

Ionic association and conductance of ionic liquids in dichloromethane at temperatures from 278.15 to 303.15 K

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Abstract The electrical conductances of very dilute solutions of the ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF₄] and 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄] in the low-permittivity solvent dichloromethane have been measured in the temperature range from 278.15 to 303.15 K at 5 K intervals. The data was analyzed assuming the possible presence of contact (CIP) and solvent-separated (SSIP) ion pairs in the solution on the basis of IcCM model to obtain ionic association constants, K_A , and the limiting molar conductivities, Λ_o , of these electrolytes. The examined ionic liquids are strongly associated in dichloromethane over the whole temperature range. From the temperature dependence of the limiting molar conductivities, the Eyring's activation enthalpy of charge transport was determined. 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 Conductance · 1-Alkyl-3-methylimidazolium tetrafluoroborate · Ion association · Thermodynamic functions

Introduction

Creating sets of data on physical and chemical properties of ionic liquids (ILs) are of essential significance for both pure scientific and industrial purposes. 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, ionic association, and solvent structure. A survey of literature indicates that most studies report only the specific conductivity data for pure ionic liquids or binary and ternary mixtures of ILs with various solvents at 298.15 K. The conductance studies of dilute solutions of ionic liquids in a wide temperature range allow the determination of the values of association constants and thermodynamic functions of association, which consequently allows the better understanding of the behavior of ILs in various solvents [1–3]. This paper is both a continuation and an extension of our and other authors' works on association of imidazolium-based ionic liquids, i.e., [emim][BF₄] and [bmim][BF₄] in water [4], 1-propanol [5], N,N-dimethylformamide [6], acetonitrile [7, 8], dimethylsulfoxide [9], and methanol [9, 10]. Moderate ionic association of ILs occurs in N,N-dimethylformamide, acetonitrile, and methanol, slight in dimethylsulfoxide, whereas it becomes significant in 1-propanol. Water promotes significantly dissociation of the ionic liquids.

According to our knowledge, conductometric data for solutions of [emim][BF₄] and [bmim][BF₄] in dichloromethane (DCM) at various temperatures have not yet been reported. The only paper is by Katsuda et al. [11], who investigated the conductance of [bmim][BF₄] in DCM exclusively at 298.15 K. Aiming to cover this topic, the present work deals with the precise conductivity measurements, which have been carried out in the concentration range $c=0.4$ to $4 \cdot 10^{-4}$ mol·dm⁻³ of [emim][BF₄] and [bmim][BF₄] in DCM at temperatures range 278.15–303.15 K at atmospheric pressure. Imidazolium-based ionic liquids were chosen because of their thermal and chemical stability and the insignificant degree of susceptibility to air and moisture. The obtained data were used to calculate the values of the limiting molar conductivities, Λ_o ,

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Table 1 Densities, ρ_o , viscosities, η , and relative permittivities, ϵ_r , of dichloromethane at different temperatures

T/K	$\rho_o/g\text{ cm}^{-3}$	$\eta/\text{mPa s}$ [13]	ϵ_r [13]
278.15	1.352778	0.505	9.61
283.15	1.343749	0.482	9.39
288.15	1.334665	0.460	9.19
293.15	1.325522	0.437	9.00
298.15	1.316310	0.415	8.82
303.15	1.307030	0.392	8.65

and the association constants, K_A on the basis of lcCM model. The Eyring activation enthalpy of charge transport, ΔH_A^\ddagger , as

well as the Gibbs energy, ΔG_A° , enthalpy, ΔH_A° , and entropy, ΔS_A° , of ion pair formation, for the electrolytes have been evaluated.

