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Conductometric Studies of 1-Ethyl-3-methylimidazolium Tetrafluoroborate and 1-Butyl-3-methylimidazolium Tetrafluoroborate in 1-Propanol at Temperatures from (283.15 to 318.15) K

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The electrical conductances of dilute solutions of the ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF_4] and 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] in 1-propanol have been measured in the temperature range from (283.15 to 308.15) K at 5 K intervals. The ionic association constant, K_A, limiting molar conductances, Λ_o, and distance parameters, R, were obtained using the low concentration Chemical Model (lcCM). The examined electrolytes are strongly associated in 1-propanol in the whole temperature range. From the temperature dependence of the limiting molar conductivities the Eyring's activation enthalpy of charge transport was estimated. The thermodynamic functions such as Gibbs energy, entropy, and enthalpy of the process of ion pair formation were calculated from the temperature dependence of the association constants.

Keywords: conductivity of ionic liquids, 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate, ion association, thermodynamic functions

1. INTRODUCTION

The data of physical and chemical properties on ionic liquids (ILs) are essential for both theoretical research and industrial application. A survey of literature indicates that physical properties of pure ionic liquids have been studied extensively, but the thermophysical and thermodynamic properties of the mixtures of ILs with aqueous or organic solvents, have not been studied in a systematic way so far. The transport properties of the mixtures of ionic liquids (conductance, viscosity, and transference numbers) are important because the values provide useful and sensitive information about ion-solvent interaction, ion-ion association, and solvent structure. Such studies allow the prediction of ILs in specific applications such as active pharmaceutical ingredients, high energy batteries or other electrochemical systems and chemical reactions [1-10].

The most intensively investigated ILs are those with imidazolium cation, but very little conductivity studies concerned the ionic association of ILs in molecular solvents [11-22]. From these papers results that the alkyl chain length of the cation, type of anion, and physical properties of the molecular solvents affect the ionic association constants. The ionic liquids are solvated to a different extent by the solvents, and the ionic association depends significantly on the ion solvation [21]. Slight ionic association of ILs occurs in the water, N,N-dimethylformamide, acetonitrile, methanol and ethanol, whereas it becomes significant in the alcohols (1-propanol, 2-propanol, 1-butanol, and 1-pentanol). In fact similar to the classical electrolytes, the ln K_A values of the ILs were found to increase linearly with the reverse of the dielectric constants of the solvents, which indicates that the electrostatic interaction between the ions are predominant for the ionic association of the ILs [11].

Therefore, we decided to study the ionic association and solvation behavior of ionic liquids in various solvents as a function of the temperature. For this purpose, in our previous paper [22], we have reported the results of the conductance measurements of 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF_4] and 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] solutions in *N*,*N*-dimethylformamide. Imidazolium ionic liquids were chosen because of their thermal and chemical stability and the insignificant impact of air and moisture. Slight ion association was found for the ionic liquids in this dipolar aprotic solvent (ε_r = 36.81 at 298.15 K [23]) in the whole investigated temperature range.

There are no experimental values of the conductometric data available in the literature about ILs tested by us, in such protic solvent as 1-propanol (ε_r = 20.45 at 298.15 K [24]) at various temperatures. Continuing our studies on electrical conductivity of ILs, in this work, precise conductivity measurements have been carried out in dilute solutions of [emim][BF_4] and [bmim][BF_4] in 1-PrOH at temperatures range (283.15K - 308.15) K and at atmospheric pressure. The obtained data were used to calculate the values of the limiting molar conductances, Λ_o, and the association constants, K_A on the basis of lcCM model. The Gibbs energy, ΔG^o_A, enthalpy, ΔH^o_A, and entropy, ΔS^o_A, of ion pair formation as well as the Eyring activation enthalpy of charge transport, $\Delta H^{\ddagger}_{\lambda}$, for the electrolytes have been evaluated.

2. EXPERIMENTAL

2.1. Reagents and chemicals

The specifications of used chemicals are summarized in Table 1.

Table 1. Specification of chemical samples

chemical name	source	initial mass fraction purity	purification method	final water mass fraction
1-PrOH	Aldrich	0.997	none	0.00005[a]
[emim][BF_4]	Fluka	0.990	none	<0.0002[a] <0.00015[b]
[bmim][BF_4]	Fluka	0.985	none	<0.0005[a] <0.0004[b]

[a] Manufacturer's analysis. [b] Our analysis (Karl Fischer coulometric titration).

2.2. Apparatus

All the solutions were prepared by mass using an analytical balance (Sartorius RC 210D) with a precision of ± $1 \cdot 10^{-5}$ g.

