

# Conductivity Studies of *n*-Tetrabutylammonium Tetraphenylborate in 3-Pentanone in the Temperature Range from 283.15 to 329.15 K

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**Abstract** The molar conductivities ( $\Lambda$ ) of solutions of *n*-tetrabutylammonium tetraphenylborate (NBu<sub>4</sub>BPh<sub>4</sub>) in 3-pentanone have been measured in the temperature range from 283.15 to 329.15 K. The conductance data have been analyzed using the Lee-Wheaton conductivity equation with the distance parameter ( $a$ ) set at Bjerrum's pairing distance, and the limiting molar conductivities ( $\Lambda_0$ ) and the association equilibrium constants ( $K_A$ ) have been derived. The limiting ion conductivities ( $\lambda_{\pm}^0$ ) have been evaluated according to the method of Krumgalz. The  $\lambda_{+}^0$  values have been compared with  $\lambda_{+}^0$  values calculated from the empirical equation of Gill. The thermodynamic functions, Gibbs energy ( $\Delta G_A^0$ ), enthalpy ( $\Delta H_A^0$ ) and entropy ( $\Delta S_A^0$ ) for the process of ion-pair formation as well as the activation energy of the ionic movement ( $\Delta H^*$ ) have been evaluated. The obtained results are discussed in terms of ion-ion and ion-solvent interactions.

**Keywords** Association constant · Limiting ionic conductivity · 3-Pentanone · *n*-Tetrabutylammonium tetraphenylborate · Thermodynamic quantities

## 1 Introduction

As pointed out in previous studies, the transport properties of electrolytes (conductivity, viscosity, transference numbers) in different solvent media give valuable information regarding the behavior of the electrolytes, because the transport properties are mainly related to the effects of collective dynamics such as ionic atmosphere relaxation on the single particle properties [1, 2]. The concept of ion association is widely used in solution chemistry. As

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it is well known, there are two different mechanisms for ionic association. The first one, proposed by Bjerrum [3] is from electrostatic association, in which the association process is due to strong Coulombic interactions. The second mechanism of ionic association is chemical association in which there is a true chemical bond. This is the case for complexes and weak acids.

In the past many researchers have investigated, using conductivity measurements, the effects of the nature of the ions, the dielectric constant and the structure of the solvent medium on the ion solvation and association. Several equations have been proposed for the analysis of conductivity data, depending on the precision required. Fuoss and co-workers [4–6] have applied the electrostatic theory to solutions of electrolytes using a model in which the ions are regarded as charged spheres in a dielectric continuum. The resulting equation shows that the decrease of conductivity with increasing concentration is a result of the long-range interionic interactions that take place in solvents with a high dielectric constant, and of short range interactions that occur in solvents with a low dielectric constant. Based on a model that is identical with the one suggested by Fuoss, Lee and Wheaton [7–9] derived a new three-parameter conductance equation that can be written in the following general form:

$$\Lambda = f(c, \epsilon, \eta, T, z, \Lambda_0, K_A, \alpha) \quad (1)$$

The known parameters in Eq. (1) are the concentration of the electrolyte ( $c$ ), the dielectric constant ( $\epsilon$ ) and viscosity ( $\eta$ ) of the solvent, the absolute temperature ( $T$ ) and the ionic charge ( $z$ ), whereas the unknown parameters are the molar conductivity at infinite dilution ( $\Lambda_0$ ), the association constant ( $K_A$ ) and the distance parameter ( $\alpha$ ). The parameter  $\alpha$  is the distance between the ions at which a stable contact or solvent-separated ion pair is formed. In this model the ions exist in one of the following three states: as free ions, as solvent-separated ion pairs and/or as contact ion pairs. The Lee-Wheaton conductivity equation is based on a more realistic picture and it has been successfully used by many researchers for the investigation of uni-univalent electrolytes in solutions in which ionic association predominates [10–15].

Recently, we investigated the transport properties of a wide variety of electrolytes in different mixed solvents [16–19]. In this article we report conductivity a study of *n*-tetrabutylammonium tetraphenylborate in 3-pentanone over the temperature range from 283.15 to 329.15 K. The experimental molar conductivity ( $\Lambda$ ) values have been analyzed using the Lee-Wheaton conductivity equation [7–9] and the values of the limiting molar conductivity ( $\Lambda_0$ ) and the association constant ( $K_A$ ) of the electrolyte have been derived. The distance parameter ( $a$ ) was assumed to be equal to the Bjerrum's critical distance [3]. The limiting ionic conductivities ( $\lambda_{\pm}^0$ ) have been calculated according to the method of Krumgalz. The Gibbs energy ( $\Delta G_A^0$ ), enthalpy ( $\Delta H_A^0$ ) and entropy ( $\Delta S_A^0$ ) for the process of ion-pair formation as well as the activation energy of the ionic movement ( $\Delta H^*$ ) have been evaluated.

A detailed search in the literature revealed that investigations of the behavior of the tetraalkylammonium ion in aqueous and non-aqueous solutions has been the focus of many researchers over the last few years, because the resulting data provide valuable information on the ion-solvent interactions [20–24]. However, to the best of our knowledge, extensive data on the transport properties of *n*-tetrabutylammonium tetraphenylborate in 3-pentanone at the experimental conditions of this study are not available in the literature. The tetraalkylammonium ions are of special interest because of their spherical shape

and large size that varies from replacing the alkyl groups [25]. The interactions between the tetraalkylammonium ions and the solvent dipoles have been found to be weaker than those of the alkali-metal cations, because of the larger size of the tetraalkylammonium-ions.

Anyhow, in water and alcohols, which exhibit a high degree of hydrogen-bonded networks, the tetraalkylammonium ions create special “hydrophobic interactions” through the hydrocarbon groups that further increase the structure of the solvent medium [26]. According to these reports, it would be of special interest to investigate the ionic interactions involving tetraalkylammonium ions in 3-pentanone, a solvent medium that exhibits dipole-dipole interactions ( $\mu = 2.88$  D) [27] in the pure state but is less structured than water or alcohols because of the absence of the hydrogen bonding.

## 2 Experimental section

### 2.1 Materials

3-Pentanone (Aldrich, puriss. grade, 99.8 mass-%) was dried by distillation over  $\text{CaCl}_2$  [28] and was stored over 0.4 nm molecular sieves. The specific conductivity of this 3-pentanone was very small ( $0.05 \mu\text{S}\cdot\text{cm}^{-1}$ ). The solvent was degassed under vacuum prior to all measurements.

