Thermodynamic properties of tetrabutylammonium iodide and tetrabutylammonium tetraphenylborate

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ABSTRACT

The heat capacities of crystalline tetrabutylammonium iodide (TBAI) and tetrabutylammonium tetraphenylborate (TBATPhB) were determined over the temperature range 5–350 K by adiabatic vacuum calorimetry, generally with an uncertainty of ±0.2%. The experimental data were used to calculate the standard thermodynamic functions of TBAI and TBATPhB, namely, the heat capacity $C_p^\circ(T)$, enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T)$ and Gibbs function $G^\circ(T) - H^\circ(0)$ at $p^\circ = 0.1$ MPa for the range from $T \to 0$ to $T = 350$ K. The standard entropy of formation $\Delta_f S^\circ$ TBAI and TBATPhB at $T = 298.15$ K was also determined. Thermodynamic characteristics of fusion and solid-state transition were determined by DSC, their comparison with literature data were carry out; numerical values of enthalpies and entropies of transitions were discussed in dependence of compounds composition.

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1. Introduction

Tetraalkylammonium cations are a series with gradually varying properties as their alkyl chains become longer, so that the physico-chemical and particularly the thermodynamic consequences of the increasing sizes of the cations can be studied and rationalized [1]. Thermodynamic functions of the tetraalkylammonium cations, such as the standard molar entropy of the aqueous ions and their molar entropy of hydration have been reported until now for the first three members of the series only [2], but not for the tetrabutylammonium one. The reason for this is the lack of the required information for any salts of the latter cation, from the data on the dissolution of which in water the desired values can be calculated. Although the relevant values may have been obtained by extrapolation from data for the first three members, it is safer to have experimental data for this cation directly. On the basis of the present work on tetrabutylammonium iodide and tetrabutylammonium tetraphenylborate the desired entropies have now been obtained [3]. These salts have been selected because of their sparing solubility in water

that facilitates the calculation of the standard Gibbs energy of solution and their ready availability in a pure form. For obtaining the required experimental entropy values of the crystalline salts at $T = 298.15$ K it is necessary to measure their heat capacities from near absolute zero up to and including the latter temperature.

In the temperature range over 400 K two-phase transitions take place in tetrabutylammonium iodide and tetrabutylammonium tetraphenylborate [4,5]. First solid-state transition is caused by a kink-block type of rearrangement of the alkyl groups within the quaternary ammonium cation [4] and according to thermodynamic classification it can be attributed to first-order phase transition. Second phase transition corresponds to fusion of salt crystals. It is interesting to discuss thermodynamic characteristics indicated transitions taking account the composition and nature of compounds.

The goal of the present work is, therefore, to measure calorimetrically the heat capacity of TBAI and TBATPhB between $T = 5$ K and $T = 350$ K and to calculate the standard thermodynamic functions $C_p^\circ(T)$, $H^\circ(T) - H^\circ(0)$, $S^\circ(T)$ and $G^\circ(T) - H^\circ(0)$ over the range from $T \to 0$ to $T = 350$ K as the standard entropy of formation $\Delta_f S^\circ$ of the studied compounds at $T = 298.15$ K. In addition, to determine the temperatures, enthalpies and entropies of melting and solid-state transition for these compounds by DSC and to interpret the

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thermodynamic characteristics of transitions with a glance of compounds composition.

2. Experimental

The white fine crystals of tetrabutylammonium iodide and tetrabutylammonium tetraphenylborate as a white powder were obtained from Sigma–Aldrich Israel Ltd. and used as-received. According to the supplier's data the impurity content was not more then 1% for both studied substances. The impurities were not identified. As determined by us calorimetrically the melting temperatures of TBAI and TBATPhB are 423.2 ± 0.3 and 512.3 ± 0.1 K, respectively.

To study the heat capacity of the tested substances from $T = 5$ to $T = 350$ K an automatic thermophysical device – a BKT-3 adiabatic vacuum calorimeter [6] – was employed. The reliability of the calorimeter operation was tested by measuring the molar heat capacity C_p of standard K-1 benzoic acid and corundum [7] prepared at the Metrology Institute of the State Standard Committee of the Russian Federation. The (iron + rhodium) resistance thermometer used was calibrated on the basis of ITS-90. The calibration of the calorimeter and test results revealed that the uncertainty of heat capacity measurements at liquid helium temperatures is within $\pm 2\%$, which decreases down to $\pm 0.5\%$ with rising temperature (up to 40 K) and becomes $\pm 0.2\%$ in the range from $T = 40$ K to $T = 350$ K.

