Thermochimica Acta, 9 (1974) 277–287
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THERMODYNAMICS OF TETRAALKYL- AND BIS-TETRAALKYLAMMONIUM BROMIDES

II. HEAT CAPACITIES OF SOLID STATE FROM 273 TO 373 K*

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(Received 27 December 1973)

ABSTRACT

The solid phase heat capacities of a number of hydrocarbon containing salts have been determined in the temperature range 273 to 373 K using a differential scanning calorimeter. The salts studied include tetramethyl-, tetraethyl-, and tetrabutylammonium bromide and the bis-tetraalkylammonium bromide series of the general formula $[R_3N(CH_2)_nNR_3]Br_2$, where $n = 2, 3, \ldots 10$, and R = ethyl or allyl. With the exception of n-Bu_4NBr, the heat capacities of the salts were found to increase linearly with temperature over the range investigated. DSC curves of the bis-tetraalkylammonium series indicated that some of them have broad thermal transitions occurring between 365 K and their decomposition point. n-Bu_4NBr was the only tetraalkylammonium salt to show any anomalous thermal transitions in the solid phase. The origin of these transitions may be due to mesophase formation.

INTRODUCTION

Aqueous tetraalkylammonium salt solutions have received considerable attention in recent years[1]. Their unusual behaviour has been attributed to the special interactions that occur between the hydrophobic alkyl groups of the ions and the polar water molecules[2–6].

A variety of thermodynamic, spectroscopic, and transport properties have been used to assess the nature of these solutions[1]. One of the most sensitive probes of structural effects in water is the partial molar heat capacity of the solute, $\bar{C}_{p,2}$. The inaccuracy in some of the methods used to obtain values of the above property at high dilution, $\bar{C}^{\circ}_{p,2}$, where ion–solvent effects are maximized, have been discussed[7].

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*This paper was taken from the work submitted by John A. Burns, to the College of Graduate Studies of the University of Saskatchewan, Saskatoon, Canada, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

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Recently, workers[8,9] have developed flow microcalorimetry techniques that provide accurate $\bar{C}_{p,2}$ values to lower concentrations than possible in the past.

An alternative way to obtain accurate $\bar{C}^{\circ}_{p,2}$ values is to measure the integral enthalpy of solution at infinite dilution as a function of temperature, thus providing values of the heat capacity of solution at infinite dilution, $\Delta C^{\circ}_{p,2}$. By means of the relation $\Delta C^{\circ}_{p,2} = \bar{C}^{\circ}_{p,2} - C_p^{\text{pure}}$, where C_p^{pure} is the heat capacity of the pure crystalline salt in its standard state, one is able to calculate $\bar{C}^{\circ}_{p,2}$. However, in order to do so, values of C_p^{pure} must be available at the same temperature as those of $\Delta C^{\circ}_{p,2}$.

The success of workers in obtaining accurate $\Delta C^{\circ}_{p,2}$ data[7,10–17] of aqueous salt solutions has been negated by their inability to evaluate $\bar{C}^{\circ}_{p,2}$ because of a lack of C_p^{pure} data. This has been particularly true of studies involving organic salts such as R_4NX[14–16] and $[R_3N(CH_2)_nNR_3]Br_2$[17]. The latter series of salts has been studied in an effort to determine to what extent the unique behaviour of R_4NX salts in water is emulated by these more complex, but somewhat similar salts. The principal aim of this study was to provide crystalline heat capacity data of these salts in the vicinity of 298 K to enable the determination of $\bar{C}^{\circ}_{p,2}$ values.