The *n*-tetrabutylammonium tetraphenylborate was prepared from sodium tetraphenylborate and *n*-tetrabutylammonium chloride as described in the literature [29]. Equimolar amounts of the salts, *n*-tetrabutylammonium chloride (Merck, puriss. grade) and sodium tetraphenylborate (Merck, puriss. grade), were dissolved in a methanol/water mixture (1:1) and mixed together. The resulting white precipitate was filtered, washed with water and diethylether, and then dried in vacuum at room temperature. The obtained solid was recrystallized from an acetone/water mixture (1:1). Yield 95%. Analysis - calculated for  $\text{C}_{40}\text{H}_{56}\text{BN}$ : C, 85.53%; H, 10.05%; N, 2.49%; found: C, 85.62%; H, 10.13%, N, 2.57%, and Cl less than 0.64%.

### 2.2 Solutions

A concentrated stock solution of  $\text{NBu}_4\text{BPh}_4$  ( $0.003 \text{ mol}\cdot\text{dm}^{-3}$ ) was prepared by mass ( $\pm 0.0001$  g, Sartorius, AG 204) and the dilute solutions (concentration range:  $0.0001$  to  $0.0015 \text{ mol}\cdot\text{dm}^{-3}$ ) were obtained by diluting the stock solution. To avoid moisture pickup, all solutions were prepared under argon gas. Under the conditions used in this work the electrolyte was completely soluble in the solvents. The conversion of molality to molarity concentrations was done using measured density values. All molar quantities are based on the relative atomic mass table of 1985 issued by IUPAC.

### 2.3 Measurements

The densities were measured with a digital densimeter (Anton Paar, model DMA 58, Austria) with a built-in solid-state thermostat. The DMA cell was calibrated with dry air and doubly distilled water [30]. The sample size was  $0.7 \text{ cm}^3$ . The uncertainty in temperature of the sample thermostat was  $\pm 0.01$  K. The uncertainties of the measured values of density were  $\pm 0.00001 \text{ g}\cdot\text{cm}^{-3}$ .

The viscosities of 3-pentanone were measured with a viscosity-measuring unit (Schott Geräte, model AVS 310, Germany) equipped with an Übbelohde capillary viscometer. The viscometer was calibrated with double-distilled water and the viscometer constant ( $K = 0.009758 \text{ mm}^2 \cdot \text{s}^{-2}$ ) was obtained. The uncertainty in the time measurement was  $\pm 0.01 \text{ s}$ . The viscometer was placed in a thermostat (Schott CT 050/2) electronically controlled at the set temperature. The temperature was maintained constant within  $\pm 0.03 \text{ K}$ . The reported kinematic viscosities ( $\nu$ ) were averaged from four readings. The absolute viscosities ( $\eta/\text{mPa}\cdot\text{s}$ ) have been calculated from the kinematic viscosities ( $\nu/\text{cm}^2 \cdot \text{s}^{-1}$ ) and the densities ( $\rho/\text{g}\cdot\text{cm}^{-3}$ ) using the relation:  $\eta = \nu\rho$ . The uncertainty in the viscosity measurements was  $\pm 0.1\%$ .

The surface tension of 3-pentanone was measured with a Du Nouy Tensiometer (A. Krüss, model K8600) equipped with a platinum-iridium ring of wire, diameter 0.37 mm. The platinum-iridium ring was cleaned with chromosulfuric acid and boiling distilled water. The sample was introduced into a double-walled glass cell connected to a thermostat, where the temperature was constant within  $\pm 0.01 \text{ K}$ . The tensiometer was calibrated with distilled water and a correction factor was employed. The uncertainty of the surface tension measurement was  $\pm 0.1 \text{ mN}\cdot\text{m}^{-1}$ .

The conductance measurements were carried out with a digital bridge-type conductivity meter (Jenway PCM 3). A conductance cell (dipping type) with electrodes coated with platinum black was used. The cell constant ( $0.98\text{--}0.01 \text{ cm}^{-1}$ ) was determined by measuring aqueous solutions of potassium chloride with molarities from 0.001 to  $0.100 \text{ mol}\cdot\text{dm}^{-3}$ , according to the method of Lind and co-workers [31]. The dissolved carbon dioxide in solution was removed by bubbling high-purity nitrogen through the solution in the cell. The cell was thermostatted using a water bath. The temperature was maintained constant within  $\pm 0.01 \text{ K}$ . All data were corrected using the specific conductance of the solvent. The correction was made by subtracting the specific conductance of the solvent medium from those of the electrolyte solutions. The molar conductivities ( $\Lambda/\text{S}\cdot\text{cm}^2 \cdot \text{mol}^{-1}$ ) were calculated from the experimental specific conductivities ( $k/\text{S}\cdot\text{cm}^{-1}$ ) and the concentrations ( $c/\text{mol}\cdot\text{dm}^{-3}$ ) of the solutions using the equation,  $\Lambda = 10^3 \times k/c$ . Experiments were repeated to ensure reproducibility. The overall uncertainty of the conductivity measurements was estimated to be 0.2%.

### 3 Results and discussion

#### 3.1 Solvent medium: 3-pentanone

According to our knowledge, detailed investigations of density ( $\rho$ ), viscosity ( $\eta$ ) and surface tension ( $\sigma$ ), over a wide range of temperatures for pure 3-pentanone, are still scarce in the literature. Therefore, in the present paper we considered it to be constructive to undertake the measurements for these properties in the temperature range from 283.15 to 329.15 K. The measured values are reported in Table 1 and are compared with the available literature values. The obtained values are in good agreement with the literature values. The values of the dielectric constant of 3-pentanone, needed for the analysis of the conductivity data, were taken from the literature [32].

The surface tension of 3-pentanone decreases linearly with increasing temperature (see Fig. 1). Application of the principle of least squares to the surface tension ( $\sigma$ ) – temperature ( $T$ ) data leads to linear equations of the form  $\sigma = \alpha - \beta T$ , in agreement with the reports of Jasper [33] and Law and Watson [34]. The slope  $\beta$  is temperature-independent and

**Table 1** Densities ( $\rho$ ), viscosities ( $\eta$ ), surface tensions ( $\sigma$ ) and dielectric constants ( $\epsilon$ ) of 3-pentanone in the temperature range from 283.15 to 329.15 K