The measurement procedure was based on the method described by Bešter-Rogač *et al.* [18, 25] and used by us in our previous works [22, 26]. Conductivity measurements were performed with a three-electrode cell with the use of a Precise Component Analyser type 6430B (Wayne-Kerr, UK) under argon atmosphere and at the different frequencies, ν, (0.2, 0.5, 1, 2, 3, 5, 10, 20) kHz. The temperature was kept constant within 0.003 K (Calibration Thermostat Ultra UB 20F with Through-flow cooler DLK 25, Lauda, Germany). The details of the experimental procedure for conductometric measurements were described in our previous paper [22]. The uncertainty of the measured values of conductivity was 0.03 %.

Densities were measured with an Anton Paar DMA 5000 oscillating U-tube densimeter equipped with a thermostat with a temperature stability within ± 0.001 K. The densimeter was calibrated with extra pure water, previously degassed ultrasonically. The uncertainty of the density is ± $2 \cdot 10^{-5}$ g · cm^{-3}.

Viscosities were measured with a AVS 350 device (Schott Instruments, Germany). The Ubbelohde viscosimeter filled with the liquid was placed vertically in a thermostat water. An optoelectronic stopwatch with a precision of 0.01 s was used for flow time measurements. The temperature was kept constant using a precision thermostat HAAKE DC30 (Thermo Scientific). The accuracy of temperature control was 0.01 K. The uncertainty in the viscosity measurements was better than 0.05%.

3. RESULTS AND DISCUSSION

Table 2. Densities, ρ_o, viscosities, η, and relative permittivities, ε_r, of 1-propanol at different temperatures

T/K	ρ_o/ g cm^{-3}	η/mPa s	ε_r
283.15	0.811462	2.837	22.61
288.15	0.807538	2.494	21.87
293.15	0.803546	2.202	21.15
298.15	0.799538	1.957	20.45
303.15	0.795502	1.729	19.78
308.15	0.791428	1.542	19.13
313.15	0.787314	1.381	18.50
318.15	0.783153	1.235	17.89

Table 3. Molar conductances, Λ, corresponding molalities, *m*, and density gradients, *b*, for solutions of [emim][BF_4] and [bmim][BF_4] in 1-PrOH over the temperature range from (283.15 to 318.15) K

10^4 *m* mol $kg^{- 1}$	Λ S cm^2 mol^{-1}	10^4 *m* mol kg^{-1}	Λ S cm^2 mol^{-1}	10^4 *m* mol kg^{-1}	Λ S cm^2 mol^{-1}	10^4 *m* mol kg^{-1}	Λ S cm^2 mol^{-1}
[emim][BF_4]							
T = 283.15 K		*T* = 288.15 K		*T* = 293.15 K		*T* = 298.15 K	
b = 0.0643 kg^2 dm^{-3} mol^{-1}		*b* = 0.0639 kg^2 dm^{-3} mol^{-1}		*b* = 0.0643 kg^2 dm^{-3} mol^{-1}		*b* = 0.0645 kg^2 dm^{-3} mol^{-1}	
1.0411	19.881	0.8667	22.830	0.7742	25.931	0.8185	29.108
3.0885	17.980	2.7295	20.701	3.8697	22.289	2.5172	26.468
6.3133	16.115	5.0877	18.965	8.7708	19.330	4.8647	24.220
7.8492	15.451	10.915	16.340	10.033	18.788	7.2383	22.585
9.8542	14.743	19.193	14.293	19.380	16.048	10.996	20.697
15.009	13.411	28.476	12.850	28.401	14.463	16.317	18.822
19.890	12.531	37.293	11.842	38.766	13.170	20.923	17.640
28.479	11.375			49.477	12.247	29.848	15.968
47.165	9.794					37.827	14.883
T = 303.15K		*T* = 308.15 K		*T* = 313.15 K		*T* = 318.15 K	
b = 0.0646 kg^2 dm^{-3} mol^{-1}		*b* = 0.0648 kg^2 dm^{-3} mol^{-1}		*b* = 0.0650 kg^2 dm^{-3} mol^{-1}		*b* = 0.0656 kg^2 dm^{-3} mol^{-1}	
0.8049	32.629	1.1911	35.509	1.0286	39.838	1.4082	43.191
2.6066	29.503	2.4621	33.192	2.1180	37.431	2.2356	41.322
4.6027	27.348	4.1677	30.947	3.8657	34.758	4.4427	37.751
6.6736	25.681	6.2462	29.002	6.1426	32.267	6.3895	35.554
11.561	22.910	9.9164	26.463	9.8529	29.392	10.138	32.422
18.901	20.255	14.512	24.183	15.288	26.511	15.808	29.100
29.545	17.877	19.684	22.309	19.647	24.842	20.225	27.254
38.797	16.500	29.973	19.804	29.244	22.187	29.950	24.316
		47.106	17.255	45.153	19.447	48.812	20.818
[bmim][BF_4]]							
T = 283.15 K		*T* = 288.15 K		*T* = 293.15 K		*T* = 298.15 K	
b = 0.0663kg^2 dm^{-3} mol^{-1}		*b* = 0.0661 kg^2 dm^{-3} mol^{-1}		*b* = 0.0659 kg^2 dm^{-3} mol^{-1}		*b* = 0.0657 kg^2 dm^{-3} mol^{-1}	
1.2613	19.036	1.1393	21.677	1.2509	24.231	1.2989	27.087
2.4422	17.927	3.3650	19.471	2.3055	22.905	2.7468	25.139
4.4292	16.600	4.3356	18.782	4.3835	21.062	4.7673	23.267
7.9837	14.957	6.4177	17.595	6.0874	19.945	6.3069	22.165
10.304	14.163	10.266	15.978	10.101	18.009	10.771	19.855
15.178	12.890	15.115	14.559	14.518	16.520	16.800	17.820
20.648	11.879	20.379	13.456	19.980	15.211	25.418	15.959
29.221	10.814	29.837	12.130	29.441	13.678	34.506	14.634
49.231	9.201	48.464	10.474	48.915	11.761	43.322	13.689

