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Thermodynamic properties of tetrabutylammonium iodide and tetrabutylammonium tetraphenylborate

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1. Introduction

Tetraalkylammonium cations are a series with gradually varying properties as their alkyl chains become longer, so that the physicochemical 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

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 $T \rightarrow 0$ to T = 350 K. The standard entropy of formation $\Delta_{\rm f}S^{\circ}$ 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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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 $T \rightarrow 0$ to T=350 K as the standard entropy of formation $\Delta_{\rm f} S^{\circ}$ 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:

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

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 ±2% for tetrabutylammonium iodide and ±1.6% for tetrabutylammonium tetraphenylborate with *n* = 7 for both substances and θ_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 ($M = 369.373 \text{ g mol}^{-1}$) and tetrabutylammonium tetraphenylborate ($M = 561.702 \text{ g mol}^{-1}$); $p^{\circ} = 0.1 \text{ MPa}$.

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1101.2.1.22.2.1.11.0.1.11102.2.9.217.3.32.2.6.017.3.51202.5.4.419.8.22.6.019.8.51502.5.4.42.2.4.22.9.019.8.51502.7.3.32.5.1.22.9.4.42.2.7.91502.7.3.32.5.1.22.9.4.42.5.1.21502.7.3.32.7.4.43.5.52.5.7.11502.7.3.32.7.4.43.5.52.5.7.11502.7.3.43.7.0.43.5.73.5.12003.3.4.44.0.2.53.8.1.63.8.4.12013.3.2.14.7.1.24.7.2.93.5.12023.3.2.14.7.1.24.7.2.95.1.92033.3.2.14.7.1.24.7.2.95.0.92043.3.5.15.7.15.6.3.55.7.12053.9.2.24.7.3.16.5.55.7.12063.9.2.23.9.27.9.2.77.9.22074.0.3.36.2.2.34.7.3.16.5.12084.0.56.3.34.86.07.0.3.12094.0.7.73.9.27.9.2.73.9.22104.0.57.9.33.9.29.0.22204.0.57.9.39.0.29.0.22304.7.78.9.29.0.29.0.22304.7.78.9.29.0.29.0.22304.9.79.0.29.0.29.0.233010.2.41.2.061.9.49.0.23301	100	204.1	10.60	187.0	8.098
1202.8.813.32.6.61.2.6.61302.54.419.322.6.6.419.81502.55.42.2.422.8.019.81502.75.32.5.122.8.02.5.371702.87.12.7.9431.6.52.5.371802.9.783.0.3034.6.63.3.0200315.43.0.03.5.53.5.1210330.440.0238.1.63.9.8.422034.74.3.6.63.9.74.7.32303.5.24.7.124.2.64.7.92403.65.150.714.7.95.9.92703.0.250.254.7.350.927040.350.714.7.95.9.927040.350.5147.74.9.6271.540.766.3.5147.86.0.327040.870.0750.2.97.2.7280446.96.3.5147.380.3729040.870.3750.2.97.2.7291.544.57.4.1350.67.4.2292.445.744.57.3.780.37293.544.57.4.1350.780.37294.544.57.4.19.0.280.37294.544.57.4.19.0.280.37294.544.57.4.19.0.280.37294.544.57.4.19.0.280.37294.544.57.4.19.0.280.37294	110	217.9	12.72	207.1	10.07
nnnnnnn1925.4100226.010.810.6190275.325.1229.422.79180275.325.1229.422.79180275.325.0225.1225.1219030.635.3035.225.12200319.437.0436.5735.1121033.440.2931.638.422031.440.2931.638.423035.247.1242.647.7924035.150.7142.951.9925037.454.4245.163.5126039.0258.2645.163.51270.540.562.347.5165.1270.540.577.443.7451.077.428045.274.1355.077.783.728044.240.867.0792.410.0339042.488.9955.292.490.1339042.410.0667.310.310.339042.410.0667.310.310.339042.410.0667.310.310.339042.410.0667.310.310.339042.410.0667.310.310.339015.072.90.00719.920.013439015.015.00.01466.80.08 <tr< td=""><td>120</td><td>230.8</td><td>17.22</td><td>220.7</td><td>14.60</td></tr<>	120	230.8	17.22	220.7	14.60