In this paper we report the molal heat capacities of the crystalline solute in the temperature range 273 to 373 K for the following salts: tetramethyl-, tetraethyl- and tetrabutylammonium bromide; the series of bolaform electrolytes of the general formula $[R_3N(CH_2)_nNR_3]Br_2$, where $n = 2, 3, \ldots, 10$, and R = ethyl and allyl. The ethyl series of bolaform compounds are abbreviated as J2, J3, ..., J10 for $n = 2, 3, \ldots, 10$. In addition the four compounds 1,2-bis-(triallylammonium) ethane dibromide, 1,2-bis-(methyldiallylammonium) ethane dibromide, 1,3-bis-(triallylammonium) propane dibromide, and 1,4-bis-(triallylammonium) butene-2-dibromide are abbreviated as TAAE, MDAAE, TAAP, and TAAB, respectively.

The experimental data were obtained by means of a differential scanning calorimeter. The crystalline heat capacities show a linear dependence on temperature over the temperature range 273 to 373 K, with a number of the salts showing an anomalous heat capacity behaviour in the temperature range 365 to 530 K.

EXPERIMENTAL

The preparation and purification of the bolaform electrolytes, Et_4NBr, and KCl have been described elsewhere[17]. n-Bu_4NBr was obtained from Baker Chemicals and recrystallized from a 1:1 (v/v) acetone–anhydrous diethyl ether mixture. Me_4NBr was synthesized and recrystallized three times from a 1:1 (v/v) methanol–ethanol mixture. C, H, N analysis indicated a purity of greater than 99.7%.

All materials were dried and stored over P_2O_5 under vacuum. The specific heat capacity and transition temperatures were obtained by means of a differential scanning calorimeter, Perkin-Elmer DSC-1B. The samples were contained in closed aluminum planchets under nitrogen. The calorimeter was purged continuously at a slow and constant flow-rate (30 ml min^{-1}) with dry nitrogen gas. Low temperature readings were attained by means of a dewar filled with liquid nitrogen and placed over the sample holder.

The instrument was calibrated for differential temperature using the fusion points of indium, 429 K, and tin, 505 K; the average temperature using the fusion point of indium and n-nonane, 222 K; and the power using the heat of fusion of indium, 16.7 $\mathrm{cal}_{th}^{*}\ \mathrm{g}^{-1}$.

The specific heat capacity data were obtained relative to an external standard aluminum oxide (sapphire) disc, the heat capacity of which was known to $\pm 1 \times 10^{-5}$ $\mathrm{cal}_{th}\ \mathrm{g}^{-1}$. Blank deflections at each temperature were obtained and applied to both the standard and sample deflections. Values of the specific heat at a given temperature were calculated by means of the relation:

$$\text{Specific heat (sample)} = \frac{\text{amplitude (sample)}}{\text{amplitude (sapphire)}} \times$$

$$\times \frac{\text{weight (sapphire)}}{\text{weight (sample)}} \times \text{specific heat (sapphire)}$$

Sample weights for the specific heat capacity measurements were determined using a Cahn gram electrobalance and were of the order 0.005–0.015 g with an absolute error of $\pm 1 \times 10^{-5}$ g.

Calorimetric measurements were conducted at a heating rate of 10 K min^{-1} and a recorder sensitivity of 2×10^{-3} $\mathrm{cal}_{th}\ \mathrm{sec}^{-1}$. DSC curves to decomposition or fusion were carried out using sample weights in the range 0.0005 to 0.001 g at a heating rate of 10 K min^{-1} and a recorder sensitivity of 8×10^{-3} $\mathrm{cal}_{th}\ \mathrm{sec}^{-1}$. The enthalpies of transition were calculated relative to the heat of fusion of tin, $\Delta H_f =$ 14.5 $\mathrm{cal}_{th}\ \mathrm{g}^{-1}$.