Table 3. (continued)

$10^4 m$ mol kg^{-1}	Λ S cm^2 mol^{-1}	$10^4 m$ mol kg^{-1}	Λ S cm^2 mol^{-1}	$10^4 m$ mol kg^{-1}	Λ S cm^2 mol^{-1}	$10^4 m$ mol kg^{-1}	Λ S cm^2 mol^{-1}
T = 303.15K		T = 308.15 K		T = 313.15 K		T = 318.15 K	
b = 0.0655 kg^2 dm^{-3} mol^{-1}		b = 0.0653 kg^2 dm^{-3} mol^{-1}		b = 0.0652 kg^2 dm^{-3} mol^{-1}		b = 0.0650 kg^2 dm^{-3} mol^{-1}	
0.9518	30.961	1.1841	33.918	1.2304	37.503	1.2168	41.507
3.0828	27.641	2.4216	31.661	2.1285	35.615	2.2809	39.042
4.9639	25.766	4.1996	29.403	4.3664	32.361	4.3773	35.714
6.9455	24.258	6.1762	27.543	6.1531	30.518	5.9287	33.903
11.751	21.692	9.8468	25.074	10.018	27.647	10.1265	30.440
19.084	19.231	15.054	22.705	14.548	25.363	14.9688	27.801
29.170	17.131	19.588	21.238	19.953	23.414	19.8060	25.918
38.753	15.770	29.473	18.983	29.492	21.032	28.8858	23.367
48.825	14.743	49.838	16.321	47.623	18.300	48.6747	20.118

The densities, viscosities, and relative permittivities of 1-propanol as a function of temperature are listed in Table 2. The values of relative permittivities were obtained by interpolation from our [27-30] and literature data [31, 32]. The values of densities and viscosities show a very good agreement with literature [24, 32, 33].

To convert molonity, $\tilde{m}$, (moles of electrolyte per kilogram of solution) into molarity, c, the values of density gradients, b, have been determined independently and used in the equation

$$c/\tilde{m} = \rho = \rho_o + b\,\tilde{m} \qquad (1a)$$

where ρ_o is the density of the solvent. Molar concentrations, c, were necessary to use the conductivity equation. The density gradients and the molar conductances of the ILs in solution, Λ, as a function of IL molality, m, (moles of electrolyte per kilogram of solvent) and temperature are presented in Table 3. The relationship among m, $\tilde{m}$, and c is the following

$$\tilde{m} = c/\rho = 1/(1 + mM) \qquad (1b)$$

where M is the molar mass of electrolyte.

The plot of molar conductances, Λ, versus the square root of the molar concentration, $c^{1/2}$, for the investigated systems monotonically decreases as shown in Figures 1 and 2.

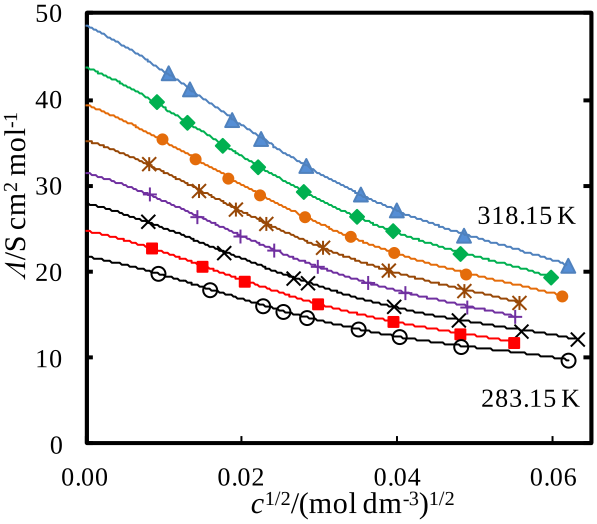

Figure 1. Molar conductance, Λ, of [emim]BF_4 solutions in 1-PrOH versus $c^{1/2}$ at experimental temperatures; ○, 283.15 K; ■, 288.15 K; ×, 293.15 K; +, 298.15 K; ⁎, 303.15 K; ●, 308.15 K; ♦, 313.15 K; ▲, 318.15 K. The lines represent the calculations according to Eqs (2) through (4).