It should be stressed that measuring the conductance in the selected systems is a difficult task, since the experiments require high accuracy. It results from the fact that the relative permittivity of dichloromethane is low, its ionization properties are relatively weak, and electrolytes dissolved in DCM are strongly associated [11–15]. Therefore, it is necessary to use the extremely low concentrations of the electrolyte. For concentrations below the limit given by Fuoss [16], $c_{\text{max}} = 3.2 \cdot 10^{-7} \cdot \epsilon_r^3 \text{ mol} \cdot \text{dm}^{-3}$ (in DCM $c_{\text{max}} = 2.3 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$), it can be expected that only the free ions and ion pairs are present in the solution [17].

Table 2 Molar conductivities, Λ , corresponding molalities, m , and density gradients, b , for solutions of [emim][BF₄] and [bmim][BF₄] in DCM over the temperature range from 278.15 to 303.15 K

	T/K					
	278.15	283.15	288.15	293.15	298.15	303.15
[emim][BF ₄]						
	$b/\text{kg}^2 \text{ dm}^{-3} \text{ mol}^{-1}$					
	0.0067	0.0082	0.0100	0.0116	0.0134	0.0150
$10^5 m/\text{mol kg}^{-1}$	$\Lambda/\text{S cm}^2 \text{ mol}^{-1}$					
2.9934	32.101	32.849	33.677	34.442	35.231	35.987
3.0273	31.978	32.742	33.552	34.335	35.136	35.903
3.7552	29.361	30.051	30.793	31.493	32.207	32.881
4.4866	27.050	27.678	28.356	29.003	29.643	30.289
5.4665	24.919	25.504	26.106	26.680	27.256	27.809
9.5666	19.066	19.491	19.940	20.364	20.796	21.186
16.047	15.286	15.626	15.981	16.313	16.660	16.980
22.151	13.309	13.596	13.903	14.193	14.486	14.770
29.957	11.617	11.862	12.126	12.378	12.632	12.877
49.726 ^a	9.405	9.605	9.814	10.007	10.209	10.391
70.244 ^a	8.158	8.329	8.512	8.689	8.859	9.024
100.34 ^a	7.085	7.233	7.391	7.537	7.685	7.823
[bmim][BF ₄]						
	$b/\text{kg}^2 \text{ dm}^{-3} \text{ mol}^{-1}$					
	-0.0183	-0.0159	-0.0136	-0.0112	-0.0080	-0.0062
3.0171	31.073	31.951	32.782	33.576	34.355	35.107
3.0895	30.710	31.565	32.463	33.116	33.888	34.618
3.7127	28.685	29.476	30.232	30.936	31.657	32.343
4.5061	26.584	27.287	28.010	28.665	29.262	29.921
5.4611	24.446	25.108	25.714	26.187	26.817	27.485
9.5947	18.548	19.049	19.522	19.965	20.027	20.610
14.933	15.344	15.750	16.131	16.491	16.820	17.116
21.967	13.047	13.401	13.728	14.033	14.315	14.572
30.573	11.277	11.573	11.849	12.101	12.554	12.704
50.099 ^a	9.139	9.375	9.590	9.791	10.013	10.303
70.352 ^a	7.956	8.164	8.350	8.526	8.715	8.909
100.63 ^a	6.895	7.071	7.235	7.388	7.530	7.658

^a These concentrations were not used for calculations of Λ_o and K_A

Experimental

Materials

[Emim][BF₄] of 99 % purity and [bmim][BF₄] of 98.5 % purity were purchased from Fluka and were used as received. The water content of the studied chemicals was determined by Karl–Fischer titration. The final water mass fraction was less than 0.015 % in [emim][BF₄] and 0.05 % in [bmim][BF₄], respectively. Dichloromethane (minimum 99.8 %, water content <0.02 %) was received from POCH Gliwice (Poland) and was used without further purification. The actual purity of DCM was estimated to be 99.97 % by gas chromatography. The specific conductance, κ , of the solvent was in the range of $2\text{--}2.5 \cdot 10^{-9} \text{ S} \cdot \text{cm}^{-1}$ at 278.15–303.15 K, which is in good agreement with available data [11, 15].