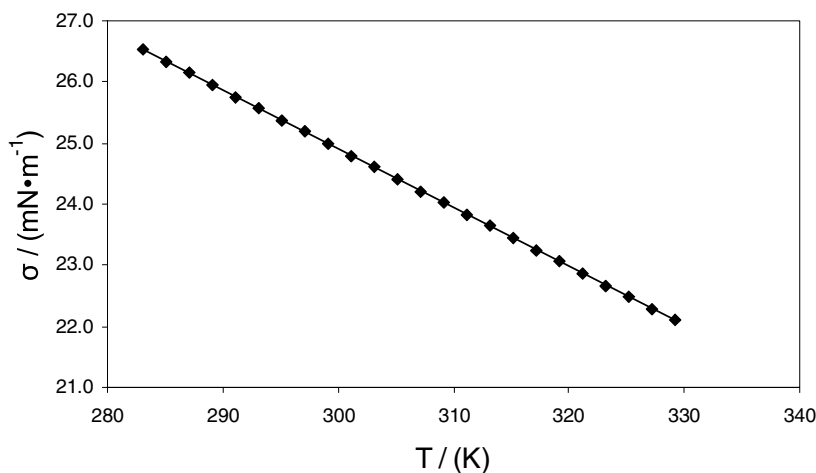
$T/K$	$\rho/\text{g} \cdot \text{cm}^{-3}$	$\eta/\text{mPa} \cdot \text{s}$	$\sigma/\text{mN} \cdot \text{m}^{-1}$	$\epsilon^a$
283.15	0.82427	0.515	26.5	17.02
285.15	0.82228	0.507	26.3	17.02
287.15	0.82030	0.499	26.1	17.01
289.15	0.81831	0.492	26.0	17.01
291.15	0.81633	0.484	25.8	17.00
293.15	0.81434	0.476	25.6	17.00
	0.8144 <sup>b</sup> /0.8138 <sup>g</sup>	0.4714 <sup>b</sup>		
295.15	0.81236	0.468	25.4	17.00
297.15	0.81037	0.460	25.2	16.99
	0.80925 <sup>c</sup> /0.81086 <sup>d</sup>	0.458 <sup>d</sup> /0.480 <sup>d</sup>		
	0.80988 <sup>e</sup>			
299.15	0.80839	0.453	25.0	16.99
301.15	0.80640	0.445	24.8	16.98
303.15	0.80442	0.437	24.6	16.98
	0.8047 <sup>b</sup> /0.80486 <sup>f</sup>	0.4231 <sup>b</sup>		
	0.80458 <sup>h,i</sup> /0.80458 <sup>j</sup>			
305.15	0.80243	0.429	24.4	16.97
307.15	0.80045	0.421	24.2	16.97
309.15	0.79846	0.414	24.0	16.96
311.15	0.79648	0.406	23.8	16.96
313.15	0.79449	0.398	23.6	16.96
	0.7949 <sup>b</sup>	0.3799 <sup>b</sup>		
315.15	0.79251	0.390	23.4	16.95
317.15	0.79052	0.382	23.3	16.95
319.15	0.78854	0.375	23.1	16.94
321.15	0.78655	0.367	22.9	16.94
323.15	0.78457	0.359	22.7	16.94
325.15	0.78259	0.351	22.5	16.93
327.15	0.78060	0.343	22.3	16.93
329.15	0.77862	0.336	22.1	16.92

<sup>a</sup>Reference [32].<sup>b</sup>Reference [22].<sup>c,d</sup>Values at 298.15 K.<sup>e</sup>Reference [65].<sup>f</sup>Reference [66].<sup>g</sup>Reference [67].<sup>h</sup>Reference [68].<sup>i</sup>Reference [69].<sup>j</sup>Reference [70].

corresponds to the surface entropy per unit surface area ( $S^S$ ) according to the modified thermodynamic equation of Clapeyron for liquid surfaces [35]:

$$S^S = - \left( \frac{\partial \sigma}{\partial T} \right)_p \quad (2)$$

Considering that the surface enthalpy ( $H^S$ ) is the sum of the surface Gibbs energy required to extend the surface (e.g., the surface tension,  $\sigma$ ) and the latent heat ( $q$ ) required to maintain



**Fig. 1** Surface tensions ( $\sigma$ ) versus the temperature ( $T$ ) for 3-pentanone in the temperature range from 283.15 to 329.15 K

isothermal conditions:  $H^S = \sigma + q$ , the surface enthalpy per unit surface area of 3-pentanone can be estimated according to the following equation:

$$H^S = \sigma - T \left( \frac{\partial \sigma}{\partial T} \right)_p = \sigma + TS^S \quad (3)$$

Both the obtained surface enthalpy ( $53.9 \text{ mJ}\cdot\text{m}^{-2}$ ) and entropy ( $0.0965 \text{ mJ}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ ) per unit surface area for 3-pentanone appear to be constant and independent of the temperature in the range from 283.15 to 329.15 K [36].

### 3.2 Electrolyte solutions

The experimental values of the molar conductivity ( $\Lambda$ ) of  $\text{NBu}_4\text{BPh}_4$  in 3-pentanone over the temperature range from 283.15 to 329.15 K are summarized in Table 2. The experimental molar conductivities were analyzed by means of the Lee-Wheaton [7–9] conductivity equation in the form suggested by Pethybridge and Taba, Eqs. (4)–(8) [37], which include the mass-action law for the ion association, Eq. (9), and the Debye-Hückel limiting law, Eq. (10), are:

$$\Lambda_{\text{Calc.}} = \gamma \Lambda_i \quad (4)$$

$$\Lambda_i = \Lambda_o \left[ 1 + C_1(\beta\kappa) + C_2(\beta\kappa)^2 + C_3(\beta\kappa)^3 \right] - \frac{\vartheta\kappa}{(1 + \kappa\alpha)} \left[ 1 + C_4(\beta\kappa) + C_5(\beta\kappa)^2 + \frac{\kappa\alpha}{12} \right] \quad (5)$$

$$\beta = \frac{|z|^2 e^2}{\epsilon_o \epsilon k_B T} \quad (6)$$

**Table 2** Molarities ( $c$ ) and molar conductivities ( $\Lambda$ ) of  $\text{NBu}_4\text{BPh}_4$  in 3-pentanone in the temperature range from 283.15 to 329.15 K