The standard atomic masses recommended by the IUPAC Commission in 2001 [8] were used in the calculation of all molar quantities.

The molar heat capacity of tetrabutylammonium iodide and tetrabutylammonium tetraphenylborate was studied between $T = 5$ K and $T = 350$ K. The sample masses inside the calorimetric ampoule were 0.7221 and 0.3501 g, respectively. In 2 series of measurements 192 and 188 experimental C_p values, respectively, were obtained both for tetrabutylammonium iodide and tetrabutylammonium tetraphenylborate. The heat capacity of the substances in the temperature range studied amounts 50–70% of the overall heat capacity of the calorimetric ampoule and the sample. The experimental C_p data were smoothed by means of degree and semilogarithmic polynomials so that the deviation of the experimental values from the corresponding smoothed $C_p = f(T)$ curve did not exceed the measurement uncertainty.

The experimental data on the thermodynamic characteristics of phase transformations were measured for tetrabutylammonium iodide and tetrabutylammonium tetraphenylborate with the DSC 204 F1 Phoenix, equipped with the μ-sensor, from Netzsch-Gerätebau GmbH. The evaluation of the DSC were executed by the Netzsch software Proteus.

The caloric calibration was performed using six reference materials according to the Netzsch procedure for enthalpy calibration. As a result, it was found, that the calorimeter and the measurement technique allow to obtain the phase transformation temperatures within to ca. ± 0.3 K and the enthalpies of the phase transformations to $\pm 1\%$. We selected aluminum pans with pierced lids and argon as purge gas. The masses of the samples inside the calorimetric ampoule were ~ 20 mg, the heating rate was 5 K min^{-1}. Additionally, it should be noted, the operation procedure was analogous to that described in Ref. [9].

3. Results and discussion

3.1. Heat capacity and standard thermodynamic functions

All experimental points of the molar heat capacity and smoothed curves in the range from $T = 5$ to $T = 350$ K are shown in Figs. 1 and 2. The molar heat capacities of tetrabutylammo-
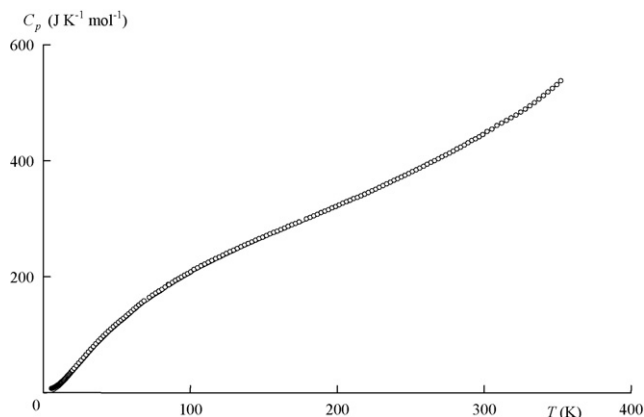

Fig. 1. Temperature dependence of heat capacity of crystalline tetrabutylammonium iodide.

nium iodide and tetrabutylammonium tetraphenylborate gradually increase as the temperature rises over the entire studied range. Numerical values of TBATPhB heat capacity higher corresponding values of TBAI within region under study, discrepancy lies from 60% to 85%. Character of C_p change with temperature increasing is the same for objects under comparison, what indicate on similarity of their crystalline structures. Thus, C_p TBAI and TBATPhB is proportional to T^1 inside temperature range from 100 to 200 K, what conform the linear structure topology.

To calculate the thermodynamic functions $C_p^\circ(T)$, $H^\circ(T) - H^\circ(0)$, $S^\circ(T)$ and $G^\circ(T) - H^\circ(0)$ of TBAI and TBATPhB (Table 1), the heat capacity of the crystalline tetrabutylammonium iodide and tetrabutylammonium tetraphenylborate was extrapolated from $T = 6$ K to $T = 0$ K by the Debye heat capacity function:

$$C_p = nD\left(\frac{\theta_D}{T}\right), \qquad (1)$$

where D is the Debye heat capacity function, n and θ_D are specific parameters. Eq. (1) describes the experimental values of heat capacity of the tested substances between $T = 6$ K and $T = 11$ K within $\pm 2\%$ for tetrabutylammonium iodide and $\pm 1.6\%$ for tetrabutylammonium tetraphenylborate with $n = 7$ for both substances and $\theta_D = 85.7$ and 57.5 K, respectively. On calculating the thermodynamic functions, it was assumed that the same accuracy holds at lower temperatures ($T < 6$ K).
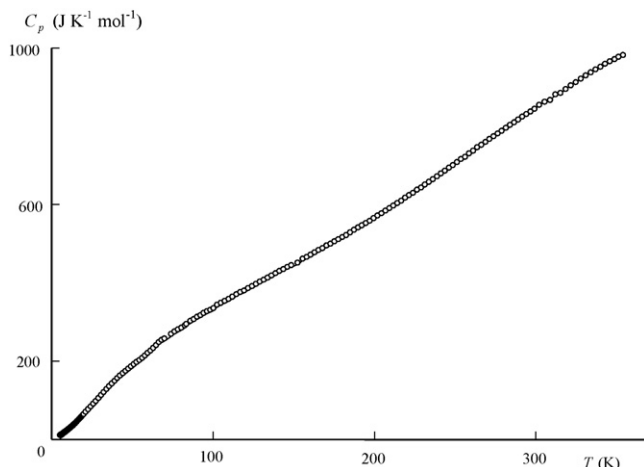

Fig. 2. Temperature dependence of heat capacity of crystalline tetrabutylammonium tetraphenylborate.

Table 1
Thermodynamic functions of crystalline tetrabutylammonium iodide (M = 369.373 g mol^{-1}) and tetrabutylammonium tetraphenylborate (M = 561.702 g mol^{-1}); $p°$ = 0.1 MPa.

T (K)	$C_p°(T)$ (J K^{-1} mol^{-1})	$H°(T) - H°(0)$ (kJ mol^{-1})	$S°(T)$ (J K^{-1} mol^{-1})	$-[G°(T) - H°(0)]$ (kJ mol^{-1})
Tetrabutylammonium iodide				
5	0.875	0.00111	0.292	0.000364
10	6.91	0.0174	2.32	0.00582
20	32.91	0.2072	14.45	0.08178
30	62.21	0.6831	33.35	0.3173
40	90.12	1.448	55.15	0.7583
50	113.7	2.471	77.88	1.423
60	135.4	3.716	100.5	2.316
70	156.1	5.177	123.0	3.434
80	172.8	6.824	145.0	4.774
90	189.7	8.636	166.3	6.331
100	204.1	10.60	187.0	8.098
110	217.9	12.72	207.1	10.07
120	230.8	14.96	226.7	12.24
130	242.9	17.33	245.6	14.60
140	254.4	19.82	264.0	17.15
150	265.4	22.42	282.0	19.88
160	276.3	25.12	299.4	22.79
170	287.1	27.94	316.5	25.87
180	297.8	30.87	333.2	29.12
190	308.6	33.90	349.6	32.53
200	319.4	37.04	365.7	36.11
210	330.4	40.29	381.6	39.84
220	341.7	43.65	397.2	43.74
230	353.2	47.12	412.6	47.79
240	365.1	50.71	427.9	51.99
250	377.4	54.42	443.1	56.35
260	390.2	58.26	458.1	60.85
270	403.3	62.23	473.1	65.51
273.15	407.6	63.51	477.8	67.01
280	416.9	66.33	488.0	70.31
290	430.8	70.57	502.9	75.27
298.15	442.5	74.13	515.0	79.42
300	445.2	74.95	517.7	80.37
310	460.1	79.47	532.6	85.62
320	475.7	84.15	547.4	91.02
330	492.4	88.99	562.3	96.57
340	511.0	94.01	577.3	102.3
350	532.3	99.22	592.4	108.1
Tetrabutylammonium tetraphenylborate				
5	2.95	0.00371	0.992	0.00124
10	16.9	0.0501	6.862	0.0185
20	57.29	0.4077	30.07	0.1936
30	102.4	1.206	61.84	0.6488
40	146.5	2.458	97.53	1.444
50	181.9	4.108	134.2	2.603
60	216.0	6.091	170.3	4.125
70	252.2	8.438	206.4	6.008
80	278.8	11.10	241.9	8.251
90	306.7	14.02	276.3	10.84
100	330.5	17.21	309.8	13.77
110	354.3	20.64	342.5	17.04
120	377.3	24.29	374.3	20.62
130	399.7	28.18	405.4	24.52
140	421.8	32.29	435.8	28.73
150	443.8	36.62	465.7	33.23
160	466.1	41.16	495.0	38.04
170	488.9	45.94	523.9	43.13
180	512.5	50.95	552.6	48.51
190	537.0	56.19	580.9	54.18
200	562.4	61.69	609.1	60.13
210	588.9	67.44	637.2	66.36
220	616.2	73.47	665.2	72.88
230	644.3	79.77	693.2	79.67
240	672.9	86.36	721.2	86.74
250	702.0	93.23	749.3	94.09
260	731.3	100.4	777.4	101.7
270	760.5	107.9	805.5	109.6
273.15	769.6	110.3	814.4	112.2
280	789.4	115.6	833.7	117.8
290	817.9	123.6	861.9	126.3