Methods

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

The measurement procedure was based on the method described by Bešter-Rogač et al. [13, 18] and used by us in our previous works [4–6, 19, 20]. Conductivity measurements were performed with a three-electrode cell with the use of a Precision Component Analyzer 6430B (Wayne-Kerr, UK) under argon atmosphere and at the different frequencies, ν , (0.2, 0.5, 1, 2, 3, 5, 10, and 20) kHz. The temperature was kept constant within 0.003 K (Calibration Thermostat 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 [6]. The estimated uncertainty of the measured values of conductivity was 0.20 %. The estimation of this uncertainty takes into account the high degree of difficulty associated with the conductivity measurements of electrolyte solutions in DCM. These difficulties, among others, are related to the use of very low concentrations of electrolytes and high ionic association.

Densities were measured with an Anton Paar DMA 5000M oscillating U-tube densimeter equipped with a thermostat with a temperature stability within $\pm 0.001 \text{ K}$. The densimeter was calibrated with extra pure water, previously degassed ultrasonically. The estimated uncertainty of the density is $\pm 2 \cdot 10^{-4} \text{ g} \cdot \text{cm}^{-3}$.

Results and discussion

The physical properties of dichloromethane are given in Table 1.

The measured density of DCM agreed well with those values published in the literature [13, 21, 22].

To convert molality, \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

$$c/\tilde{m} = \rho = \rho_0 + b\tilde{m} \quad (1a)$$

where ρ_0 is the density of the solvent. Molar concentrations, c , were necessary to use the conductivity equation. The density gradients and the molar conductivities 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 2. The relationship among m , \tilde{m} , and c is the following

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

where M is the molar mass of electrolyte.

The plot of molar conductivity, Λ , versus the square root of the molar concentration, $c^{1/2}$, for the investigated systems monotonically decreases as shown in Figs. 1 and 2, respectively, over the temperature range from 273.15 to 303.15 K. The values of Λ for ionic liquids in DCM are smaller than in DMF [6], water [4], and 1-propanol [5]. With a change of temperature, they change very slightly, in contrast to the above-mentioned solvents.

The conductivity data were analyzed in the framework of the low concentration Chemical Model (lcCM) [23]. This approach uses the following set of equations

$$\Lambda = \alpha \left[\Lambda_0 - S(\alpha c)^{1/2} + E(\alpha c) \ln(\alpha c) + J_1(\alpha c) + J_2(\alpha c)^{3/2} \right] \quad (2)$$

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

and

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

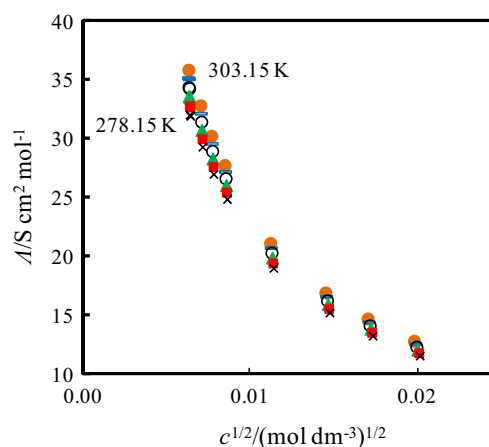


Fig. 1 Molar conductivity, Λ , of [emim][BF₄] solutions in DCM versus $c^{1/2}$ at experimental temperatures; \times 278.15 K, \blacksquare 283.15 K, \blacktriangle 288.15 K, \circ 293.15 K, \blacksquare 298.15 K, \bullet 303.15 K