nononononono10276.325.1229.4422.5717027.3127.94316.525.8718029.7830.8735.2321.1219030.6633.9034.6535.13200318.440.0238.1639.8420133.0440.2938.1639.8420235.1247.1241.2647.7920335.247.1241.2647.7920435.150.7142.6945.9920537.4450.7142.6945.9920640.350.7142.6945.9120740.362.3344.9165.33208416.963.3147.7945.9120940.870.3750.297.27200416.963.3147.7940.31200416.963.3147.7940.31201445.274.1351.507.27202416.963.3349.2449.1165.24203445.274.1351.617.2720445.17.3710.239.029.02205442.574.1351.617.2720645.274.1351.617.2720745.274.147.3310.4420845.274.147.3310.4420945.27.447.3310.4421015.2 <td< td=""><td>140</td><td>242.9</td><td>10.82</td><td>243.0</td><td>17.15</td></td<>	140	242.9	10.82	243.0	17.15
no266325122942942279170287125423132221918025783087333222111803764365132533406325320031943704365735113514210330440293816339843322220341.74365397247.79230353247.1242.6447.79240355.150.7142.7951.99250377.454.2243.3165.31270.5403.362.3347.3165.31270.4403.362.3347.3165.11271.540.76.563.5147.3165.11271.540.75.663.5147.8247.77281.544.2544.1351.5077.7281.544.2544.1351.5077.74280.444.5244.1351.6249.62290445.784.9952.390.22280.445.145.1549.6249.6130.442.488.9950.2390.2330.442.443.8956.2340.8120047.5741.1040.940.230.442.50.00716.6620.0018530.442.50.00719.02.39.5730.529.50.00719.02.39.5730.442.51.0066.6620.00185	150	254.4	22 42	204.0	10.88
PPP2P2P2P2P2P2P2180257.80.077333.222.1218030.6633.30349.632.53200319.440.2936.5735.11201330.440.29381.637.2203353.247.12412.647.79204355.150.71427.951.99250377.454.4243.166.35200390.282.6438.160.8520030.362.2347.3165.5120140.362.31477.367.0128046.963.31477.367.0128046.970.3151.079.4228046.970.3151.079.4228046.274.5551.780.731046.179.4752.979.4231046.274.5552.385.6231046.179.4752.485.6231046.179.4752.485.6231046.179.4752.485.6231046.179.4752.485.6231140.0157.385.6285.6231240.157.385.6285.6231340.167.385.6285.6231440.063.397.331.4431542.279.563.31.4431640.170.486.9 <td>160</td> <td>203.4</td> <td>25.12</td> <td>299.4</td> <td>22 79</td>	160	203.4	25.12	299.4	22 79
No2978008733229.12190308.63390349.632.53200319.4370.4365.735.11200319.443.65397.247.7023035.3247.12412.647.79240365.150.7147.9351.99250377.454.2243.3165.35260390.258.26458.165.5127.1547.663.5147.867.0127.1444.2347.3165.5127.1547.663.5147.867.0128.1544.2574.1351.5079.7228.1544.2574.1351.5079.4230.045.2179.4732.2685.6230.045.2179.4732.2685.6230.045.2179.4730.7102.330.045.2390.2052.2190.2030.045.248.9956.2390.6730.045.2410.00716.8620.018530.016.90.05016.8620.018530.016.90.05016.8620.01330.016.241.20661.840.648830.016.241.20661.840.648830.016.90.05016.86210.9130.016.90.05016.8620.018530.016.90.05016.86210.8430.016.9<	170	287.1	27.94	316.5	25.87
19030.6633.0034.8632.5320033.0440.2936.5735.1121033.0440.2936.5737.4423035.3247.1241.2647.7923035.3247.1241.2647.7924035.150.71427.950.5325037.7454.4243.1165.51260390.252.6247.3165.5127040.3362.2347.3165.51280416.963.31477.8167.01280416.963.3148.8070.31281.544.2.274.9551.5079.42281.544.2.374.9551.7780.7230.044.5274.9551.7780.7231.040.1780.9057.3310.4332051.099.262.3310.332051.099.260.0370.9232051.099.20.012410.6332051.099.20.012410.6332140.0157.30.01340.4332252.280.9313.440.6432397.290.00370.9920.012432410.0513.422.6313.4432510.016.90.01340.643252.280.4897.331.4444014.632.4397.331.4445018.194.05<	180	297.8	30.87	333.2	29.12