$10^3 \times c/\text{mol}\cdot\text{dm}^{-3}$	$\Lambda/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$c/\text{mol}\cdot\text{dm}^{-3}$	$\Lambda/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$c/\text{mol}\cdot\text{dm}^{-3}$	$\Lambda/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$
$T = 283.15 \text{ K}$		$T = 285.15 \text{ K}$		$T = 287.15 \text{ K}$	
0.2150	79.10	0.2145	81.86	0.2140	84.00
0.4227	77.56	0.4216	79.82	0.4206	81.73
0.5792	76.74	0.5778	78.64	0.5764	80.21
0.7423	75.15	0.7405	76.96	0.7387	78.88
0.8989	74.33	0.8967	76.28	0.8945	78.11
1.0670	73.16	1.0644	74.93	1.0618	76.69
1.1699	72.86	1.1671	74.75	1.1643	76.55
1.2795	72.13	1.2764	73.85	1.2733	75.54
1.3660	71.73	1.3627	73.49	1.3594	75.23
1.5020	70.93	1.4983	72.56	1.4947	74.32
$T = 289.15 \text{ K}$		$T = 291.15 \text{ K}$		$T = 293.15 \text{ K}$	
0.2135	85.92	0.2129	87.65	0.2124	89.38
0.4196	83.69	0.4186	85.51	0.4175	87.33
0.5750	82.22	0.5736	84.15	0.5722	86.02
0.7369	80.76	0.7351	82.61	0.7333	84.56
0.8923	79.95	0.8901	81.74	0.8880	83.52
1.0592	78.51	1.0566	80.37	1.0540	82.27
1.1614	78.32	1.1586	80.03	1.1557	81.79
1.2702	77.34	1.2671	79.12	1.2640	80.96
1.3561	77.00	1.3528	78.78	1.3494	80.54
1.4910	75.93	1.4874	77.70	1.4837	79.44
$T = 295.15 \text{ K}$		$T = 297.15 \text{ K}$		$T = 299.15 \text{ K}$	
0.1748	91.56	0.1744	93.49	0.1739	95.81
0.3645	90.68	0.3636	92.49	0.3627	94.68
0.5583	89.84	0.5570	91.93	0.5556	93.93
0.7214	88.75	0.7196	90.78	0.7178	92.66
0.8654	87.76	0.8633	89.72	0.8611	91.66
0.9894	86.99	0.9869	88.97	0.9845	90.84
1.0956	86.39	1.0929	88.29	1.0902	90.22
1.1841	85.96	1.1812	87.91	1.1782	89.70
1.2608	85.60	1.2577	87.51	1.2546	89.42
1.3572	85.21	1.3538	87.11	1.3505	88.86
$T = 301.15 \text{ K}$		$T = 303.15 \text{ K}$		$T = 305.15 \text{ K}$	
0.1735	97.95	0.1731	100.10	0.1221	101.24
0.3618	96.83	0.3609	99.04	0.2240	99.83
0.5542	95.98	0.5528	98.04	0.3050	98.60
0.7160	94.69	0.7143	96.79	0.3707	97.40
0.8590	93.64	0.8569	95.63	0.4442	96.30
0.9821	92.78	0.9796	94.89	0.4940	95.68
1.0875	92.14	1.0848	94.14	0.5407	95.07
1.1753	91.62	1.1724	93.56	0.5819	94.67
1.2515	91.41	1.2484	93.30	0.6560	93.79
1.3471	90.78	1.3438	92.73	0.7558	92.51

**Table 2** Continued

$10^3 \times c/\text{mol}\cdot\text{dm}^{-3}$	$\Lambda/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$c/\text{mol}\cdot\text{dm}^{-3}$	$\Lambda/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$c/\text{mol}\cdot\text{dm}^{-3}$	$\Lambda/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$
<i>T</i> = 307.15 K		<i>T</i> = 309.15 K		<i>T</i> = 311.15 K	
0.1218	103.48	0.1215	105.06	0.1212	107.70
0.2235	101.89	0.2229	103.95	0.2224	106.53
0.3042	100.74	0.3035	103.08	0.3027	105.39
0.3698	99.82	0.3689	102.25	0.3680	104.79
0.4431	99.14	0.4420	101.47	0.4409	103.81
0.4927	98.49	0.4915	100.58	0.4903	102.97
0.5394	97.87	0.5380	100.25	0.5367	102.43
0.5804	97.48	0.5790	99.59	0.5775	101.75
0.6543	96.57	0.6527	98.91	0.6511	101.03
0.7539	95.49	0.7521	97.51	0.7502	99.63
<i>T</i> = 313.15 K		<i>T</i> = 315.15 K		<i>T</i> = 317.15 K	
0.1209	109.88	0.1206	112.06	0.1203	114.16
0.2218	108.62	0.2213	110.97	0.2207	113.08
0.3019	107.79	0.3012	109.78	0.3004	111.78
0.3670	106.84	0.3661	108.96	0.3652	111.16
0.4398	105.90	0.4387	108.00	0.4376	110.38
0.4890	104.99	0.4878	107.50	0.4866	109.66
0.5353	104.62	0.5340	107.04	0.5326	109.25
0.5761	103.81	0.5746	106.67	0.5732	108.93
0.6494	102.88	0.6478	105.77	0.6462	108.10
0.7483	101.43	0.7464	104.62	0.7445	107.04
<i>T</i> = 319.15 K		<i>T</i> = 321.15 K		<i>T</i> = 323.15 K	
0.1200	116.65	0.0786	120.69	0.0784	122.64
0.2201	115.45	0.1493	120.45	0.1489	122.49
0.2997	114.36	0.2515	120.10	0.2509	122.27
0.3643	113.34	0.3301	119.84	0.3292	122.10
0.4365	112.50	0.4008	119.60	0.3998	121.94
0.4854	111.81	0.4873	119.31	0.4860	121.76
0.5313	111.37	0.5737	119.02	0.5723	121.57
0.5717	111.04	0.6602	118.73	0.6585	121.38
0.6445	110.27	0.7388	118.46	0.7369	121.21
0.7426	109.22	0.8802	117.99	0.8780	120.90
<i>T</i> = 325.15 K		<i>T</i> = 327.15 K		<i>T</i> = 329.15 K	
0.0782	124.80	0.0780	127.64	0.0778	129.62
0.1486	124.71	0.1482	127.43	0.1478	129.47
0.2502	124.58	0.2496	127.13	0.2489	129.24
0.3284	124.48	0.3276	126.89	0.3267	129.06
0.3988	124.39	0.3978	126.68	0.3967	128.90
0.4848	124.28	0.4835	126.43	0.4823	128.71
0.5708	124.17	0.5693	126.17	0.5679	128.51
0.6568	124.06	0.6551	125.92	0.6534	128.32
0.7350	123.96	0.7331	125.68	0.7312	128.14
0.8757	123.78	0.8735	125.26	0.8712	127.83



$$\kappa = \left( \frac{8\pi N_A e^2 |z|^2 \gamma c}{1000 \epsilon_0 \epsilon k_B T} \right)^{1/2} \quad (7)$$