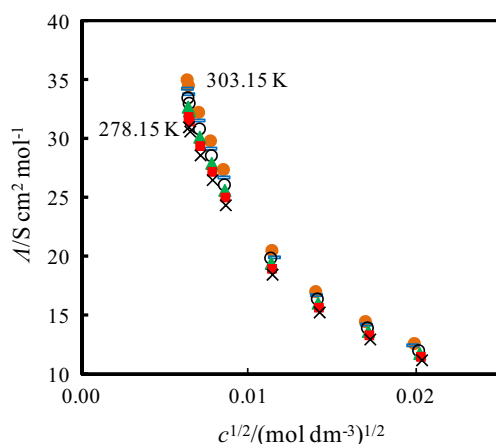


Fig. 2 Molar conductivity, Λ , of [bmim][BF₄] solutions in DCM versus $c^{1/2}$ at experimental temperatures; \times 278.15 K, \blacksquare 283.15 K, \blacktriangle 288.15 K, \circ 293.15 K, \bullet 298.15 K, \bullet 303.15 K

In these equations, Λ_0 is the limiting molar conductivity, 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, and A and B are the Debye–Hückel equation coefficients. The analytical form of the parameters S , E , J_1 , and J_2 was presented previously [23].

In all previous papers [4–6, 19, 20], the values of Λ_0 , K_A , and R were obtained using the well-known procedure given by Fuoss [24]. However, in this case, we were unable to optimize the values of R in a sufficiently reliable manner. Therefore, we calculated the values of R independently, assuming the possible existence of contact (CIP) and solvent-separated (SSIP) ion pairs in the solution. For this purpose, the distance of closest approach (contact distance) of cation and anion,

$R = a = a_+ + a_-$, we calculated from the ionic radius of BF_4^- , $a_- = 0.227$ and $a_+ = 0.331$ nm for [bmim]⁺ and $a_+ = 0.310$ nm for [emim]⁺ [11]. The latest value was extrapolated by us from the radii of ions [bmim]⁺, [hmim]⁺, and [omim]⁺ [11]. In the case of solvent-separated ion pair, $R = a + s$, where s is the length of an orientated solvent molecule, we assumed according to [13, 25] $s = 0.177$ nm. The results obtained by a two-parameter fit (Λ_0 and K_A) are collected in Table 3. For the last three concentrations from Table 2, the calculated values of Λ were lower than the experimental ones. Moreover, the differences between calculated and experimental values of Λ increase with an increase of concentration. This suggests that in solution form higher aggregates such as triple ion formation. Therefore, we did not use the last three concentrations for calculations, and we used a range of concentrations ($c = 0.4$ to $4 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) consistent with the Fuoss condition [16].

As seen from Table 3, the limiting molar conductivities increase as the temperature increases since the mobility of free ions is higher. The values of Λ_0 for [emim][BF₄] are higher compared to those values for [bmim][BF₄] because the Λ_0 values increase with decreasing alkyl chain length of the ILs. Furthermore, the differences between the Λ_0 values for both ionic liquids increase with increasing temperature. The limiting molar conductivities for [emim][BF₄] and [bmim][BF₄] presented in Table 3 are much higher than corresponding values determined in 1-propanol, DMF, and water [4–6]. However, one should pay attention to the fact that the determining factor that affects the Λ_0 value, a macroscopic viscosity of the solvent, in the case of dichloromethane, is very small (see Table 1). The value of Λ_0 for [bmim][BF₄] at 298.15 K is in good agreement with this reported by Katsuta et al. [11] ($\Lambda_0 = 162.5 \text{ S cm}^2 \text{ mol}^{-1}$). Obtained values of standard deviations, $\sigma(\Lambda)$, may be considered to be high, but

Table 3 Limiting molar conductivities, Λ_0 , association constants, K_A , and standard deviations, $\sigma(\Lambda)$, for the investigated electrolytes in DCM at different temperature