200319437.0436.7436.7436.7421033.4443.0537.1443.0537.1443.0522035.1257.1247.2943.2443.1156.3525037.458.2647.3165.5165.5127.140.3362.2347.3165.5127.140.3470.7663.3148.0070.3128.041.6963.3148.0070.3129.040.8470.5751.5079.4229.140.5274.3351.5079.4230.045.2174.9551.780.3730.045.2174.9551.780.3730.045.2174.9551.2075.2730.045.2174.9551.2079.4230.045.2174.9753.2685.6230.045.2174.9753.2685.6230.045.2174.9773.2770.2730.045.2174.9773.2770.2730.045.2170.9770.3770.3730.010.2410.06768.820.018530.010.2412.06768.820.018530.010.2412.06763.2112.4430.010.2412.06730.0710.4430.010.2412.0613.7713.2730.010.2412.0613.7713.2430.010.2412.0613.7713.27<	190	308.6	33.90	349.6	32.53
21030.440.2981.699.2439.43220341.743.65397.243.74230353.247.1242.943.94240365.150.71427.951.99250377.454.4245.160.85270403.362.347.165.51270403.362.347.867.01280416.963.3147.867.01280416.963.3147.870.31290430.870.4750.079.27281.5442.574.1351.780.37310460.179.4752.685.62320475.784.15547.491.02320492.489.952.390.292.435052.392.292.410.2335052.392.292.410.2330010.241.2066.8820.01841016.90.05016.8820.01853010.241.2061.440.4684014.652.4537.531.4445018.194.108142.22.6031016.52.573.0310.445018.194.1022.731.4445018.194.1023.731.4445018.194.1023.731.4445018.194.1023.731.4445018.194.102 <t< td=""><td>200</td><td>319.4</td><td>37.04</td><td>365.7</td><td>36.11</td></t<>	200	319.4	37.04	365.7	36.11
22034.1743.6537.247.78230353.247.12412.647.79240365.150.71472.951.99250377.454.42443.160.85260390.258.26473.165.51273.15407.663.51477.867.01273.15407.663.51478.070.31280416.963.31488.070.31280.4445.274.13515.079.42300445.274.9551.679.42301460.179.47532.685.62320475.784.1557.3102.3350531.090.259.4102.3350531.090.20.012.4102.3350531.090.06.820.012.430102.41.20.66.8420.018.530102.41.05.01.4441.4443016.52.45897.531.44430102.41.06.06.8620.018.530102.41.06.013.422.60330102.41.06.910.4414.6530126.06.09110.3410.6430126.06.09110.3410.6430126.06.09110.4410.6430126.16.09110.4410.6430127.1108.410.6410.6430137.114	210	330.4	40.29	381.6	39.84
230353247,1241,2647,79240365150,71427.951.90250377.454.4243.156.35250390.258.26458.160.85270403.362.2347.3165.51280416.966.3348.070.31280416.966.3348.070.31280445.274.1351.5079.42281.5442.574.1351.079.42300445.274.9551.780.37310460.179.4753.685.62320475.784.15547.491.02330422.488.9956.2.396.5734051.099.20012410.235052.392.292.410.313010.2.412.0661.84001241016.90.003110.9920.01241016.90.0031130.070.13353010.2.41.20661.840.04883010.2.41.20661.840.04883010.2.41.20661.840.04883010.2.41.20661.840.0243010.2.41.20661.840.0243010.2.41.20661.840.0243010.2.41.20661.840.0243010.2.41.20661.840.0243013.514.44	220	341.7	43.65	397.2	43.74
240365.150.7147.951.99250377.454.42443.166.35260390.252.6645.8160.85273.15407.665.5147.3165.51273.15407.665.3147.8467.01280416.966.33488.0070.31290430.870.5750.9075.27290.4445.274.9551.5079.42300445.274.9557.7780.37301460.179.4752.6685.62300475.784.1557.3296.57300475.784.1557.3310.2330140.2489.9956.2396.5730252.2390.0037199.9200.012430116.90.005116.8620.01853010.241.20661.840.648840146.52.45897.531.4445018.194.108134.22.60330102.41.20661.840.60880278.811.1024.98.251100330.517.21308.813.7710154.32.606442.517.04102330.517.21308.813.7710339.6722.9458.826.62104330.517.21308.813.7710530.6245.1645.9445.9410644.88 <td>230</td> <td>353.2</td> <td>47.12</td> <td>412.6</td> <td>47.79</td>	230	353.2	47.12	412.6	47.79