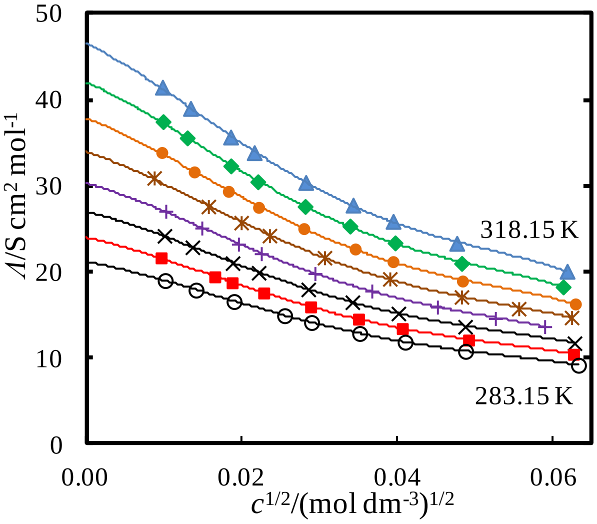

Figure 2. Molar conductance, Λ, of [bmim]BF_4 solutions in 1-PrOH versus $c^{1/2}$ at experimental temperatures; ○, 283.15 K; ■, 288.15 K; ×, 293.15 K; +, 298.15 K; ⁎, 303.15 K; ●, 308.15 K; ♦, 313.15 K; ▲, 318.15 K. The lines represent the calculations according to Eqs (2) through (4).

The conductivity data were analyzed in the framework of the low concentration Chemical Model (lcCM) [34]. This approach uses the set of equations

$$\Lambda = \alpha\,[\Lambda_o - S(\alpha c)^{1/2} + E(\alpha c)\ln(\alpha c) + J(\alpha c) + J_{3/2}(\alpha c)^{3/2}] \qquad (2)$$

$$K_A = (1 - \alpha) / (\alpha^2 c y_{\pm}^2) \qquad (3)$$

and

$$\ln y_{\pm} = -\,(A\alpha^{1/2}c^{1/2}) / (1 + BR\alpha^{1/2}c^{1/2}) \qquad (4)$$

In these equations, Λ_o is the limiting molar conductance; α is the dissociation degree of an electrolyte; K_A is the ionic association constant; R is the distance parameter of ions; $y_{\pm}$ is the activity coefficient of ions on the molar scale; A and B are the Debye–Hückel equation coefficients. The analytical form of the parameters S, E, J, and $J_{3/2}$ was presented previously [34]. The values of Λ_o, K_A, and R were obtained using the well-known procedure given by Fuoss [35] and are collected in Table 4.

Table 4. Limiting molar conductances, Λ_o, association constants, K_A, distance parameters, R, and standard deviations, $\sigma(\Lambda)$, for the investigated ionic liquids in 1-PrOH at different temperatures[a]

T/K	Λ_o/S cm^2 mol^{-1}	K_A/dm^3 mol^{-1}	R/nm	$\sigma(\Lambda)$
[emim][BF$_4$]				
283.15	21.748± 0.024	906 ± 6	1.23 ± 0.07	0.018
288.15	24.708 ± 0.026	916 ± 8	1.42 ± 0.08	0.020
293.15	27.908 ± 0.018	932 ± 4	1.45 ± 0.03	0.015
298.15	31.426 ± 0.027	943 ± 6	1.58 ± 0.05	0.021
303.15	35.212 ± 0.046	951± 9	1.66 ± 0.06	0.036
308.15	39.364 ± 0.061	968 ± 9	1.70 ± 0.06	0.046
313.15	43.719 ± 0.039	979 ± 6	1.71 ± 0.04	0.032
318.15	48.556 ± 0.064	985± 8	1.83 ± 0.04	0.047
[bmim][BF$_4$]				
283.15	21.141± 0.044	907 ± 12	1.55 ± 0.09	0.034
288.15	23.495 ± 0.049	938 ± 12	1.47 ± 0.10	0.036
293.15	26.983 ± 0.044	964 ± 10	1.42 ± 0.08	0.033
298.15	30.290± 0.043	987 ± 9	1.41 ± 0.07	0.029
303.15	33.911 ± 0.034	1018 ± 7	1.35 ± 0.05	0.026
308.15	37.781 ± 0.036	1046 ± 6	1.31 ± 0.05	0.027
313.15	41.943± 0.020	1065 ± 3	1.35 ± 0.02	0.015
318.15	46.461 ± 0.028	1095 ± 3	1.32 ± 0.02	0.016

As seen from Table 4, both ionic liquids are highly associated. For molar concentrations of about 3-5·10^{-3} mol dm^{-3}, half of the examined electrolytes occurs in the undissociated form in 1-propanol. In the case of the same ionic liquids solutions in DMF, the association constants are practically negligible and one can assume that these electrolytes exist essentially as free ions [22]. Therefore, it is possible that an essential role in the ionic association process plays the relative permittivity of the solvent. The linear dependence of $\ln K_A = f\,(1/\varepsilon_r)$, shown in Figure 3, suggest that the electrostatic interactions between ions are mainly responsible for their association.