<i>T</i> /K	$\Lambda_0/\text{S cm}^2 \text{ mol}^{-1}$ CIP	$K_A/\text{dm}^3 \text{ mol}^{-1}$	$\sigma(\Lambda)$	$\Lambda_0/\text{S cm}^2 \text{ mol}^{-1}$ SSIP	$K_A/\text{dm}^3 \text{ mol}^{-1}$	$\sigma(\Lambda)$
[emim][BF ₄]						
278.15	149.74	467,030	0.13	151.20	477,780	0.13
283.15	156.39	491,840	0.13	157.78	502,200	0.13
288.15	164.56	525,200	0.13	166.07	536,530	0.13
293.15	172.51	558,210	0.14	173.82	568,340	0.14
298.15	181.07	595,110	0.14	182.96	609,480	0.14
303.15	190.63	640,300	0.15	192.41	654,130	0.15
[bmim][BF ₄]						
278.15	136.49	402,980	0.20	137.65	411,280	0.20
283.15	142.24	418,760	0.20	143.54	427,990	0.20
288.15	147.93	434,990	0.20	149.72	447,400	0.20
293.15	155.01	463,310	0.20	156.26	473,640	0.20
298.15	161.08	478,920	0.13	162.56	489,420	0.13
303.15	168.50	510,440	0.22	170.18	522,420	0.22

Table 4 Comparison of limiting molar conductivities, Λ_o , association constants, K_A , and Gibbs-free energy ΔG_A^o , for solutions of [emim][BF₄] and [bmim][BF₄] in various molecular solvents of viscosity, η , and relative permittivity, ϵ_r , at 298.15 K

Solvent	η /mPa s	ϵ_r	Λ_o /S cm ² mol ⁻¹	K_A /dm ³ mol ⁻¹	ΔG_A^o /kJ mol ⁻¹	Ref.
DCM	0.415 [13]	8.82 [10]	181.07 ^a	595,110 ^a	-33.0	<i>c</i>
			161.08 ^b	478,920 ^b	-32.4	<i>c</i>
PrOH	1.957 [5]	20.45 [26]	31.43 ^a	943 ^a	-17.0	[5]
			30.29 ^b	987 ^b	-17.1	[5]
MeOH	0.5438 [9]	32.63 [9]	134.0 ^a	66.1 ^a	-10.4	[10]
			121.84 ^b	37.7 ^b	-9.0	[9]
			126.9 ^b	53.7 ^b	-9.9	[10]
ACN	0.3413 [13]	35.96 [7]	197.10 ^a	15.9 ^a	-6.9	[7]
			198.3 ^a	17.9 ^a	-7.2	[8]
			189.29 ^b	15.7 ^b	-6.8	[7]
			190.3 ^b	18.2 ^b	-7.2	[8]
DMF	0.8455 [6]	36.81 [27]	93.47 ^a	11.30 ^a	-6.0	[6]
			89.83 ^b	10.57 ^b	-5.9	[6]
DMSO	1.9946 [9]	46.52 [9]	41.51 ^b	4.6 ^b	-3.8	[9]
Water	0.8903 [26]	78.36 [27]	114.27 ^a	0.89 ^a		[4]
			107.39 ^b	016 ^b		[4]

^a [Emim][BF₄]^b [Bmim][BF₄]^c This paper

should be noted that the conductometric measurements of analyzed systems are very difficult to be performed.

From data collected in Table 4 for investigated ILs in various solvents results that the values of limiting molar conductivities, Λ_o , follow the order: acetonitrile > dichloromethane > methanol > water > N,N-dimethylformamide > dimethyl sulfoxide > 1-propanol. As mentioned above, the conductivity increase is related to the decrease in solvent viscosity. However, for the series given above, this relationship is not entirely fulfilled. But if we consider the protic and aprotic character of solvents, the conductivity decreases in the order: MeOH > Water > 1-PrOH, and for aprotic: ACN > DCM > DMF > DMSO, which correlates very well with viscosity increase.