$$\vartheta = \frac{F \xi e |z|}{3\pi \eta} \quad (8)$$

$$K_A = \frac{(1 - \gamma)}{\gamma^2 f_{\pm}^2 c} \quad (9)$$

$$f_{\pm}^2 = \exp \left[ \frac{-\beta \kappa}{(1 + \kappa \alpha)} \right] \quad (10)$$

where  $C_1$  through  $C_5$  are functions of the product  $(\kappa\alpha)$  and are given in Ref. [37];  $K_A$  is the thermodynamic ion-pair association constant for the equilibrium:  $\text{NBu}_4^+ + \text{BPh}_4^- \rightleftharpoons \text{NBu}_4\text{BPh}_4$ ,  $\gamma$  the degree of dissociation,  $c$  the electrolyte concentration,  $f_{\pm}$  the mean ion activity coefficient of the dissociated species (the activity coefficient of the non-conducting species was assumed to be equal to 1),  $e$  the electronic charge,  $z_{\pm}$  the ionic charge,  $\epsilon_0$  the permittivity of vacuum,  $\epsilon$  the dielectric constant of the solvent,  $\eta$  the viscosity of the solvent,  $F$  the Faraday constant,  $k_B$  the Boltzmann's constant,  $N_A$  the Avogadro's number,  $T$  the absolute temperature, and the symbol  $\xi$  is equal to  $1/299.79$ . The parameter  $a$  represents the center-to-center distance between the ions in the ion pairs. At separations beyond this distance, the ions are considered to be unassociated.

The computations for calculating the limiting molar conductivity ( $\Lambda_0$ ), the association constant ( $K_A$ ) and the distance parameter ( $a$ ) were performed on a computer using the program of successive approximations suggested by Pethybridge and Taba [37] following the three-parameter optimization method. The initial  $\Lambda_0$  values for the procedure were obtained from the Debye-Hückel-Onsager equation [38] following the suggestion of Shedlovsky [39]. The formation of tripl ions was regarded as being negligible [40]. The calculations were made by finding the values of  $\Lambda_0$ ,  $K_A$  and  $\alpha$  after obtaining the minimal standard deviation ( $\sigma_{\Lambda}$ ) between the calculated ( $\Lambda_{\text{Calc.}}$ ) and experimental ( $\Lambda_{\text{Exp.}}$ ) conductivity values for a sequence of different  $a$  values. The standard deviation  $\sigma_{\Lambda}$  is given from the equation:

$$\sigma_{\Lambda} = \left[ \sum_{j=1}^n (\Lambda_{j(\text{Calc.})} - \Lambda_{j(\text{Exp.})})^2 / (N_p - 1) \right]^{1/2} \quad (11)$$

In other words, a reliable value for the distance parameter  $a$  will correspond to the minimum of the plot,  $\sigma_{\Lambda}$  versus  $a$ . The distance  $a$ , which has been selected for the computations, was varied from 9.0 Å, which is the sum of the crystallographic radii of the  $\text{NBu}_4^+$  and  $\text{BPh}_4^-$  ions ( $r_{C_{r+}} = 4.94$  Å,  $r_{C_{r-}} = 4.20$  Å) [41], to a maximum value of 40.0 Å. The variation of  $\Lambda_0$  and  $K_A$  with  $a$  was insignificant. Because a rough scan involving increasing the  $a$  value from 9.0 to 40.0 Å in 0.5 Å steps gave no significant minima in the  $\sigma_{\Lambda}$  versus  $a$  curves, the  $a$  value of  $\text{NBu}_4\text{BPh}_4$  was assumed to be equal with the Bjerrum's critical distance [3] as recommended by Justice [42]:

$$a = \frac{z_+ z_- e^2}{8\pi \epsilon_0 \epsilon k_B T} \quad (12)$$

This assumption has been considered since the sum of the cationic and anionic crystallographic radii (9.0 Å) [41] is smaller than the Bjerrum's distance for all the cases studied [43]. The derived values of limiting molar conductance  $\Lambda_o$  ( $\pm 0.3\%$ ), association constant  $K_A$  ( $\pm 5\%$ ) and Bjerrum's distance ( $a$ ) of  $\text{NBu}_4\text{BPh}_4$  in 3-pentanone in the temperature range from 283.15 to 329.15 K are reported in Table 3 along with their standard deviations  $\sigma_\Lambda$ . The maximum deviation that was found in this work was relatively small ( $\sigma_\Lambda = 0.75 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ) indicating a satisfactory fitting of our experimental  $\Lambda$  values with the Lee-Wheaton equation.

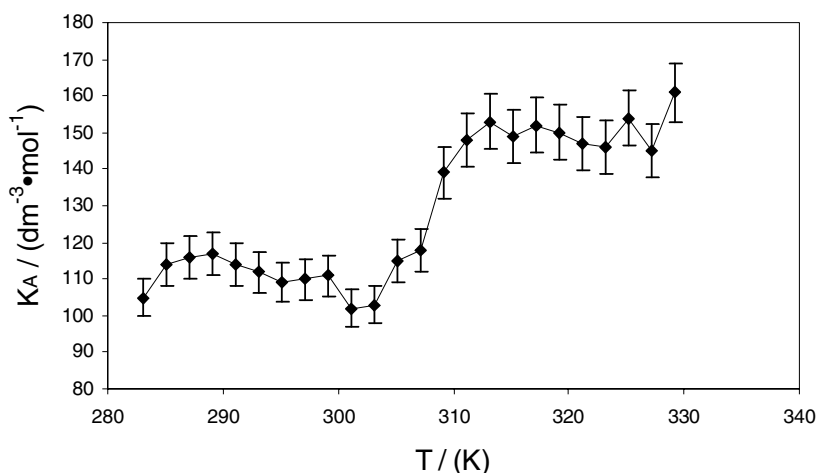
Expectedly, the  $\Lambda_o$  values increase linearly with the increase in temperature because the mobility of the free ions is enhanced. The values of  $\Lambda_o$  vary almost inversely with the viscosity of 3-pentanone and the Walden product ( $W = \eta\Lambda_o$ ) is nearly constant and independent of the temperature (Table 3). These results indicate that the mobility of the "free" ions is completely controlled by the bulk viscosity, confirming that the  $\text{NBu}_4^+$  and  $\text{BPh}_4^-$  ions are likely to be poorly solvated.

In spite of the bulkiness of the  $\text{NBu}_4^+$  and  $\text{BPh}_4^-$  ions, the  $K_A$  values show that association of the investigated electrolyte generally increases with the increase of the temperature, following the decrease of the dielectric constant of the solvent medium (Fig. 2).