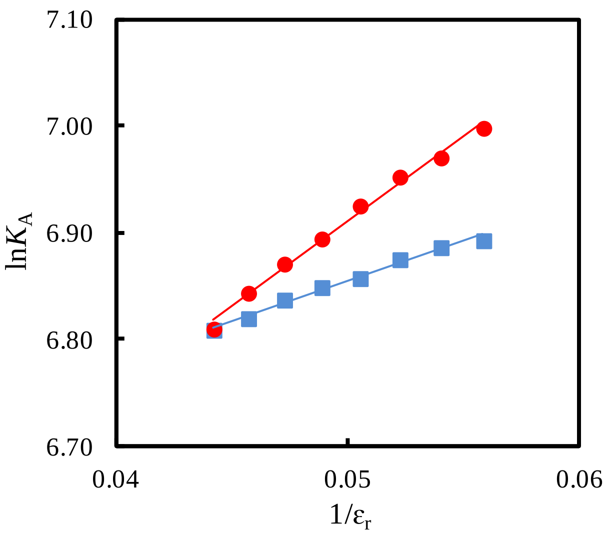

Figure 3. Plot of the logarithm of the association constant for the ■, [emim][BF_4]; and ●, [bmim][BF_4] versus the reciprocal of the relative permittivity of 1-PrOH.

The data collected in Table 4 also show that the ionic association phenomenon increases with increasing temperature, and the effect is much more pronounced in the case of [bmim][BF_4]. In the case of DMF solutions, the association constants were small and slightly higher for [emim][BF_4], but they increase with increasing temperature to a similar extent. These facts prove that the ion-pairing process does not depend only on the dielectric properties of the solvent. An important role play the ion-solvent interactions and the size of the alkyl substituent in the imidazolium cation. One should also pay attention to the fact that the temperature dependences of R values in the ion pairs have a different character for both investigated ionic liquids, ie, in the case of [emim][BF_4] the values of R increase, and in the case of [bmim][BF_4] they decrease with increasing temperature. This may explain why in the case of [bmim][BF_4] the K_A values increase more intensively with increasing temperature.

The limiting molar conductances increase as the temperature increases since the mobility of free ions is higher. However, the values of Λ_o for [emim][BF_4] are higher from those values for [bmim][BF_4]. This indicates that the Λ_o values decrease with increasing alkyl chain length of the ILs. Furthermore, the differences between the Λ_o values for both ionic liquids increase with increasing temperature, from about 0.6 units (at 283.15 K) to about 2.1 units (at 318.15 K). In the case of aprotic DMF the values of Λ_o were also higher for [emim][BF_4]. However, the differences between the Λ_o values for both ionic liquids practically did not depend on the temperature, and they were about 4.6-4.8 units [22]. This may mean that the effect of temperature on the ion-pairing process and on the mobility of ions may depend on the alkyl chain length of the ILs and the ion-solvent interactions.

The limiting molar conductances for [emim][BF_4] and [bmim][BF_4] presented in Table 4 are about three times smaller than those values determined in DMF. The simple hydrodynamic models assume that the values of limiting molar conductance, Λ_o, and macroscopic viscosity of the solvent, η, are offset and the Walden product value, $\Lambda_o\eta$, should be independent of temperature. The values presented in Table 5 show that for examined ionic liquids the Walden rule is well fulfilled both in 1-

propanol as well as in *N,N*-dimethylformamide. It can also be noted that the values of $\Lambda_o\eta$ are much smaller in the case of 1-propanol.

The same simple thermodynamic models assume that the $\Lambda_o\eta$ values are reciprocally proportional to the effective size of ions according to the equation $\Lambda_o\eta = \text{const} / r_s$. Therefore, it can be assumed that the effective size of ions in 1-PrOH are much greater than in DMF. It is possible that this is due to the poor solvation of BF_4^- anions in an aprotic DMF compared with a protic 1-PrOH. Although the crystallographic radius of BF_4^- ion is slightly larger than the Br^- and Cl^-, the values of limiting molar conductivities for these ions in DMF are very similar. The fact that the little polarized anions are poor solvated in dipolar aprotic solvents seems to be fairly well substantiated [36-39]. However, the evaluation of effective size of ions $[emim]^+$, $[bmim]^+$, and BF_4^- requires determining the limiting ionic conductivities values using the procedures applied in our previous work [26]. On the basis of data presented in Tables 4 and 5, respectively, it can be concluded that the limiting ionic conductivities, λ_o^+, and thus the ionic Walden products, $\lambda_o^+\eta$, for $[emim]^+$ are higher than those for $[bmim]^+$, both in 1-PrOH and in DMF. From Table 5 it follows that the differences between the values of $\lambda_o^+\eta$ for $[emim]^+$ and $[bmim]^+$ with increasing temperature increase slightly in the case of 1-PrOH (from 0.017 to 0.026), and decrease slightly (from 0.035 to 0.030) in the case of DMF.