Table 1 (*Continued*)

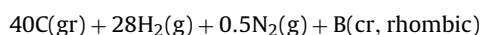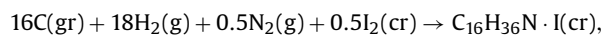| T (K)	$C_p^\circ(T)$ (J K^{-1} mol^{-1})	$H^\circ(T) - H^\circ(0)$ (kJ mol^{-1})	$S^\circ(T)$ (J K^{-1} mol^{-1})	$-[G^\circ(T) - H^\circ(0)]$ (kJ mol^{-1})
298.15	840.7	130.4	884.9	133.4
300	845.8	132.0	890.1	135.1
310	873.0	140.6	918.3	144.1
320	899.3	149.4	946.4	153.4
330	925.0	158.5	974.5	163.0
340	949.8	167.9	1002	172.9
350	974.1	177.5	1030	183.1

As can see from comparison of the values of characteristics Debye's temperature θ_D that have been calculated for temperature interval $6 \leq T \leq 12$ K, the $\theta_D(\text{TBAI}) > \theta_D(\text{TBATPhB})$ take place. It is very likely that TBAI have more hard crystalline lattice than TBATPhB.

The thermodynamic functions $H^\circ(T) - H^\circ(0)$ and $S^\circ(T)$ were estimated from the results based on the relationship $C_p^\circ = f(T)$ using the known procedures [10]. The values of $G^\circ(T) - H^\circ(0)$ were obtained by Eq. (2) using the corresponding values of $H^\circ(T) - H^\circ(0)$ and $S^\circ(T)$:

$$G^\circ(T) - H^\circ(0) = [H^\circ(T) - H^\circ(0)] - TS^\circ(T). \tag{2}$$

The results for both compounds are shown in Table 1. We suggest that for TBAI and TBATPhB the error of the calculated values of the functions is within about 1.5–2% at $T < 20$ K, 0.5% between $T = 20$ K and $T = 80$ K, 0.3% in the range from $T = 80$ K to $T = 350$ K. Hence, the absolute entropies at $T = 298.15$ K are $S^\circ(\text{TBAI, cr}) = 515.0 \pm 1.5$ J K^{-1} mol^{-1} and $S^\circ(\text{TBATPhB, cr}) = 884.9 \pm 2.5$ J K^{-1} mol^{-1}, to be used for the calculation of the standard entropies of the aqueous tetrabutylammonium cation and its entropy of hydration [3].

From the values of the absolute entropy of the tetrabutylammonium iodide and tetrabutylammonium tetraphenylborate (Table 1), carbon in the form of graphite [11], gaseous hydrogen, nitrogen, crystalline iodine [12] as well as crystalline boron [11] the standard molar entropies of formation at $T = 298.15$ K were calculated: $\Delta_f S^\circ(\text{TBAI, cr}) = -2083 \pm 9$ J K^{-1} mol^{-1} and $\Delta_f S^\circ(\text{TBATPhB, cr}) = -3105 \pm 13$ J K^{-1} mol^{-1}. They correspond to the processes:

$$16\text{C(gr)} + 18\text{H}_2\text{(g)} + 0.5\text{N}_2\text{(g)} + 0.5\text{I}_2\text{(cr)} \rightarrow \text{C}_{16}\text{H}_{36}\text{N} \cdot \text{I(cr)},$$

$$40\text{C(gr)} + 28\text{H}_2\text{(g)} + 0.5\text{N}_2\text{(g)} + \text{B(cr, rhombic)}$$

$$\rightarrow \text{C}_{16}\text{H}_{36}\text{N} \cdot \text{C}_{24}\text{H}_{20}\text{B(cr)},$$

where in the brackets the physical states of reagents are indicated: (gr), graphite; (g), gaseous; (cr), crystalline.

3.2. Temperatures and enthalpies of phase transitions

DSC curves of studied substances are shown in Figs. 3 and 4. As can see, the curves have two endothermic effects. Curves run were reproduced at repeated measurements after consecutive cooling and heating (see Figs. 3 and 4 and Tables 2 and 3). The observed transitions are reversible. The low-temperature phase transition relates to solid-to-solid transition state II to state I at heating [4] as the high-temperature transition caused by melting.

