various alkyl chain lengths are approximately: butyl = 11.5, amyl = 17, hexyl = 23, heptyl = 47 eu. The agreement is only fair, and for heptyl, the calculated value is too high. This probably results from steric restrictions, and these are not readily accounted for by this model without further assumptions. The occurrence of two or more solid-state transitions, as are observed in some of the longer chain salts, confirms that this approach to the melting behavior, while informative, is but a first approximation for this series of compounds.

If the enthalpy changes are examined from the Blasenbrey and Pechhold kink-block approach and normal melting for ionic crystals, the results are qualitatively in accord with the concepts of paraffin and alkali halide melting behavior. Thus, one predicts that the introduction of two *gauche* bonds increases the energy by 1.5 kcal/mol, and for the series butyl–heptyl, ΔH_{tot} would range from 8 to 12 kcal/mol. The ΔH_{tot} values of most salts in Table I fall within this range.

Another approach would be to treat the transition and melting steps as a single process. The solid transitions in n-paraffins are frequently difficult to characterize precisely,[18] and some authors prefer to combine the calorimetric data for transition and melting and thus to consider the total change as due to one melting process.[19,20] Following the suggestions of Oriani[21] from this viewpoint, namely that the melting process (*i.e.*, combined melting and transition steps) is equivalent to expansion at constant order followed by disordering at constant volume, one obtains for the overall entropy change

$$\Delta S_{tot} = R \ln x + \Delta S_{expansion} \qquad (2)$$

where the value for $\Delta S_{expansion}$ can be calculated from[22]

$$\Delta S_{expansion} = 2.34[10^{-3}(\alpha/\beta)\Delta V] \qquad (3)$$

Here x depends on the number of configurations available to the molecule. Aranow, Witten, and Andrews[20] have proposed that the entropy of fusion of long-chain paraffins increases by a factor close to $R \ln 3$ for each additional methylene group, and this is in accord with experiment.[19]

Table III shows that, with a value rather lower than $R \ln 3$, the total entropy can be accounted for fairly well if it is assumed that the eight nearest CH_2 groups to the nitrogen contribute little to the entropy change. Examination of models reveals that the two innermost CH_2 groups of the cation of each alkyl chain are sterically hindered from rotation, and the preceding argument is thus not unreasonable. An investigation of steric hindrance and the entropy changes of the series Et_2CH_2, Et_3CH, Et_4C by Bondi[19] established that the steric effect is not insignificant; in the present series, because of the smaller radius of N^+ compared to C, a comparable, or more probably larger, steric effect

Table III. Comparison of ΔS_{config} Calculated with Estimated Experimental Values (eu)

Quaternary ammonium salt	$\Delta S_{expansion}$[a]	$\Delta S_{tot} - \Delta S_{vol}$	ΔS_{config}, calcd[a]
$(n\text{-}C_4H_9)_4NBr$	3.1	15.7	14.0
$(n\text{-}C_4H_9)_4NI$	4.4	18.2	14.0
$(n\text{-}C_5H_{11})_4NBr$	4.2	22.1	21.0
$(n\text{-}C_5H_{11})_4NI$	4.6	28.5	21.0
$(n\text{-}C_5H_{11})_4NSCN$	1.9	29.5	21.0
$(n\text{-}C_5H_{11})_4NNO_3$	1.4	24.5	21.0
$(i\text{-}C_5H_{11})_4NI$	2.7	21.0	21.0
$(n\text{-}C_6H_{13})_4NBr$	2.5	22.0	28.0
$(n\text{-}C_6H_{13})_4NI$	4.2	29.4	28.0
$(n\text{-}C_6H_{13})_4NBF_4$	5.6	21.0	28.0
$(n\text{-}C_6H_{13})_4NClO_4$	6.9	26.3	28.0
$(n\text{-}C_7H_{15})_4NI$	4.3	26.5	35.0

[a] ΔS_{config} calculated from $0.875\,(x - 8)$, where x is the number of C atoms in the cation. The number 8 allows for the nonparticipation of the two innermost methylene groups to the entropy change. $\Delta S_{expansion}$ is calculated assuming $\alpha = 1.0 \times 10^{-4}$ deg^{-1}, $\beta = 2.0 \times 10^{-8}$ cm^2 g^{-1} in eq 3. The values were taken from A. Müller, *Proc. Roy. Soc., Ser. A*, **178**, 227 (1941).

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would be expected (*i.e.*, an increase in ΔS_f of less than $R \ln 3$ for each methylene group).

The effect of steric hindrance on rotation is seen by comparison of the compounds (n-$C_5H_{11})_4NI$ and (i-$C_5H_{11})_4NI$. Although the solid transitions are roughly similar, the ΔH_f and ΔS_f for the *i* compound are found to be smaller than for the *n* compound. This assumes that the crystal structures are similar in this series.

The heats of fusion of straight-chain hydrocarbons have been found to increase with increasing chain length. Billmeyer[23] has reported a linear relationship between chain length and ΔH_f, increasing 0.9 kcal/mol for each CH_2. Inspection of ΔH_{tot} for the present quaternary ammonium compounds shows that while there is a similar trend (for ΔH_{tot} to increase with increasing chain length), the scatter in the data is too much to allow definitive conclusions.

The general tendency for the values of ΔS_{tot} and ΔH_{tot} to increase with increasing chain length is thus in accord with the predictions from hydrocarbon analogs. Examining the results for a series of halides (with cation invariant), it is seen (Table I) that the values (for both ΔH_{tot} and ΔS_{tot}) decrease in the order I > Br > Cl. If allowance is made for the differences in volume change on melting between Br and I, this trend still holds (see Table III). The melting points of the quaternary salts decrease in the same order. For purely normal melting, as in the alkali halide series, the volume change on melting is in the inverse order, *i.e.*, F > Cl > Br > I[16,24] (the cesium halides are exceptions); the melting points and ΔH_f values also follow this trend, while the ΔS_f values are approximately constant (apart from the lithium salts).

Compared to alkali halides and hydrocarbons, the volume changes of the quaternary ammonium salts on melting (Table II) are small. Thus for the alkali halides the values range from 11 to 30%;[14] for straight-chain hydrocarbons, having even numbers of C atoms, the values are above 16%;[25] for the quaternary ammonium salts, the range of the values is 3–12%. The smaller volume change for fusion of such quaternary ammonium compounds was previously predicted[26] from consideration of viscosity and electrical conductance data and indicates a similarity between liquid and solid packing.

The trend of ΔS_{tot} with anion is additional support for a similarity between liquid and solid molecular packing. It follows that the larger the anion, the less is the overlap between the alkyl groups of neighboring cations, and the less the need for the alkyl groups to adopt coiled-up configurations; this results in a greater freedom for rotation of each CH_2 about its bonds, and consequently larger ΔS_{tot} values.

Inspection of the results for the series of salts having the cations $(C_6H_{13})_4N^+$, $(C_6H_{13})_3(C_7H_{15})N^+$, $(C_6H_{13})_2(C_7H_{15})_2N^+$, and $(C_7H_{15})_4N^+$ shows that ΔS_{tot} remains relatively constant, but that ΔS_{tr} decreases along the series and ΔS_f, correspondingly, increases. Apparently the heptyl chains (more sterically hindered) attain rotational freedom less easily than the hexyl chains.

The melting behavior of the quaternary ammonium salts thus bridges the concepts of paraffinic melting and normal ionic melting. X-Ray diffraction data appear to be needed for these compounds, especially to further the understanding of the process of fusion for quaternary ammonium salts, and more generally, ionic compounds of the weak-field cation class.

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