250377.454.4244.1156.35260390.258.26458.160.85270403.362.23473.165.51270.4416.966.3348.070.31280416.966.3348.070.31280430.870.57502.975.27281.544.2574.1351.5079.42300445.274.95517.780.37310460.179.4753.2685.62320475.784.15547.491.02330452.488.9956.2396.5734051.099.2259.2108.1350512.399.2259.4108.12052.399.2259.4108.12052.90.003710.9920.001242052.90.003710.9920.012330102.41.20561.840.648840166.52.45897.531.44450181.94.108134.22.60360216.06.091170.24.12570252.28.438206.46.00880278.811.1024.98.251100306.714.02276.310.4411034.832.064342.517.04120377.32.2935.13.33130132.555.955.648.51100366.14.164	240	365.1	50.71	427.9	51.99
260390258,2648,8160.85270403.362.23473.165.51273.15407.663.51477.867.01280416.966.33488.070.3128040.870.57502.975.27300445.274.95517.780.37310460.179.47532.685.62320475.784.15547.491.02330492.488.99562.396.5734051.1094.0157.3102.335052.392.292.400.12.4160.05016.6620.01852057.290.003710.9920.001241016.90.05016.6620.01852057.290.003719.0920.01241016.90.05016.6620.01852057.290.003719.0920.01241016.90.05016.6620.01852057.290.407730.070.193630102.41.20661.840.648850181.94.108134.22.60360216.66.091170.34.12570252.28.438276.310.84100306.714.02276.310.84110354.32.646.0083.04110354.32.662457.33.23110399.728.18 <td< td=""><td>250</td><td>377.4</td><td>54.42</td><td>443.1</td><td>56.35</td></td<>	250	377.4	54.42	443.1	56.35
270403.362.2347.3165.51273.15407.663.51477.867.01280416.966.33448.070.31280.1440.570.57502.975.27288.15442.574.13515.079.42300445.274.95517.780.37310460.179.47532.685.62320475.784.15547.491.02330492.488.99562.396.57340511.099.22592.4108.121016.90.003716.8620.0185350532.399.22592.4108.121116.90.05016.8620.018530102.41.2066.1840.644830102.41.2066.1840.644830102.41.2066.1840.644830102.41.2061.3422.60330102.41.2061.3422.60330102.41.061134.22.60330252.28.438206.46.0083030.6.71.10124.193.233030.6.71.40227.6310.843030.6.71.40227.6310.843030.6.71.40227.633.33310.4433.6245.743.333130.99.728.18405.424.523130.99.7<	260	390.2	58.26	458.1	60.85
273.15407.663.51477.867.01280416.966.33488.07.31290430.870.57502.975.27300445.274.95515.07.94.2300445.274.95532.685.62300457.784.15547.491.02300492.488.99562.396.5730051.094.01577.3102.3350552.392.259.20.0012435052.30.005116.8620.01852057.290.005116.8620.01852057.290.005016.8620.01852057.290.407730.070.193630102.41.20661.840.648840146.52.45897.531.44450181.94.108134.22.60360216.06.091170.34.12570252.28.438206.46.00890306.714.02276.310.84110354.32.064342.517.04120377.32.29343.32.64130399.728.18405.42.45214041.832.2934.32.64150443.836.6245.733.33160466.141.16495.038.0417048.955.156.056.218051.250.95 <td>270</td> <td>403.3</td> <td>62.23</td> <td>473.1</td> <td>65.51</td>	270	403.3	62.23	473.1	65.51
280416.966.33488.070.31290430.870.5750.975.27298.15442.574.13515.079.42310460.179.47532.685.62310490.179.47532.685.62320475.784.15547.491.02330492.488.99562.396.57340511.094.01577.3102.3350522.399.22592.4108.1Tertabutylamonium terphenylborateTertabutylamonium terphenylborateTertabutylamonium terphenylborate1.00.003710.9920.001241016.90.05016.8620.01852057.290.407730.070.19363010.241.2066.1840.648840146.52.45897.531.44450181.94.108134.22.60360216.06.091170.34.12570252.28.438206.46.08880278.811.1024.937.3100330.517.21309.813.77110354.3206.4355.828.73150443.836.62455.824.52150443.836.6233.23150443.836.6233.23150443.836.5136.916057.463.527.88 <td>273.15</td> <td>407.6</td> <td>63.51</td> <td>477.8</td> <td>67.01</td>	273.15	407.6	63.51	477.8	67.01