The limiting molar conductances of the electrolyte were divided into limiting ionic conductances according to the method of Krumgalz using the following relation [44, 45]:

$$\lambda^\circ(\text{NBu}_4^+) = 0.517\Lambda_o(\text{NBu}_4\text{BPh}_4) \quad (13)$$

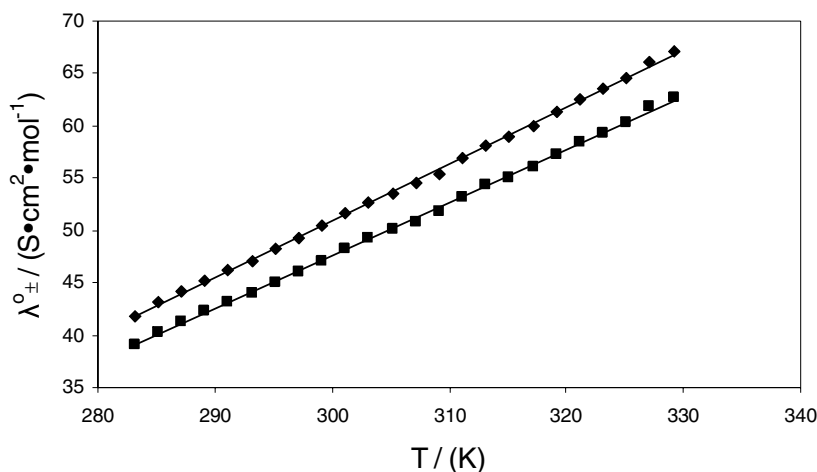
This method is based on the assumption that the large unsolvated spherical ions  $\text{NBu}_4^+$  and  $\text{BPh}_4^-$  have almost the same effective volume in solution and consequently should have the same transference number. This assumption, which was made first by Fuoss and co-workers



**Fig. 2** Association constants ( $K_A$ ) versus the temperature ( $T$ ) for  $\text{NBu}_4\text{BPh}_4$  in 3-pentanone in the temperature range from 283.15 to 329.15 K

**Table 3** Limiting molar conductivities ( $\Lambda_0$ ,  $\pm 0.3\%$ ), association constants ( $K_A$ ,  $\pm 5\%$ ), Bjerrum's distances ( $a$ ), limiting ion conductivities ( $\lambda_0^\pm$ ) and values of the Walden product ( $W = \eta\Lambda_0$ ) of NBu<sub>4</sub>BPh<sub>4</sub> in 3-pentanol in the temperature range from 283.15 to 329.15 K

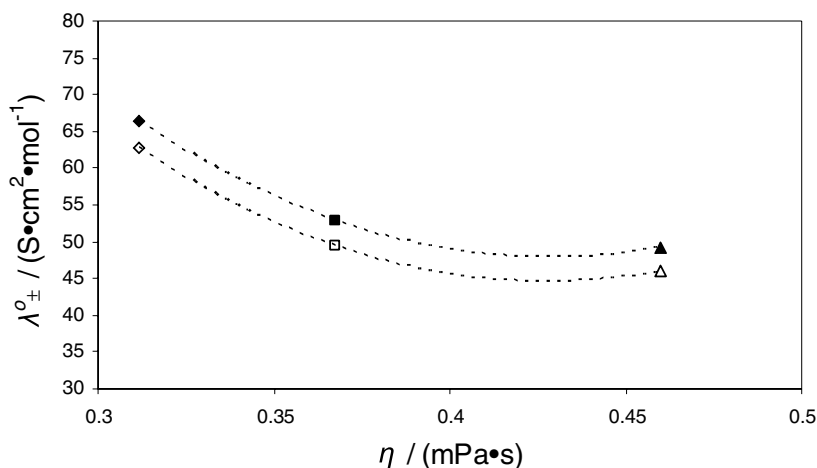
T/K	$\Lambda_0/S\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$K_A/\text{dm}^3\cdot\text{mol}^{-1}$	$a/\text{\AA}$	$W = (\eta\Lambda_0)$	$\lambda_0^+/S\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\lambda_0^-/S\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\sigma_A/S\cdot\text{cm}^2\cdot\text{mol}^{-1}$
283.15	80.9 ± 0.2	105 ± 5	17.3	41.72	41.8	39.1	0.25
285.15	83.4 ± 0.3	114 ± 6	17.3	42.28	43.1	40.3	0.67
287.15	85.5 ± 0.3	116 ± 6	17.4	42.48	44.2	41.3	0.75
289.15	87.5 ± 0.3	117 ± 6	17.4	42.70	45.2	42.3	0.70
291.15	89.3 ± 0.3	114 ± 6	17.4	42.77	46.2	43.1	0.59
293.15	91.2 ± 0.3	112 ± 6	17.4	42.84	47.1	44.0	0.41
295.15	93.2 ± 0.3	109 ± 5	17.4	42.98	48.2	45.0	0.28
297.15	95.2 ± 0.3	110 ± 6	17.4	43.04	49.2	46.0	0.36
299.15	97.5 ± 0.3	111 ± 6	17.4	43.11	50.4	47.1	0.28
301.15	99.7 ± 0.3	102 ± 5	17.4	43.19	51.6	48.2	0.28
303.15	102.0 ± 0.3	103 ± 5	17.4	43.24	52.7	49.3	0.28
305.15	103.6 ± 0.3	115 ± 6	17.4	43.00	53.6	50.0	0.07
307.15	105.4 ± 0.3	118 ± 6	17.4	42.77	54.5	50.9	0.06
309.15	107.2 ± 0.3	139 ± 7	17.4	42.47	55.4	51.8	0.14
311.15	110.1 ± 0.3	148 ± 7	17.4	42.59	56.9	53.2	0.14
313.15	112.4 ± 0.3	153 ± 8	17.4	42.50	58.1	54.3	0.18
315.15	114.0 ± 0.3	149 ± 7	17.4	42.07	58.9	55.1	0.08
317.15	115.9 ± 0.3	152 ± 8	17.4	41.62	59.9	56.0	0.08
319.15	118.5 ± 0.4	150 ± 8	17.4	41.49	61.3	57.2	0.09
321.15	121.1 ± 0.4	147 ± 7	17.4	44.44	62.6	58.5	0.10
323.15	122.9 ± 0.4	146 ± 7	17.4	44.14	63.5	59.4	0.12
325.15	125.0 ± 0.4	154 ± 8	17.4	43.88	64.6	60.4	0.20
327.15	128.0 ± 0.4	145 ± 7	17.4	43.91	66.2	61.8	0.11
329.15	129.9 ± 0.4	161 ± 9	17.5	43.66	67.2	62.7	0.13