Enthalpies of transitions ($\Delta_{tr}H^\circ$ and $\Delta_{fus}H^\circ$) were calculated from the areas under the DSC peaks. The temperature corresponding to the minimum value of the specific heat flow rate in the transition range is regarded as transition temperature (T_{fus}° and T_{tr}°). The entropies of transitions ($\Delta_{fus}S^\circ$ and $\Delta_{tr}S^\circ$) were estimated from the temperatures and enthalpies of transition according to Eqs. (3) and (4), respectively:

$$\Delta_{fus}S^\circ = \frac{\Delta_{fus}H^\circ}{T_{fus}^\circ}, \tag{3}$$
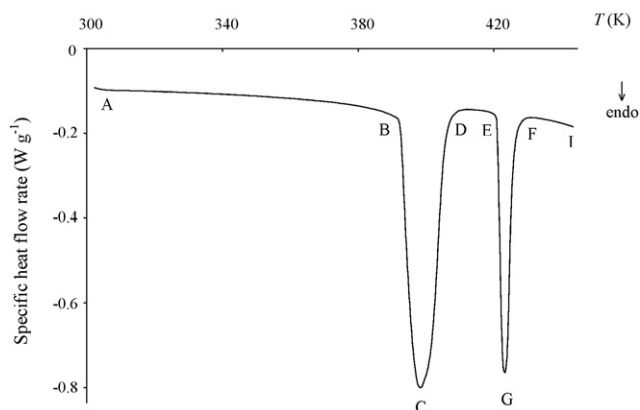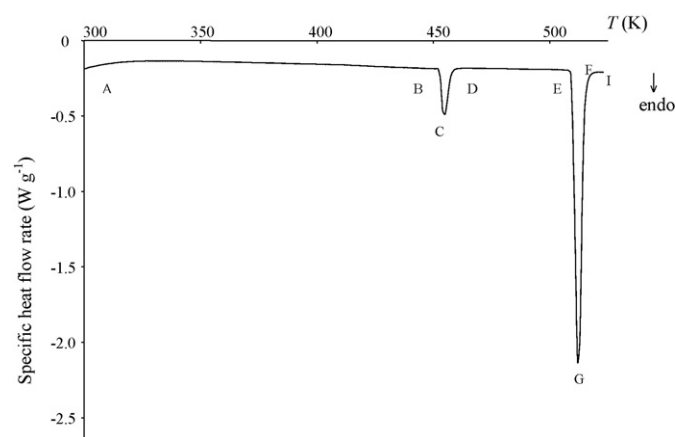

Fig. 3. Plot of the DSC-signal against temperature for tetrabutylammonium iodide: AB—state II; DE—state I; FI—liquid; BCD and EGF—in the transition state II ⇌ state I and the melting intervals, respectively.

$$\Delta_{tr}S^\circ = \frac{\Delta_{tr}H^\circ}{T_{tr}^\circ}. \tag{4}$$

The resulting thermodynamic characteristics of transitions in TBAI and TBATPhB are given in Table 4.

Earlier, for TBAI and TBATPhB the phase transitions were revealed and the values of temperatures, enthalpies and entropies of transitions were presented by authors [4]. As can see from Table 4, the results of phase transition calorimetric study which were obtained by us and published in Ref. [4] are in good agreement. The value 416.5 K, which authors of Ref. [5] gives as fusion temperature of TBAI, is correspond to beginning of solid-state transition according to our data as well as results of Ref. [4].

First solid-state transition is caused by a kink-block type of rearrangement of the alkyl groups within the quaternary ammonium

Fig. 4. Plot of the DSC-signal against temperature for tetrabutylammonium tetraphenylborate: AB—state II; DE—state I; FI—liquid; BCD and EGF—in the transition state II ⇌ state I and the melting intervals, respectively.

Table 2
Thermodynamic characteristics of fusion of tetrabutylammonium iodide and tetrabutylammonium tetraphenylborate ($p° = 0.1$ MPa).