290430.870.57502.975.27288.15442.574.13515.075.42300445.274.95517.780.37310460.179.4753.2685.62320475.784.15547.491.02330492.488.99562.396.57340511.094.01577.3102.3350522.399.2292.4108.1252.950.003710.9920.001241016.90.50516.8620.01852057.290.407730.070.193630102.41.20661.840.648840146.52.45897.531.44450181.94.108134.22.60360216.06.091170.34.12570252.28.438206.46.00880278.811.1024.517.04100354.320.64342.517.04101354.320.64342.517.04102376.314.2432.9343.3103397.723.236.332.3150443.8366.245.832.3150443.8366.245.832.3150443.8366.232.334.3150443.8366.232.334.3150443.836.6245.832.3150443.836.6245.	280	416.9	66.33	488.0	70.31
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 85.62 330 492.4 88.99 562.3 96.57 340 511.0 90.22 59.24 102.3 50 532.3 99.22 59.4 108.1 Tetraburylammonium tetraphenylborate - - - 0.0071 0.992 0.0014 10 16.9 0.0501 6.862 0.0185 0.0124 0.0164 0.6488 20 57.29 0.4077 3.0.07 0.1936 0.148 0.6488 40 146.5 2.458 197.3 1.444 0.6488 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 80 378.8 11.10 241.9 324.9 </td <td>290</td> <td>430.8</td> <td>70.57</td> <td>502.9</td> <td>75.27</td>	290	430.8	70.57	502.9	75.27
300 445.2 74.95 51.7.7 80.37 310 460.1 79.47 53.26 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 57.73 102.3 350 532.3 99.22 50.4 108.1 Tetrabutylammonium tetraphemylborate 0.00124 10 16.9 0.00501 6.862 0.00185 20 57.2.9 0.4077 30.07 0.1936 30 102.4 1.206 61.84 6.6488 40 146.5 2.458 97.53 1.444 50 181.9 4.108 134.2 2.603 60 216.0 6.091 17.3 42.51 70 252.2 8.438 206.4 6.008 80 377.3 24.29 374.3 20.62 90 306.7	298.15	442.5	74.13	515.0	79.42
310 400.1 74/4 52.b 85.b2 320 475.7 84.15 67.4 91.02 330 492.4 88.99 562.3 96.57 350 532.3 99.22 592.4 108.1 Tetrabutylammonium tetraphenylborate 5 2.95 0.001371 0.992 0.01185 20 57.29 0.4077 30.07 0.1936 20 57.29 0.4077 30.07 0.1936 20 57.29 0.4077 30.07 0.1936 20 57.29 0.4077 30.07 0.1936 20 16.0 6.091 170.3 4.125 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 30.9 10.84 100 330.5 17.21 39.9 13.7 10.4 120 377.3 24.29 374.3	300	445.2	74.95	517.7	80.37
2.0 47.3.7 88.15 947.4 91.02 300 492.4 88.99 562.3 965.7 340 511.0 94.01 577.3 102.3 350 532.3 99.22 592.4 108.1 Tetrabutylammonium tetraphenylborate	310	460.1	/9.4/	532.6	85.62
3.0 4.92.4 86.99 302.3 90.37 340 511.0 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 6.18.4 0.6488 40 146.5 2.45.8 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 30.5 90 306.7 14.02 276.3 10.84 100 330.5 17.21 309.8 13.77 110 354.3 20.62 37.43 20.62 130 399.7 28.18 405.4 2	320	4/5./	84.15	547.4	91.02
340 511.0 94.01 57.3 102.3 350 532.3 99.2 592.4 108.1 Tetrabutylammonium tetraphenylborate 592.4 0.00124 0.00124 10 16.9 0.05010 6.862 0.00185 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 20.62 374.3 20.62 120 377.3 24.29 374.3 20.62 140 421.8	330	492.4	88.99	502.3	96.57
3.0 3.52 3.52 3.54 1.05.4 Tetraburylammonium tetraphenylborate 0.00124 10 16.9 0.00371 0.992 0.00124 10 16.9 0.00371 30.07 0.1936 20 57.29 0.4077 30.07 0.1936 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 2064 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 20.62 37.3 20.62 130 399.7 28.18 405.4 24.52 140 41.8 36.62 465.7 33.23 150 465.1 41.6	340 250	522.2	94.01	502.4	102.3
Tetraburplamonium tetraphenylbrate 9 0.000371 0.902 0.0018 10 16.9 0.00501 6.862 0.0185 20 57.29 0.4077 30.07 0.1936 30 102.4 1.206 6.18.4 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 11.0 241.9 8.251 90 306.7 14.02 276.3 10.84 100 33.0.5 17.21 309.8 13.77 110 354.3 2.064 342.5 17.04 120 377.3 24.29 374.3 2.662 130 399.7 28.18 32.0 38.04 150 443.8 36.62 45.94 52.69 45.11	220	332.3	33.22	332.4	100.1