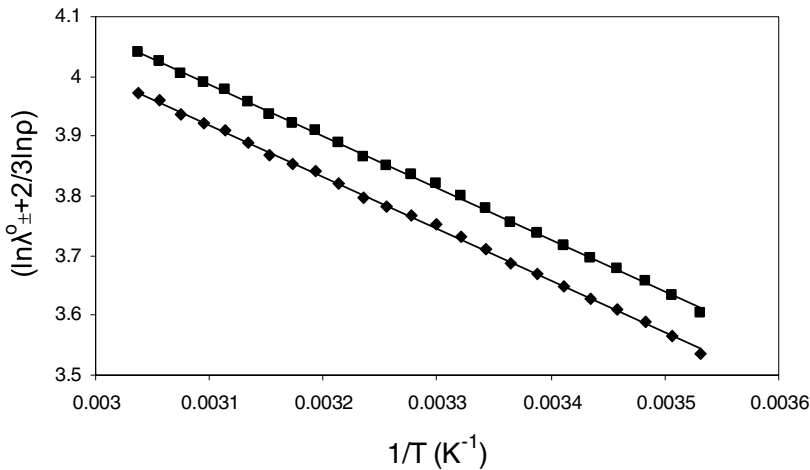
**Fig. 3** Limiting ionic conductivities ( $\lambda_{\pm}^{\circ}$ ) versus the temperature ( $T$ ) for  $\text{NBU}_4^+$  ( $\blacklozenge$ ) and  $\text{BPh}_4^-$  ( $\blacksquare$ ) ions in 3-pentanone in the temperature range from 283.15 to 329.15 K

[46, 47] and adopted later by other researchers [48–52], appears to be valid and independent of the solvent and the temperature. The resulting limiting ionic conductivities of  $\text{NBU}_4^+$  and  $\text{BPh}_4^-$  ( $\lambda_{\pm}^{\circ}$ ) are reported in Table 3 and presented graphically in Fig. 3.

It is very useful to compare our  $\lambda_{\pm}^{\circ}$  values for  $\text{NBU}_4^+$  and  $\text{BPh}_4^-$  with those reported in the literature in solutions of other ketones of smaller size. Consequently, the  $\lambda_{\pm}^{\circ}$  values of  $\text{NBU}_4^+$  and  $\text{BPh}_4^-$  in 3-pentanone obtained in this work at 297.15 K, along with the literature  $\lambda_{\pm}^{\circ}$  values in propanone and 2-butanone at 298.15 K [53, 54], are presented graphically against the viscosity of the solvent medium in Fig. 4. As can be seen from Fig. 4, the  $\lambda_{\pm}^{\circ}$  values decrease with the increase of the size of the ketone molecule followed by the increase of the



**Fig. 4** Limiting ionic conductivities ( $\lambda_{\pm}^{\circ}$ ) versus the viscosity of the solvent medium ( $\eta$ ) for  $\text{NBU}_4^+$  (solid symbols) and  $\text{BPh}_4^-$  (open symbols) in propanone at 298.15 K ( $\blacklozenge$ ) [53], 2-butanone at 298.15 K ( $\blacksquare$ ) [54], and 3-pentanone at 297.15 K ( $\blacktriangle$ )



**Fig. 5** Plot of  $(\ln\lambda_{\pm}^{\circ} + 2/3\ln\rho)$  versus the inverse of the temperature  $(1/T)$  {according to Eq. (14)} for  $\text{NBu}_4\text{BPh}_4$  in 3-pentanone in the temperature range from 283.15 to 329.15 K. The symbols are denoted as follows: (■)  $\text{NBu}_4^+$  and (◆)  $\text{BPh}_4^-$

bulk viscosity. In addition, our experimental values in 3-pentanone and the literature values in propanone and 2-butanone appear to be in reasonable agreement.

The obtained limiting ionic conductivity ( $\lambda_{\pm}^{\circ}$ ) values were used to evaluate the activation energy of the ionic movement ( $\Delta H^*$ ). The temperature dependence of the limiting ionic conductances may be represented in the framework of the kinetic conductance theory by the following equation [55, 56]:

$$\ln \lambda_{\pm}^{\circ} + \frac{2}{3} \ln \rho = -\frac{\Delta H^*}{RT} + B \tag{14}$$

where  $\rho$  is the density of the solvent and  $\Delta H^*$  is the Eyring activation enthalpy of the ionic movement. From the slope of the linear function of  $(\ln\lambda_{\pm}^{\circ} + 2/3\ln\rho)$  versus the inverse of the temperature  $(1/T)$ , which is shown in Fig. 5, we obtained identical  $\Delta H^*$  values for both  $\text{NBu}_4^+$  and  $\text{BPh}_4^-$  ions ( $\Delta H^* = 7.22 \text{ kJ}\cdot\text{mol}^{-1}$ ). This result demonstrates that the energy needed for the rearrangement of the solvent molecules in the area surrounding the  $\text{NBu}_4^+$  and  $\text{BPh}_4^-$  ions is identical. The observed similarity can be ascribed to the similarity in the ion sizes and charges, and implies that they are unaffected by the presence of the solvent molecules.

The experimental limiting ion conductances ( $\lambda_{\pm}^{\circ}$ ) for the  $\text{NBu}_4^+$  cation were compared with the values estimated from the empirically adjusted equation of Gill [57, 58]:

$$\lambda_{+}^{\circ} = \frac{z_+ F^2}{6\pi N_A \eta_0 [r_{\text{Cr}+} - 0.0103\epsilon - r_y]} \tag{15}$$

where  $r_y = 0.85 \text{ \AA}$  [57, 58] for 3-pentanone, which has very little association. The results are presented in Table 4. It is recognized that the error between the experimental and the estimated values of  $\lambda_{\pm}^{\circ}$  from Eq. (15) is about 3 to 10%, and is significantly higher than the error of 1% that has been proposed [57, 58]. Because Eq. (15) can be applied to solvent

**Table 4** Experimental  $\lambda_+^{\circ}$  (Exp.) and estimated  $\lambda_+^{\circ}$  (Est.) values from Eq. (15) for the limiting ionic conductivities of  $\text{NBU}_4^+$  in 3-pentanone in the temperature range from 283.15 to 329.15 K