Table 5. Comparison of the Walden product $\Lambda_o\eta$, as a function of temperature for the investigated ionic liquids in 1-PrOH and DMF [26].

T/K	$10^{-2}\ \Lambda_o\eta$/Scm^2 mol^{-1} mPa s			
	[emim][BF$_4$] + 1-PrOH	[bmim][BF$_4$] + 1-PrOH	[emim][BF$_4$] + DMF	[bmim][BF$_4$] + DMF
283.15	0.617	0.600	0.747	0.712
288.15	0.616	0.597	0.748	0.716
293.15	0.615	0.594	0.748	0.718
298.15	0.615	0.593	0.746	0.717
303.15	0.609	0.586	0.745	0.716
308.15	0.607	0.583	0.742	0.713
313.15	0.604	0.579	0.740	0.711
318.15	0.600	0.574	0.739	0.709

From the temperature dependence of Λ_o, the Eyring activation enthalpy of charge transport, $\Delta H_\lambda^\ddagger$, was obtained

$$\ln \Lambda_o + 2/3 \ln \rho_o = -\frac{\Delta H_\lambda^\ddagger}{RT} + D \qquad (5)$$

where *D* is an empirical constant. From the slope of the linear function of $\ln \Lambda_o + 2/3 \ln \rho_o$ versus the inverse of the temperature (1/*T*), which is shown in Figure 4, we obtained $\Delta H_\lambda^\ddagger$ values. $\Delta H_\lambda^\ddagger$ values are 16335 J mol^{-1} and 16665 J mol^{-1} for [emim][BF$_4$] and [bmim][BF$_4$], respectively. For [bmim][BF$_4$], the value of $\Delta H_\lambda^\ddagger$ is thus higher by 330 units. In the case of aprotic DMF the $\Delta H_\lambda^\ddagger$ values were 8541 J mol^{-1} and 8669 J mol^{-1} for [emim][BF_4] and [bmim][BF_4], respectively [22]. Thus, for [bmim][BF_4], the value of $\Delta H_{\lambda}^{\ddagger}$ was also higher, but only by 128 units. It is the result of the presence of a larger substituent in the [bmim]$^+$ cation compared to [emim]$^+$. It seems that this conclusion applies to both protic 1-propanol and aprotic *N*,*N*-dimethylformamid.

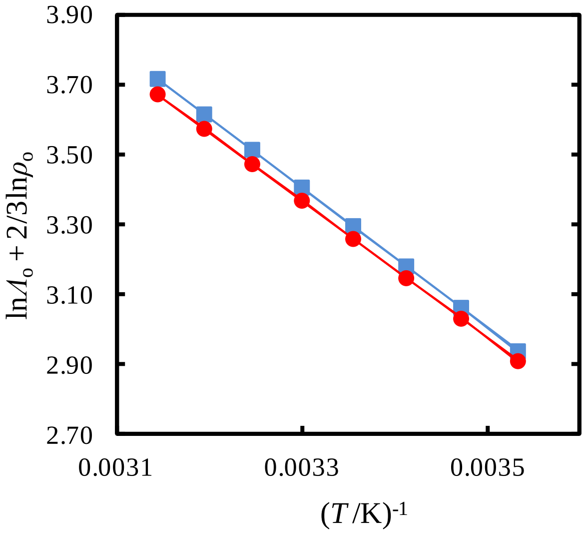

Figure 4. Plot of ln Λ_o + 2/3 ln ρ_o as a function of 1/T for ■, [emim][BF_4]; and ●, [bmim][BF_4] in 1-PrOH.

The temperature dependence of the association constant was used to calculation of Gibbs free energy of ion formation, ΔG_A^o

$$\Delta G_A^o\ (T) = -RT\ ln\ K_A(T) \qquad (6)$$

$\Delta G_A^o(T)$ can also be expressed by the polynomial

$$\Delta G_A^o\ (T) = A_o + A_1 T + A_2 T^2 \qquad (7)$$

The values of parameters A_o, A_1, and A_2 of Eq. (7) and correlation coefficients, r^2, are summarized in Table 6.