The chart areas of the DSC curves were measured with a planimeter. Each sample was checked for equivalence in transition temperatures and heats of transition by repetitive thermogram scanning of a given sample. No less than two runs were made on samples of each compound. The heat of fusion of the bolaform salts could not be obtained as they decomposed prior to melting. The accuracy of the instrument was verified by determining the specific heat capacity of KCl and $\mathrm{Me_4NBr}$. The molar heat capacity value found at 298 K for KCl was 12.2±0.25 $\mathrm{cal}_{th}\ \mathrm{K}^{-1}\ \mathrm{mol}^{-1}$ as compared to literature values of 12.05±0.25 $\mathrm{cal}_{th}\ \mathrm{K}^{-1}\ \mathrm{mol}^{-1}$ (Ref. 18) and 12.31 $\mathrm{cal}_{th}\ \mathrm{K}^{-1}\ \mathrm{mol}^{-1}$ (Ref. 19). The molar heat capacity values of $\mathrm{Me_4NBr}$ were calculated to be 38.1±0.8 and 42.9±0.8 $\mathrm{cal}_{th}\ \mathrm{K}^{-1}\ \mathrm{mol}^{-1}$ at 298 and 345.6 K, respectively. These are to be compared with the values 38.64±0.04 and 43.51±0.04 $\mathrm{cal}_{th}\ \mathrm{K}^{-1}\ \mathrm{mol}^{-1}$ obtained by Chang and Westrum[20] using equilibrium calorimetry. Therefore the estimated accuracy of the experimental values is ±2% over this temperature range. In addition, the reproducibility was found to be ±2% while the standard deviations quoted in the data are somewhat less.

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[*] Throughout this paper 1 $\mathrm{cal}_{th} = 4.184$ J.

TABLE 1

EXPERIMENTAL SPECIFIC HEAT CAPACITIES OF PURE CRYSTALLINE SALTS

Temperature range 273 to 373 K. 1 cal_{th} = 4.184 J.

Compound	*T±0.5* (*K*)	C_p^{pure} (*experimental*) ($cal_{th}\ K^{-1}\ g^{-1}$)	*Linear least squares equation*		C_{p298}^{pure} ($cal_{th}\ K^{-1}\ g^{-1}$)
			Intercept at 273K ($cal_{th}\ K^{-1}\ g^{-1}$)	*Slope×10*^{4} ($cal_{th}\ K^{-2}\ g^{-1}$)	
J2	273	0.233, 0.235	0.235±0.002[a]	6.92±0.23[a]	
	298	0.256, 0.249			0.252±0.005[b]
	323	0.273, 0.267			
	348	0.288, 0.285			
	373	0.305, 0.302			
J3	273	0.241, 0.240, 0.238, 0.243	0.242±0.002	7.35±0.15	
	298	0.258, 0.261, 0.259, 0.265			0.260±0.005
	323	0.279, 0.278, 0.275, 0.281			
	348	0.296, 0.295, 0.295, 0.300			
	373	0.316, 0.312, 0.314, 0.316			
J4	273	0.245, 0.244, 0.244, 0.244	0.245±0.002	7.60±0.17	
	298	0.265, 0.268, 0.262, 0.260			0.264±0.005
	323	0.283, 0.287, 0.284, 0.280			
	348	0.300, 0.303, 0.304, 0.298			
	373	0.317, 0.323, 0.324, 0.318			
J5	273	0.252, 0.255, 0.250, 0.255	0.253±0.002	8.07±0.25	
	298	0.270, 0.273, 0.270, 0.276			0.273±0.005
	323	0.288, 0.293, 0.295, 0.300			
	348	0.307, 0.313, 0.312, 0.320			
	373	0.327, 0.334, 0.333, 0.340			
J6	273	0.257, 0.260, 0.259	0.258±0.002	8.44±0.15	
	298	0.279, 0.278, 0.278			0.279±0.005
	323	0.302, 0.299, 0.298			
	348	0.321, 0.322, 0.321			
	373	0.338, 0.345, 0.345			