$T/\text{K}$	$\lambda_+^{\circ}(\text{Exp.})/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\lambda_+^{\circ}(\text{Est.})/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	% difference
283.15	41.8	40.7	2.6
285.15	43.1	41.3	4.1
287.15	44.2	42.0	5.0
289.15	45.2	42.6	5.7
291.15	46.2	43.3	6.3
293.15	47.1	44.0	6.5
295.15	48.2	44.8	7.1
297.15	49.2	45.6	7.4
299.15	50.4	46.3	8.2
301.15	51.6	47.1	8.7
303.15	52.7	48.0	9.0
305.15	53.6	48.9	8.9
307.15	54.5	49.8	8.7
309.15	55.4	50.6	8.6
311.15	56.9	51.6	9.3
313.15	58.1	52.7	9.4
315.15	58.9	53.7	8.8
317.15	59.9	54.9	8.4
319.15	61.3	55.9	8.8
321.15	62.6	57.1	8.8
323.15	63.5	58.4	8.1
325.15	64.6	59.7	7.6
327.15	66.2	61.1	7.7
329.15	67.2	62.4	7.2

media that have a dielectric constant ( $\varepsilon$ ) in the region:  $17 < \varepsilon < 77$ , the large divergence that has been observed can be attributed to the  $\varepsilon$  value of 3-pentanone which is near to the lower limit ( $\varepsilon = 16.99$  at 298.15 K) [32].

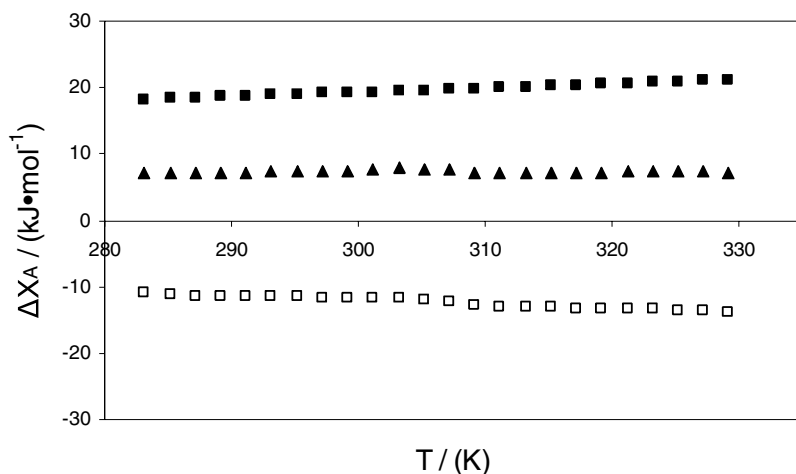
The obtained equilibrium constant ( $K_A$ ) for the ion association reaction served to study the thermodynamics of this process. Consequently, the standard Gibbs energy ( $\Delta G_A^{\circ}$ ), enthalpy ( $\Delta H_A^{\circ}$ ) and entropy ( $\Delta S_A^{\circ}$ ) of the ion-association process have been calculated according to following equations [59–61]:

$$\Delta G_A^{\circ} = -RT \ln K_A \quad (16)$$

$$\Delta S_A^{\circ} = - \left( \frac{\partial \Delta G_A^{\circ}}{\partial T} \right)_p \quad (17)$$

$$\Delta H_A^{\circ} = -T^2 \left( \frac{\partial (\Delta G_A^{\circ}/T)}{\partial T} \right)_p \quad (18)$$

The values of  $\Delta G_A^{\circ}$ ,  $\Delta H_A^{\circ}$  and  $T \Delta S_A^{\circ}$  are presented graphically *versus* the temperature in Fig. 6. It can be seen from Fig. 6 that the ion-association process exhibits negative values of Gibbs energy (the process is recognized as an exergonic process) that becomes



**Fig. 6** Thermodynamic functions ( $\Delta X_A$ ) for ion-pair formation versus the temperature ( $T$ ) for  $\text{NBu}_4\text{BPh}_4$  in 3-pentanone in the temperature range from 283.15 to 329.15 K. The symbols are denoted as follows: ( $\square$ )  $\Delta G_A^\circ$ , ( $\blacktriangle$ )  $\Delta H_A^\circ$ , and ( $\blacksquare$ )  $T\Delta S_A^\circ$

more negative with increasing temperature. In addition, the entropy and enthalpy values are positive and stable over the whole temperature range ( $\Delta S_A^\circ = 0.064 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ,  $\Delta H_A^\circ = 7.5 \text{ kJ}\cdot\text{mol}^{-1}$ ).

The stability of the  $\Delta S_A^\circ$  values upon ion-pair formation indicates that the number of the degrees of freedom does not change significantly with the rise of the temperature, probably due to weak solvation of the  $\text{NBu}_4^+$  and  $\text{BPh}_4^-$  ions. Furthermore, the positive value of  $\Delta H_A^\circ$  indicates that the process of ion-pair formation is endothermic in nature and energy consuming. Anyhow, the entropy term  $T\Delta S_A^\circ$  is sufficiently positive to compensate for the positive contribution of the enthalpic term  $\Delta H_A^\circ$ . Consequently, the increase of temperature leads to more negative  $\Delta G_A^\circ$  values, demonstrating that the ion-association equilibrium is shifted toward the ion pairs at elevated temperatures.

#### 4 Conclusions

In the present paper we have presented experimental molar conductivities ( $\Lambda$ ) of *n*-tetrabutylammonium tetraphenylborate in 3-pentanone over a wide temperature range from 283.15 to 329.15 K. The conductivity data have been analyzed using the Lee-Wheaton conductivity equation [7–9] and the values of the limiting molar conductivity ( $\Lambda_o$ ) and the association constant ( $K_A$ ) have been derived. The limiting ion conductivities ( $\lambda_{\pm}^\circ$ ) have been evaluated according to the method proposed by Krumgalz [44, 45]. The thermodynamic quantities such as Gibbs energy ( $\Delta G_A^\circ$ ), enthalpy ( $\Delta H_A^\circ$ ) and entropy ( $\Delta S_A^\circ$ ) for the ion-pair formation process, as well as the activation energy of the ionic movement ( $\Delta H^*$ ), have been evaluated. The  $K_A$  and  $\Delta G_A^\circ$  values of the ion-association process show that association of the investigated electrolyte generally increases to some extent with the rise of the temperature, that follows the decrease of the dielectric constant of the solvent medium. The  $\lambda_{\pm}^\circ$  values increase linearly with increasing temperature and the consequent decrease of the viscosity of 3-pentanone. Consequently, the Walden product ( $W = \eta\Lambda_o$ ) is nearly constant and independent of the temperature, confirming that the  $\text{NBu}_4^+$  and  $\text{BPh}_4^-$  ions are weakly

solvated. The constancy of the entropy ( $\Delta S_{\lambda}^0$ ) of the ion-association process over the whole temperature range supports the last conclusion.

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