It is observed from Table 3 that both ionic liquids are very highly associated in DCM. This observation stays in agreement with literature data for various imidazolium ILs in DCM ($K_A \approx 1 \cdot 10^4$ – $38 \cdot 10^4$ dm³ mol⁻¹) [11, 13]. The value of $K_A = 384300$ dm³ mol⁻¹ for [bmim][BF₄] in DCM at 298.15 K presented in paper [11] is slightly lower than ours. This can be explained by different procedure used for experimental data analysis and the different measuring procedure. As we can see from the Table 3, K_A values depend significantly on the adopted model of ion pairs. In the case of solvent-separated (SSIP) ion pairs, the K_A and Λ_o values are higher. The data collected in Table 3 also show that the association constants increase with increasing temperature, and the effect is much more pronounced in the case of

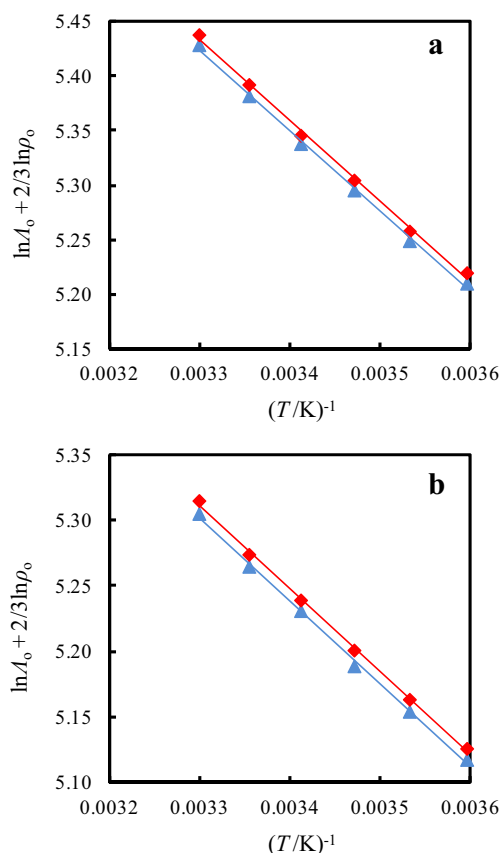
**Fig. 3** a, b Plot of $\ln \Lambda_o + 2/3 \ln \rho_o$ as a function of $1/T$ for a [emim][BF₄] and b [bmim][BF₄] in DCM: (▲), CIP, and (●), SSIP

Table 5 Coefficients of Eq. (7) and correlation coefficients, r^2 , for [emim][BF₄] and [bmim][BF₄] in DCM

		$A/\text{kJ mol}^{-1}$	$B/\text{J mol}^{-1} \text{K}^{-1}$	$C/\text{J mol}^{-1} \text{K}^{-2}$	r^2
[emim][BF ₄]	CIP	-14.656	21.71	-0.279	0.99998
[bmim][BF ₄]		-15.556	21.70	-0.263	0.99984
[emim][BF ₄]	SSIP	-17.338	39.99	-0.311	0.99998
[bmim][BF ₄]		-11.815	-4.16	-0.219	0.99987

[emim][BF₄]. This can be due to decrease in ILs-DCM interactions with increasing temperature.

In the case of [emim][BF₄] and [bmim][BF₄] solutions in dimethyl sulfoxide [9] and N,N-dimethylformamide [6], the association constants are practically negligible; in methanol and acetonitrile [7–10], ion association is rather weak. In turn, in water [4], both ionic liquids are practically fully dissociated, whereas in 1-propanol [5] and especially in dichloromethane, they were definitely associated. The data are consistent with the classical ionic association theory of electrolytes [28]. Similar behavior of other ionic liquids in various solvents was also observed [1, 3, 29–34]. In turn, in very low-permittivity tetrahydrofuran ($\epsilon_r = 7.58$), ionic liquid (1-butyl-2,3-dimethylimidazolium tetrafluoroborate [bmmim][BF₄]) form not only ion pairs but also triple ions [29]. It means that ions are more associated in the solvent possessing a low-relative permittivity. However, not only the relative permittivity of the solvent plays an essential role in the ionic association process, but also the participation of the ion–solvent interactions and the alkyl chain length of the ILs should be considered too.