J8	273	0.263, 0.268, 0.265	0.267±0.002	9.29±0.17	
	298	0.291, 0.288, 0.287			0.290±0.005
	323	0.309, 0.310, 0.310			
	348	0.334, 0.336, 0.333			
	373	0.358, 0.360, 0.357			
J10	273	0.281, 0.286, 0.282	0.280±0.002	10.16±0.20	
	298	0.301, 0.303, 0.307			0.305±0.005
	323	0.330, 0.330, 0.331			
	348	0.357, 0.358, 0.354			
	373	0.386, 0.383, 0.382			
TAAE	273	0.252, 0.246, 0.246, 0.249	0.248±0.002	8.32±0.25	
	298	0.274, 0.268, 0.271, 0.266			0.269±0.005
	323	0.294, 0.290, 0.294, 0.284			
	348	0.309, 0.305, 0.312, 0.306			
	373	0.329, 0.338, 0.334			
MDAAE	273	0.237, 0.236	0.247±0.002	9.40±0.24	
	298	0.260, 0.259			0.271±0.005
	323	0.285, 0.282			
	348	Transition occurs			
	373				
TAAP	273	0.250, 0.245, 0.250	0.250±0.002	7.87±0.17	
	298	0.270, 0.270, 0.274			0.270±0.005
	323	0.288, 0.289, 0.285			
	348	0.305, 0.308, 0.309			
	373	0.328, 0.330, 0.328			
TAAB	273	0.273, 0.262, 0.265, 0.258	0.262±0.002	9.09±0.24	
	298	0.290, 0.280, 0.282, 0.280			0.285±0.0005
	323	0.309, 0.309, 0.305, 0.305			
	348	0.330, 0.331, 0.328, 0.330			
	373	0.355, 0.354, 0.356, 0.354			
$(CH_3)_4NBr$	273	0.228, 0.232, 0.232, 0.228	0.231±0.002	6.56±0.18	
	298	0.247, 0.250, 0.250, 0.245			0.247±0.005
	323	0.263, 0.268, 0.266, 0.261			
	348	0.278, 0.284, 0.280, 0.276			
	373	0.293, 0.300, 0.299, 0.293			

(*Continued on p. 282*)

TABLE 1 (*continued*)

Compound	*T*±*0.5* (*K*)	C_p^{pure} (*experimental*) (*cal*$_{th}$ *K*$^{-1}$ *g*$^{-1}$)	*Linear least squares equation*		C_{p298}^{pure} (*cal*$_{th}$ *K*$^{-1}$ *g*$^{-1}$)
			Intercept at 273K (*cal*$_{th}$ *K*$^{-1}$ *g*$^{-1}$)	*Slope* × *10*^{4} (*cal*$_{th}$ *K*$^{-2}$ *g*$^{-1}$)	
$(C_2H_5)_4NBr$	273	0.268, 0.265, 0.265	0.264±0.002	6.56±0.15	
	298	0.283, 0.281, 0.278			0.281 ±0.005
	323	0.299, 0.297, 0.296			
	348	0.313, 0.314, 0.313			
	373	0.330, 0.332, 0.330			
$(C_4H_9)_4NBr^c$	273	0.330, 0.330, 0.331, 0.330	0.330±0.003	29.75±0.30	
	298	0.357, 0.351, 0.355, 0.350			0.353 ±0.006
	323	0.383, 0.377, 0.379, 0.375			
	348	0.414, 0.406, 0.411, 0.410			
	373	0.444, 0.443, 0.444, 0.447			
KCl	273	0.166, 0.160, 0.158	0.162±0.002	0.466±0.27	
	298	0.168, 0.163, 0.159			0.163 ±0.005
	323	0.169, 0.162, 0.161			
	348	0.170, 0.163, 0.162			
	373	0.171, 0.165, 0.163			

[a] Standard deviation. [b] Estimated error. [c] Computer-fit to an exponential function.

RESULTS

The experimental specific heat capacities are presented in Table 1 as a function of temperature. The data are stated in terms of the defined thermochemical calorie equal to 4.184 absolute joules. The data, with one exception, were fitted to a linear least squares equation using a Hewlett-Packard time shared computer program. The heat capacity of n-Bu_4NBr versus temperature appeared to give a more suitable fit to an exponential function ($C_p = Ae^{BT}$). The evaluated coefficients and the associated standard deviations are listed in Table 1. Interpolated values of the specific heat at 298 K (Table 1) were calculated from the appropriate equations.