Substance	Experiment number	$T_i - T_f$ (K)[a]	$T_{fus}°$ (K)[b]	$\Delta_{fus}H°$ (kJ mol^{-1})[c]	$\Delta_{fus}S°$ (J K^{-1} mol^{-1})[d]
TBAI	1	419–430	423.3	9.0	21.3
	2	419–430	422.9	9.0	21.3
	3	419–430	423.4	9.1	21.5
	Mean value[e]		423.2 ± 0.3	9.0 ± 0.1	21.4 ± 0.3
TBATPhB	1	509–518	512.3	44.2	86.3
	2	509–518	512.4	43.5	84.9
	3	509–518	512.3	43.9	85.7
	Mean value[e]		512.3 ± 0.1	43.9 ± 0.5	85.6 ± 0.9

[a] T_i and T_f the temperatures of the beginning and the end of melting, respectively.
[b] $T_{fus}°$ the temperature of melting corresponding to the minimum specific heat flow rate in the melting interval.
[c] $\Delta_{fus}H°$ the molar enthalpy of melting.
[d] $\Delta_{fus}S°$ the molar entropy of melting.
[e] The values are indicated within apparatus uncertainty.

Table 3
Thermodynamic characteristics of transition in tetrabutylammonium iodide and tetrabutylammonium tetraphenylborate ($p° = 0.1$ MPa).

Substance	Experiment number	$T_i - T_f$ [a] (K)	$T_{tr}°$ (K)[b]	$\Delta_{tr}H°$ (kJ mol^{-1})[c]	$\Delta_{tr}S°$ (J K^{-1} mol^{-1})[d]
TBAI	1	391–409	398.4	27.8	69.8
	2	391–409	398.6	27.7	69.5
	3	391–409	399.1	27.9	69.9
	Mean value[e]		398.7 ± 0.4	27.8 ± 0.3	69.7 ± 0.9
TBATPhB	1	452–461	454.6	6.57	14.5
	2	452–461	454.8	6.49	14.3
	3	452–462	454.7	6.52	14.3
	Mean value[e]		454.7 ± 0.1	6.53 ± 0.07	14.3 ± 0.2

[a] T_i and T_f the temperatures of the beginning and the end of transition, respectively.
[b] $T_{tr}°$ the temperature of transition corresponding to the minimum specific heat flow rate in the transition interval.
[c] $\Delta_{tr}H°$ the molar enthalpy of transition.
[d] $\Delta_{tr}S°$ the molar entropy of transition.
[e] The values are indicated within apparatus uncertainty.

Table 4
Standard thermodynamic characteristics of phase transitions for the tetrabutylammonium iodide and tetrabutylammonium tetraphenylborate.

Substance	$T_{tr}°$ (K)	$\Delta_{tr}H°$ (kJ mol^{-1})	$\Delta_{tr}S°$ (J K^{-1} mol^{-1})	$T_{fus}°$ (K)	$\Delta_{fus}H°$ (kJ mol^{-1})	$\Delta_{fus}S°$ (J K^{-1} mol^{-1})	$\Delta H°_\Sigma$ (kJ mol^{-1})[a]	$\Delta S°_\Sigma$ (J K^{-1} mol^{-1})[b]	Ref.
TBAI	398.7	27.8	69.7	423.2	9.0	21.4	36.8	91.1	Our paper
	392.2	28.0	71.5	419.2	9.6	23.0	37.6	94.5	[4]
TBATPhB	454.7	6.53	14.3	512.3	43.9	85.6	50.4	99.9	Our paper
	458.2	6.69	14.2	502.2	38.5	77.0	45.2	91.2	[4]

[a] $\Delta H°_\Sigma$ the total enthalpy of transitions.
[b] $\Delta S°_\Sigma$ the total entropy of transitions.

cation [4], second corresponds to fusion. The some dependences of thermodynamic characteristics of phase transitions from compound compositions are given below. Thus, some more spatial substituent, tetraphenylborate, obviously, bring to more friable structure of TBATPhB in comparison with TBAI. The relative structure hardness of salts is confirmed by values of characteristic Debye temperatures and $\Delta_{tr}H°/\Delta H°_\Sigma$ ration, here $\Delta H°_\Sigma$ the total enthalpy of transitions. For TBAI and TBATPhB the contribution of solid-to-solid transition enthalpy in the total enthalpy is 76% and 13%, respectively. The replace of orientations of group-substituents into ionic salts structure proceeds for TBATPhB with small energetic consumptions. However the state I for TBAI is less thermal stable in comparison with state I for TBATPhB. The last sentence is followed from Table 4. The identical structure topology of objects under comparison is confirmed by practically similar the total entropy of transitions ($\Delta S°_\Sigma$) values.

Thus, should be noted results of analysis of low-temperature heat capacity and thermodynamic characteristics of phase transitions for ammonium salts under study are in good agreement with the structural models.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2008.10.017.

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