From the temperature dependence of Λ_o , the Eyring activation enthalpy of charge transport, $\Delta H_{\lambda}^{\ddagger}$, was obtained by using Eq. 5

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

where D is an empirical constant. From the slope of the linear dependencies of $\ln \Lambda_o + 2/3 \ln \rho_o$ versus the inverse of the temperature ($1/T$), which are shown in Fig. 3(a, b), we obtained the following $\Delta H_{\lambda}^{\ddagger}$ values 6,138 (CIP) and 6,142 (SSIP) for [emim][BF₄] and 5,257 (CIP) and 5,271 (SSIP) for [bmim][BF₄] (all in $\text{J} \cdot \text{mol}^{-1}$), respectively. For [emim][BF₄], the value of $\Delta H_{\lambda}^{\ddagger}$ is thus higher than [bmim][BF₄] by 881 (CIP) and 871 (SSIP) units. It is somewhat surprising, considering the fact that in other solvents [4–7, 9], the values of $\Delta H_{\lambda}^{\ddagger}$ are higher for [bmim][BF₄] than [emim][BF₄]. It is the result of the presence of a larger substituent in the [bmim]⁺ cation compared to [emim]⁺. In the case of dichloromethane, it may suggest that the effective ionic radius of [emim]⁺ is larger than the [bmim]⁺. Taking into account the values of the Eyring activation enthalpy of charge transport for other solvents, we

Table 6 Thermodynamic functions of association of [emim][BF₄] and [bmim][BF₄] solutions in DCM at different temperatures

T/K	ΔG_A^o J mol^{-1} CIP	ΔS_A^o $\text{J mol}^{-1} \text{K}^{-1}$	ΔH_A^o J mol^{-1}	ΔG_A^o J mol^{-1} SSIP	ΔS_A^o $\text{J mol}^{-1} \text{K}^{-1}$	ΔH_A^o J mol^{-1}
[emim][BF ₄]						
278.15	-30,190	133.4	6,910	-30,240	132.7	6,690
283.15	-30,850	136.2	7,700	-30,900	135.9	7,560
288.15	-31,560	138.9	8,490	-31,610	139.0	8,440
293.15	-32,250	141.7	9,300	-32,300	142.1	9,345
298.15	-32,960	144.5	10,130	-33,020	145.2	10,260
303.15	-33,700	147.3	10,960	-33,750	148.3	11,200
[bmim][BF ₄]						
278.15	-29,850	124.4	4,770	-29,890	125.8	5,110
283.15	-30,470	127.1	5,510	-30,530	128.0	5,720
288.15	-31,100	129.7	6,260	-31,170	130.2	6,350
293.15	-31,800	132.3	7,020	-31,850	132.4	6,980
298.15	-32,420	135.0	7,800	-32,480	134.6	7,630
303.15	-33,130	137.6	8,590	-33,180	136.8	8,280

can conclude that ΔH_A^\ddagger depends mainly on the solvent. In the case of protic solvents (water and 1-propanol) values are very similar (about $16,000 \text{ J}\cdot\text{mol}^{-1}$) and almost twice or more higher than those for DMF, DCM, and ACN. It can be concluded that the value of ΔH_A^\ddagger depends on the formation of hydrogen bonds between molecules of the solvent and its structure.

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

$$\Delta G_A^\circ(T) = -RT \ln K_A(T) \tag{6}$$

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

$$\Delta G_A^\circ(T) = A + BT + CT^2 \tag{7}$$

The values of parameters A , B , and C of Eq. (7) and correlation coefficients, r^2 , are summarized in Table 5.

The entropy and enthalpy of ion association are defined as

$$\Delta S_A^\circ = -(\partial \Delta G_A^\circ / \partial T)_p = -B - 2CT \tag{8}$$

$$\Delta H_A^\circ = \Delta G_A^\circ + T\Delta S_A^\circ = A - CT^2 \tag{9}$$

The thermodynamic functions of the ion pair formation (ΔG_A° , ΔS_A° , ΔH_A°) at different temperatures are presented in Table 6 and in Figs. 4, 5, and 6, respectively.