5 2.95 0.00371 0.992 0.00124 10 16.9 0.00371 30.07 0.1936 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 2.16.0 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 10 354.3 20.64 342.5 17.04 120 377.3 24.29 374.3 20.62 140 421.8 32.29 435.8 28.73 150 443.8 36.62 455.7 33.23 160 466.1 41.16 495.0 38.04 170 488.9 67	Tetrabutylammo	onium tetraphenylborate			
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 20.62 140 421.8 32.29 435.8 28.73 150 443.8 36.62 455.7 33.23 160 466.1 41.16 495.0 38.04 170 488.9 65.6	5	2.95	0.00371	0.992	0.00124
20 57.29 0.40/7 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 28.73 150 433.8 36.62 455.7 33.23 160 466.1 41.16 495.0 38.04 170 488.9 65.1	10	16.9	0.0501	6.862	0.0185
30 102.4 1.200 $0.1.84$ 0.0485 40 1465 2.458 97.53 1.444 50 181.9 4.108 134.2 2.603 60 216.0 6.091 70.3 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 56.19 609.1 60.13 210 58.9 67.44 637.2 66.36 220 616.2 73.47 665.2 72.88 230 64.3 79.77 693.2 79.67 240 672.9 86.36 721.2 86.74 250 70.0 93.23 749.3 94.09 260 731.3 100.4 77.74 101.7 270 760.5 107.9 805.5 109.6 <td< td=""><td>20</td><td>57.29</td><td>0.4077</td><td>30.07</td><td>0.1936</td></td<>	20	57.29	0.4077	30.07	0.1936
400140.52.4589.7.331.44450181.94.108134.22.60360216.06.091170.34.12570252.28.438206.46.00880278.811.10241.98.25190306.714.02276.310.84100330.517.21309.813.77110354.320.64342.517.04120377.324.29374.320.62130399.728.18405.424.52140421.832.29435.828.73150443.836.62465.733.23160466.141.16495.038.04170488.945.94523.943.13180512.550.95552.648.51190537.056.19509.160.13210588.967.44637.266.36220616.273.47665.272.88230644.379.77693.279.67240672.986.36721.286.74250702.093.23749.394.09260731.3100.477.74101.7270760.5107.9805.5109.6273.15769.6110.3814.4112.228078.4115.692.7117.6	30	102.4	1.200	07.52	0.0488
30 161.9 4.105 194.2 2.003 60 216.0 6.091 170.3 4.125 70 252.2 8.438 2064 6.008 80 278.8 11.10 241.9 8.251 90 306.7 14.02 276.3 1084 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 56.19 609.1 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 70.67 240 672.9 86.36 721.2 86.74 250 70.0 93.23 749.3 94.09 273.15 79.6 100.3 814.4 112.2 280 79.6 110.3 814.4 112.2	40	140.5	2.436	97.33	1.444
00 216.0 60.01 10.0.5 11.0.5 41.1.5 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 60.13 212	50	216.0	4.108	134.2	2.005
70 278.8 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 48.51 200 562.4 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 94.09 270 760.5 107.9 805.5 109.6 273.15 769.6 110.3 814.4 112.2 280 789.4 115.6 812.7 117.6	70	210.0	8.438	206.4	6.008
00 306.7 11.0 21.63 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 45.54 523.9 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 78.8 220 616.2 73.47 655.2 72.88 230 644.3 79.77 693.2 79.67 240 672.9 86	80	232.2	11 10	241 9	8 251
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 94.09 270 760.5 107.9 805.5 109.6 273.15 769.6 110.3 814.4 112.2 280 780.4 115.6 292.7 117.2	90	306.7	14.02	276.3	10.84
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 32.33 749.3 94.09 260 731.3 100.4 777.4 101.7 270 760.5 107.9 805.5 109.6 273.15 78.94 115.6 814.4 112.2	100	330.5	17.21	309.8	13.77