The molal values of the thermodynamic functions at constant pressure are presented in Table 2. They were obtained from the computer-fitted equations through

TABLE 2

MOLAR HEAT CAPACITY AT 298 K AND ENTROPY CHANGE FROM 273 TO 373 K FOR PURE CRYSTALLINE SALTS

Compound	*Mol. wt.* (*g g-mol*$^{-1}$)	$C_{p298}^{pure} \pm 2\%^{a}$ (*cal*$_{th}$ K^{-1} mol^{-1})	$\Delta S_{273\to373}^{pure} \pm 4\%^{a}$ (*cal*$_{th}$ K^{-1} mol^{-1})
J2	390.3	98.4	32.6
J3	404.3	105.0	34.9
J4	418.3	110.5	36.7
J5	432.4	118.0	38.8
J6	446.4	124.6	41.6
J8	474.4	137.7	46.3
J10	502.5	153.0	51.5
TAAE	462.3	124.4	41.5
MDAAE	410.3	111.2	36.0
TAAP	476.4	128.6	42.7
TAAB	488.4	139.2	46.5
$(CH_3)_4NBr$	154.1	38.1 (38.7)[b]	12.6 [9.8(9.9)[b]][c]
$(C_2H_5)_4NBr$	210.2	59.0	19.6
$(C_4H_9)_4NBr$	322.4	114.2	38.6
KCl	74.55	12.1	

[a] Estimated deviation. [b] From Ref. 20. [c] $\Delta S_{273\to350}^{pure}$.

the data points in the temperature range 273 to 373 K. Anomalous thermal transitions were observed above 365 K for a number of the salts. The temperature ranges of these transitions and the derived thermodynamic functions and estimated errors are shown in Table 3.

The experimental heat capacity values for n-Bu_4NBr reported in Table 1 were those obtained from a second or subsequent temperature scan of a given sample. It was found that initial runs on fresh samples of n-Bu_4NBr were not as reproducible as subsequent temperature scans. This was thought to be a consequence of the absorption of a small amount of moisture in handling. Corrections were made for the small anomalous transitions occurring below 370 K when calculating heat capacity values of n-Bu_4NBr. The estimated error in the C_p values obtained by this method is less than 2%.

TABLE 3

TRANSITIONS OF TETRAALKYL- AND bis-TETRAALKYLAMMONIUM BROMIDES

Compound	*Transition temp. (K)*	*ΔH transition ±2%*[a] *(kcal$_{th}$ mol^{-1})*	*Decomposition temp. (K)*
J2	—		450
J3	—		470
J4	503–530	12.0	480
J5	458–471	5.8_5	485
J6	482–505	4.5	490
J8	430–446	2.9	485
J10	437–452	0.20	500
TAAE	—		400
MDAAE	370–372	0.72	455
TAAP	—		450
TAAB	425–436	2.2	445
$(CH_3)_4NBr$	623 (>633)[b]	[c]	505 (>503)[d]
$(C_2H_5)_4NBr$	446–448	4.8_5 (fusion)	
$(C_4H_9)_4NBr$	A 293–295	<0.016	
	B 366.0–369	0.39	
	C 382–383.5	0.08	
	394.5–395.5	3.8_6 (fusion)	

[a] Estimated deviation. [b] Sublimation, from Ref. 24. [c] Not possible to calculate, decomposition occurred partially. [d] From Ref. 24.