Table 6. Coefficients of Eq. (7) and correlation coefficients, r^2, for [emim][BF_4] and [bmim][BF_4] in 1-PrOH

	A_o /kJ mol^{-1}	A_1/J mol^{-1} K^{-1}	A_2/J mol^{-1} K^{-2}	r^2
[emim][BF_4]	2.916	-70.22	0.012	0.99995
[bmim][BF_4]	5.160	-78.58	0.013	0.99995

The entropy and enthalpy of ion association are defined as

$$\Delta S_{\mathrm{A}}^{\mathrm{o}} = -\left(\frac{\partial \Delta G_{\mathrm{A}}^{\mathrm{o}}}{\partial T}\right)_{\mathrm{p}} = -A_1 - 2A_2\,T \qquad (8)$$

$$\Delta H_{\mathrm{A}}^{\mathrm{o}} = \Delta G_{\mathrm{A}}^{\mathrm{o}} + T\,\Delta S_{\mathrm{A}}^{\mathrm{o}} = A_{\mathrm{o}} - A_2 T^{2} \qquad (9)$$

The thermodynamic functions of the ion pair formation $(\Delta G_{\mathrm{A}}^{\mathrm{o}}, \Delta S_{\mathrm{A}}^{\mathrm{o}}, \Delta H_{\mathrm{A}}^{\mathrm{o}})$ at different temperatures are presented in Table 7 and in Figures 5, 6, and 7, respectively.

Table 7. Thermodynamic functions of association of [emim][BF_4] and [bmim][BF_4] solutions in 1-PrOH at different temperatures

T/K	$\Delta G_{\mathrm{A}}^{\mathrm{o}}$ J mol^{-1}	$\Delta S_{\mathrm{A}}^{\mathrm{o}}$ J $mol^{-1}K^{-1}$	$\Delta H_{\mathrm{A}}^{\mathrm{o}}$ J mol^{-1}
	[emim][BF_4]		
283.15	-16029	63.6	1978
288.15	-16338	63.5	1944
293.15	-16665	63.4	1910
298.15	-16978	63.2	1876
303.15	-17284	63.1	1841
308.15	-17614	63.0	1805
313.15	-17928	62.9	1769
318.15	-18233	62.8	1732
	[bmim][BF_4]		
283.15	-16033	71.1	4102
288.15	-16395	71.0	4065
293.15	-16745	70.8	4026
298.15	-17090	70.7	3987
303.15	-17456	70.6	3948
308.15	-17813	70.4	3907
313.15	-18147	70.3	3866
318.15	-18511	70.2	3824

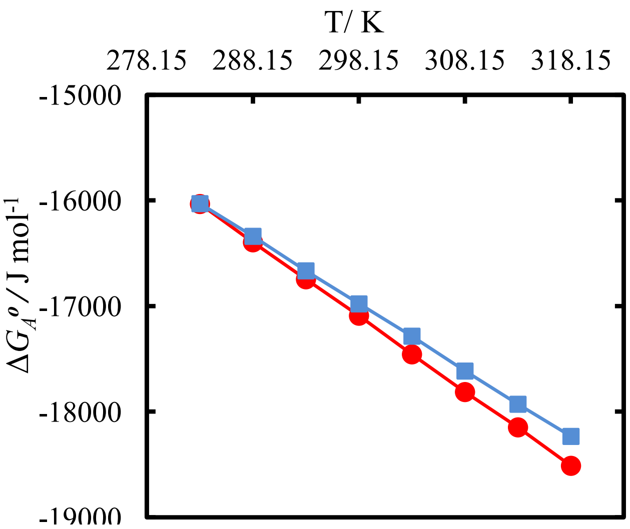

Figure 5. Variation of Gibbs free energy, $\Delta G_{\mathrm{A}}^{\mathrm{o}}$, as a function of temperature *T* of ■, [emim][BF$_4$]; and ●, [bmim][BF$_4$] in 1-PrOH.

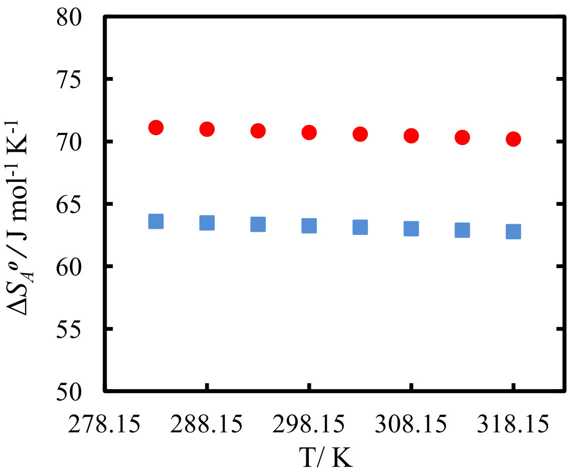

Figure 6. Variation of association entropies, $\Delta S_{\mathrm{A}}^{\mathrm{o}}$, as a function of temperature of ■, [emim][BF$_4$]; and ●, [bmim][BF$_4$] in 1-PrOH.