120377.324.29374.320.62130399.728.18405.424.52140421.832.29435.828.73150443.836.62465.733.23160466.141.16495.038.04170488.945.94523.943.13180512.550.95552.648.51190537.056.19580.954.18200562.461.69609.160.13210588.967.44637.266.36220616.273.47665.272.88230644.379.77693.279.67240672.986.36721.286.74250702.093.23749.394.09260731.3100.4777.4101.7270760.5107.9805.5109.6273.15769.6110.3814.4112.2280780.4115.6823.7117.2	110	354.3	20.64	342.5	17.04
130399.728.18405.424.52140421.832.29435.828.73150443.836.62465.733.23160466.141.16495.038.04170488.945.94523.943.13180512.550.95552.648.51190537.056.19580.954.18200562.461.69609.160.13210588.967.44637.266.36220616.273.47665.272.88230644.379.77693.279.67240672.986.36721.286.74250702.093.23749.394.09260731.3100.4777.4101.7270760.5107.9805.5109.6273.15769.6110.5823.7112.2	120	377.3	24.29	374.3	20.62
140421.832.29435.828.73150443.836.62465.733.23160466.141.16495.038.04170488.945.94523.943.13180512.550.95552.648.51190537.056.19580.954.18200562.461.69609.160.13210588.967.44637.266.36220616.273.47665.272.88230644.379.77693.279.67240672.986.36721.286.74250702.093.23749.394.09260731.3100.4777.4101.7270760.5107.9805.5109.6273.15769.6110.3814.4112.2280780.4115.6823.7172.7	130	399.7	28.18	405.4	24.52
150443.836.62465.733.23160466.141.16495.038.04170488.945.94523.943.13180512.550.95552.648.51190537.056.19580.954.18200562.461.69609.160.13210588.967.44637.266.36220616.273.47665.272.88230644.379.77693.279.67240672.986.36721.286.74250702.093.23749.394.09260731.3100.4777.4101.7270760.5107.9805.5109.6273.15769.6110.3814.4112.2280780.4115.6823.7172.5	140	421.8	32.29	435.8	28.73
160466.141.16495.038.04170488.945.94523.943.13180512.550.95552.648.51190537.056.19580.954.18200562.461.69609.160.13210588.967.44637.266.36220616.273.47665.272.88230644.379.77693.279.67240672.986.36721.286.74250702.093.23749.394.09260731.3100.4777.4101.7270760.5107.9805.5109.6273.15769.6110.3814.4112.2280780.4115.6823.7117	150	443.8	36.62	465.7	33.23
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	160	466.1	41.16	495.0	38.04
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	170	488.9	45.94	523.9	43.13
190 537.0 56.19 580.9 54.18 200 56.4 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 94.09 260 731.3 100.4 777.4 101.7 270 760.5 107.9 805.5 109.6 273.15 769.6 110.3 814.4 112.2 280 789.4 115.6 823.7 117.2	180	512.5	50.95	552.6	48.51
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	190	537.0	56.19	580.9	54.18
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	200	562.4	61.69	609.1	60.13
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	210	588.9	67.44	637.2	66.36
230 644.3 /9.// 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	220	616.2	/3.4/	665.2	72.88
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	230	644.3	/9.//	693.2	/9.6/
230 702.0 93.23 749.3 94.09 260 731.3 100.4 777.4 101.7 270 760.5 107.9 805.5 109.6 273.15 769.6 110.3 814.4 112.2 280 789.4 115.6 823.7 117.9	240	672.9 702.0	80.30 02.22	721.2	δb./4 04.00
260 751.3 100.4 777.4 101.7 270 760.5 107.9 805.5 109.6 273.15 769.6 110.3 814.4 112.2 280 789.4 115.6 823.7 117.9	250	702.0	93.23	749.3	94.09
270 700.5 107.9 805.5 109.6 273.15 769.6 110.3 814.4 112.2 280 789.4 115.6 \$22.7 117.9	200	751.5	100.4	///.4 205 5	101.7
213.13 703.0 110.5 514.4 112.2 280 780.4 115.6 622.7 117.0	270	760.5	107.9	003.3 914.4	109.0
	275.15	789.4	115.6	833.7	112.2
290 8179 1236 8619 1263	290	817.9	123.6	861.9	126.3