DISCUSSION

The results* reported here for $C_{p,298}^{pure}$ of Me_4NBr and n-Bu_4NBr, (38.1 ± 0.8) and (114.2 ± 2.2) cal$_{th}$ K^{-1} mol^{-1}, respectively, can be compared with those derived from previously reported values of $\bar{C}_{p,2}^{\circ}$ and $\Delta C_{p,2}^{\circ}$. The $\bar{C}_{p,2}^{\circ}$ values of aqueous Me_4NBr and n-Bu_4NBr solutions, obtained from extrapolation of $\bar{C}_{p,2}$ data to infinite dilution[9], are (26.05 ± 0.2) and (289.1 ± 0.3) cal$_{th}$ K^{-1} mol^{-1}, respectively. The values of ΔC_p° derived from interpolation of ΔC_p° data[15] for aqueous Me_4NBr and n-Bu_4NBr solutions at 298 K are (–14.1 ± 1.0) and (174.2 ± 1.1) cal$_{th}$ K^{-1} mol^{-1}, respectively. Using these data the values of $C_{p,298}^{pure}$ for Me_4NBr and n-Bu_4NBr are calculated to be (40.1 ± 1.2) and (114.9 ± 1.4) cal$_{th}$ K^{-1} mol^{-1}, respectively. A comparison of the

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*Recently, Somsen and de Visser, *J. Chem. Thermodyn.*, 5 (1973) 147, have reported a value of 98.5 cal$_{th}$ K^{-1} mol^{-1} for $C_{p,298}^{pure}$ of n-Bu_4NBr. However, the good agreement between the experimental results in this work and those previously reported for KCl and Me_4NBr, and the agreement between the value of $C_{p,298}^{pure}$ for n-Bu_4NBr reported here and that calculated from independent studies (see above) and Ref. 21 seems to favor the higher value.

calculated and experimental C_p^{pure} values for these salts shows good agreement within the estimated error.

It has been reported[15] that an apparent discrepancy exists between the temperature dependence of $\bar{C}_{p,2}$ values[22] of aqueous n-Bu_4NBr solutions (0.7 kg mol^{-1}) and indirect estimates[15] of $\bar{C}^{\circ}_{p,2}$ at infinite dilution. The C_p^{pure} data for n-Bu_4NBr may be used to reassess these results. The $\bar{C}^{\circ}_{p,2}$ values calculated from ΔC°_p data[15] and C_p^{pure} (Table 2), indicate an increase of 6.5 cal_{th} K^{-1} mol^{-1} (287.6 to 294.1) over the temperature range 10 to 90 °C, whereas $\bar{C}_{p,2}$ (0.7 kg mol^{-1}) (Ref. 22) shows a decrease of 50 cal_{th} K^{-1} mol^{-1} over the same temperature range.

Recent work by Philip and Desnoyers[9] on the concentration dependence of $\bar{C}_{p,2}$ of R_4NBr solutes up to 0.4 kg mol^{-1} indicates that long range coulombic ion–ion interactions and modification of structural hydration between ions have a marked effect on $\bar{C}_{p,2}$ of these solutions. Structural interference will decrease as temperature increases and this will be more apparent in the case of higher concentration, as opposed to infinite dilution conditions where maximization of ion–solvent interactions occurs. The small increase in $\bar{C}^{\circ}_{p,2}$ with increasing temperature indicates the predominance of the intrinsic heat capacity of the ion as opposed to a decreasing contribution of the component of $\bar{C}_{p,2}$ resulting from the water structure surrounding the ion. Therefore it would appear, that based on recent studies[9], the results obtained[15,22] are not in conflict but can be rationalized on the basis of structural models[23] describing the behaviour of aqueous solutions of R_4NBr salts.

The data in Table 2, although lacking the ultimate precision and accuracy obtained in classical equilibrium calorimetry, indicate that the molal heat capacity increases linearly with molecular weight. At 25 °C the average change in molal heat capacity per methylene group between the nitrogen centers of the bis-tetraalkylammonium salts and the alkyl chain of the R_4NBr salts are (6.7 ± 0.5*) and (6.3 ± 0.6*) cal_{th} K^{-1} mol^{-1}, respectively. There appears to be an irregular variation in the values as one ascends the homologous series in both cases. However, the difference between the average values is within the sum of the estimated absolute errors.