The values of $\Delta G_{\mathrm{A}}^{\mathrm{o}}$ presented in Table 7 and Figure 5 indicate that the spontaneity of the ion pair formation at 298.15 K is comparable for both salts examined. With increasing temperature the spontaneity of the ion pair formation becomes smaller in the case of salt containing the smaller cation, ie [emim][BF$_4$]. The differences between values of $\Delta G_{\mathrm{A}}^{\mathrm{o}}$ at 318.15 K, however, does not exceed 300 J, which represents only about 1.7 % of the free enthalpy of association value. One should pay attention that in the case of [emim][BF$_4$] and [bmim][BF$_4$] w *N,N*-dimethylformamide the situation was reversed, ie the spontaneity of the ionic association was somewhat higher for salt containing the smaller cation, ie [emim][BF$_4$] [22]. However, in this case, the K_{A} values are very small (about 10 units), and the differences between the K_{A} values for both the salts are very small and do not exceed the unit. For example, using different conductance equations can obtain comparable or even greater differences between values of the association constant.

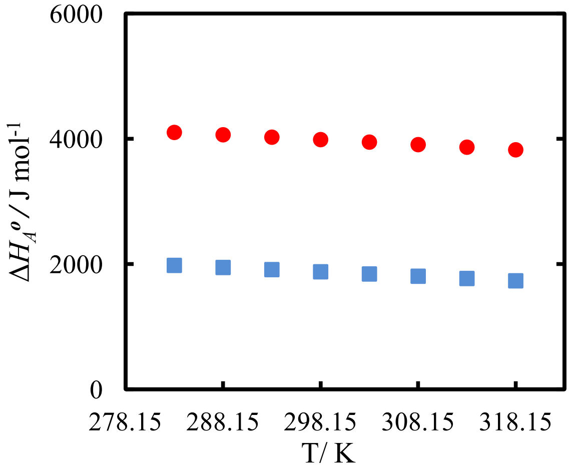

Figure 7. Variation of enthalpies, $\Delta H_{\mathrm{A}}^{\mathrm{o}}$, as a function of temperature of ■, [emim][BF$_4$]; and ●, [bmim][BF$_4$] in 1-PrOH**.**

The increase of temperature leads to more negative $\Delta G_{\mathrm{A}}^{\mathrm{o}}$ values, which means shifting the equilibrium towards the formation of ion pairs. As can be seen in Figures 6 and 7, both the values of entropy and enthalpy of association are positive and greater for [bmim][BF$_4$]. Moreover, the values of $\Delta S_{\mathrm{A}}^{\mathrm{o}}$ and $\Delta H_{\mathrm{A}}^{\mathrm{o}}$ slightly decrease with increasing temperature for both tested electrolytes. Positive values of entropy prove that the transition from the free solvated ions into the ion pairs causes that system becomes less ordered. It is possible that this is related to the partial desolvation of ions prior to the formation of ion pair. This effect is more pronounced in the case of [bmim][BF$_4$]. The positive values of $\Delta H_{\mathrm{A}}^{\mathrm{o}}$ indicate that the ion pair forming processes are endothermic, particularly in the case of [bmim][BF$_4$]. From Eq. (10)

$$\Delta G_{\mathrm{A}}^{\mathrm{o}}(T) = \Delta H_{\mathrm{A}}^{\mathrm{o}}(T) - T\,\Delta S_{\mathrm{A}}^{\mathrm{o}}(T) \qquad (10)$$

it follows that entropic effects seem to dominate over the enthalpic effects, because the Gibbs free energy, $\Delta G_{\mathrm{A}}^{\mathrm{o}}$, is negative, and thus the ion pair formation is exoergic in both cases.

4. CONCLUSIONS

Molar conductances of solutions of ionic liquids, [emim][BF$_4$] and [bmim][BF$_4$ in 1-propanol have been reported at T = (283.15 to 318.15) K. Analyses of the conductivity data on the basis of Barthel's low concentration Chemical Model (lcCM) provided important information about the ion association of investigated ionic liquid solutions. Both examined ionic liquids behave like classical electrolytes in solvent with low dielectric constant, and the electrostatic interactions between ions is mainly responsible for their association. A strong ionic association was observed for the ILs in protic solvent 1-PrOH at all experimental temperatures. The K_{A} values increase as the temperature increases (with decreasing relative permittivity of the solvent) and increase with an increase in the alkyl chain length of the ILs. The limiting molar conductances of ILs are influenced by the ionic solvation. The evaluated values of thermodynamic functions of association suggest the spontaneity of the association process. The values of ΔH_A^o are positive and suggest that the ion-pairing process is endothermic. Because the Gibbs free energy is negative, entropic effects seem to dominate over the enthalpic effects, and thus the ion pair formation of ionic liquids in 1-propanol is exoergic.

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