Table 1	Continued
Table I	<i>Continuea</i>)

•	•			
T (K)	$C_p^{\circ}(T)$ (J K ⁻¹ mol ⁻¹)	$H^{\circ}(T) - H^{\circ}(0) (\text{kJ mol}^{-1})$	$S^{\circ}(T)$ (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 $6 \le T \le 12$ K, the θ_D (TBAI)> θ_D (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 $S^{\circ}(T)$:

$$G^{\circ}(T) - H^{\circ}(0) = [H^{\circ}(T) - H^{\circ}(0)] - TS^{\circ}(T).$$
(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° (TBAI, cr) = 515.0 ± 1.5 J K⁻¹ mol⁻¹ and S° (TBATPhB, cr) = 884.9 ± 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: $\Delta_{\rm f}S^{\circ}$ (TBAI, cr) = -2083 ± 9 J K⁻¹ mol⁻¹ and $\Delta_{\rm f}S^{\circ}$ (TBATPhB, cr) = -3105 ± 13 J K⁻¹ mol⁻¹. They correspond to the processes:

 $16C(gr) + 18H_2(g) + 0.5N_2(g) + 0.5I_2(cr) \rightarrow C_{16}H_{36}N \cdot I(cr),$

 $40C(gr) + 28H_2(g) + 0.5N_2(g) + B(cr, rhombic)$

 $\rightarrow C_{16}H_{36}N\cdot C_{24}H_{20}B(cr),$

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 $(T_{fus}^{\circ} \text{ and } T_{tr}^{\circ})$. 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:

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



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 *i* state I and the melting intervals, respectively.

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

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	$T_{i} - T_{f} (K)^{a}$	$T_{\rm fus}^{\circ}$ (K) ^b	$\Delta_{ m fus} H^\circ$ (kJ mol $^{-1}$) ^c	$\Delta_{\mathrm{fus}}S^{\circ}(\mathrm{J}\mathrm{K}^{-1}\mathrm{mol}^{-1})^{\mathrm{d}}$
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 $T_{\rm fric}^{\circ}$ the temperature of melting corresponding to the minimum specific heat flow rate in the melting interval.

^c $\Delta_{\text{fus}}^{\text{nus}} H^{\circ}$ the molar enthalpy of melting.

^d $\Delta_{fus} S^{\circ}$ 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	$T_{\rm i}-T_{\rm f}$ ^a (K)	$T_{\rm tr}^{\circ}$ (K) ^b	$\Delta_{ m tr} H^{\circ} (m kJ mol^{-1})^{c}$	$\Delta_{\mathrm{tr}} S^{\circ} (\mathrm{J} \mathrm{K}^{-1} \mathrm{mol}^{-1})^{\mathrm{d}}$
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	2	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	2	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 $\Delta_{tr}^{u}H^{\circ}$ the molar enthalpy of transition.

 $^{\rm d}~\Delta_{tr}S^{\circ}$ 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	$T_{ m tr}^{\circ}$ (K)	$\Delta_{ m tr} H^{\circ}$ (kJ mol ⁻¹)	$\Delta_{\mathrm{tr}}S^{\circ}$ (J K ⁻¹ mol ⁻¹)	$T_{\rm fus}^{\circ}$ (K)	$\Delta_{ m fus} H^{\circ} (m kJ mol^{-1})$	$\Delta_{\rm fus}S^\circ({\rm JK^{-1}mol^{-1}})$	$\Delta H^{\circ}{}_{\Sigma} (\mathrm{kJ}\mathrm{mol}^{-1})^{\mathrm{a}}$	$\Delta S^{\circ}{}_{\Sigma}$ (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 $\Delta H^{\circ}_{\Sigma}$ the total enthalpy of transitions.

^b $\Delta S^{\circ}{}_{\Sigma}$ 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 $\Delta_{tr} H^{\circ} / \Delta H^{\circ} \Sigma$ ration, here $\Delta H^{\circ} \Sigma$ 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 ($\Delta S^{\circ}\Sigma$) 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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