Within a homologous series entropy should increase linearly with molecular weight. Examination of the solid lattice entropy change for the various series of salts in the temperature range 273 to 373 K (Table 2) corroborates this view.

The course of the solid state thermograms of several of the bolaform salts between 373 K and the decomposition temperatures is marked by an anomalous thermal transition that is broad and symmetrical in nature. These transitions did not reappear in subsequent curves after initially heating the sample through the transition region to a temperature just below the onset of decomposition. As well cooling the samples to 298 and 248 K for periods of 24 h and 30 min, respectively, after the initial curve was carried out did not induce recurrence of the transition. The weight of the samples was checked after each run and no loss of material was observed for

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*Average deviations.

any of the compounds in which this phenomenon occurred as long as the anomalous transition was below the onset of the decomposition temperature.

Values of the enthalpies of transition and the transition temperature range are shown in Table 3. The magnitude of the transition enthalpy is seen to decrease as the homologous series is ascended. The transition temperature range was determined by constructing a straight baseline from the onset to the end of the endotherm and noting the points of departure of the curve line running into and out of the straight baseline. Similarly, the decomposition temperature was recorded as the initial temperature at which the curve started to deviate from a straight line running out of the pre-decomposition range. This latter method gives rise to a very long tail for the onset of decomposition that extends over a wide temperature range. In the case of the bis-tetraalkylammonium salts, J4 and J6, where the thermal anomalies are located at the beginning of the decomposition wing, it was possible to approximate a smooth curve for the decomposition endotherm and to subtract its contribution in the region where the larger anomalous transition occurs. This method allows for a reasonable estimate of the anomalous transition enthalpy, however, the transition range temperatures are in greater error, ± 3 K.

The origin of these transitions is difficult to rationalize from calorimetric work alone. The absence of a simple melting process and a value for the heat of fusion precludes a clear consideration as to the monotropic nature of these transitions. To resolve unequivocally whether these transitions are solid–solid or solid–mesophase will require studies of other properties of these salts. At this time the observation of what appears to be a turbid liquid during these transitions would favor the solid–mesophase case.

The heats of fusion of Et_4NBr and n-Bu_4NBr were found to be $(4.8_5 \pm 0.1)$ $kcal_{th}\ mol^{-1}$ (446 K) and (3.86 ± 0.08) $kcal_{th}\ mol^{-1}$ (395 K), respectively. Several other transitions were observed for n-Bu_4NBr.

Peak A (Table 3) is a small broad transition that occurs at 293 K; peak B, an unusual transition occurs at 366 K; and peak C is a small sharp transition occurring at 382 K. Peaks A and C occur on first and subsequent heating of the solid and on cooling from the isotropic liquid. The enthalpies of transition obtained from both cycles are invariant within the reproducibility of the present data. However, the positions of peaks A and C on cooling were found to be 281 and 377 K, respectively. Peak B is always noted on the initial heating scan, however, on cooling from the melt there is no sign of this transition. If a second heating of the melt-recrystallized material is carried out within 10 min after cooling to 298 K, peak B is not observed. Either extending the above time to 1 h or cooling the melt to 273 K for 15–20 min causes peak B to reappear at the same temperature and with the original enthalpy of transition during a second heating of the recrystallized melt.

The complex thermal behaviour of the n-Bu_4NBr compound suggests that several mesophases exist between the true solid and isotropic liquid. In addition, transitions A and C appear to be of a monotropic type. The dependence of these transitions on conditions of recrystallization can be ruled out as similar results were obtained with samples recrystallized from different solvent systems. A more detailed study of the optical and structural properties of the compounds reported in this work are required to completely resolve the observed transitions.

ACKNOWLEDGMENTS

The authors acknowledge financial support of this work from the National Research Council (Canada). J. A. Burns acknowledges the award of a N.R.C. (Canada) Scholarship.

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