The values of ΔG_A° presented in Table 6 and Fig. 4 indicate that the spontaneity of the ion pair formation in the case of both ionic liquids is comparable. The increase of temperature leads to more negative ΔG_A° values, which means shifting the equilibrium toward the formation of ion pairs due to reduction in preferential solvation of ions by temperature (interactions

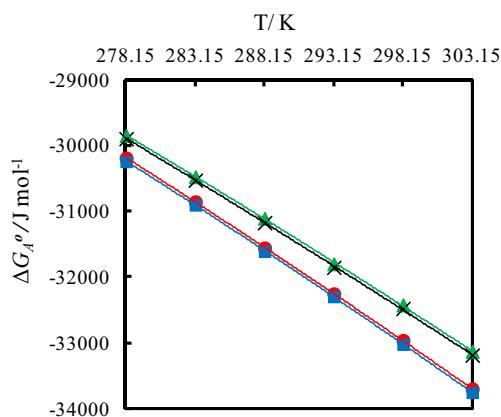


Fig. 4 Variation of Gibbs-free energy, ΔG_A° , as a function of temperature T of [emim][BF₄]: (■), SSIP, (●), CIP, and [bmim][BF₄] in DCM, (×), SSIP, (▲), CIP

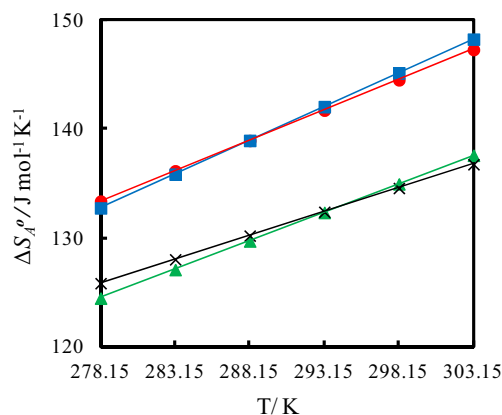


Fig. 5 Variation of association entropies, ΔS_A° , as a function of temperature of [emim][BF₄], (■), SSIP, (●), CIP, and [bmim][BF₄] in DCM, (×), SSIP, (▲) CIP

between IL and DCM become weaker with increasing temperature).

The data collected in Table 4 show that the values of Gibbs-free energy of the studied ILs in other solvents are also negative (and become more negative as temperature increases).

As can be seen in Figs. 5 and 6, both the values of entropy and enthalpy of association are positive and greater for [emim][BF₄]. Moreover, the values of ΔS_A° and ΔH_A° increase 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. This is related to the partial desolvation of ions prior to the formation of ion pair. The positive values of ΔH_A° indicate that the ion pair-forming processes are endothermic, particularly in the case of [emim][BF₄]. From Eq. (10)

$$\Delta G_A^\circ(T) = \Delta H_A^\circ(T) - T\Delta S_A^\circ(T) \tag{10}$$

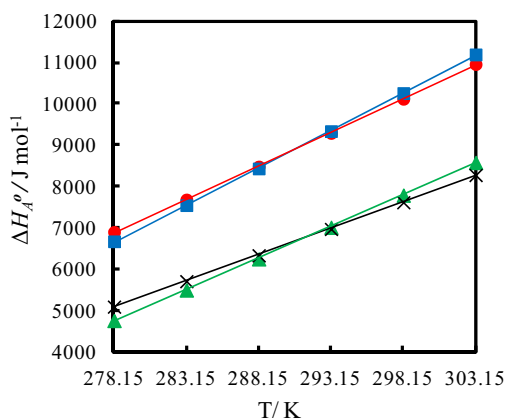


Fig. 6 Variation of enthalpies, ΔH_A° , as a function of temperature of [emim][BF₄], (■), SSIP, (●), CIP and [bmim][BF₄] in DCM, (×), SSIP, (▲) CIP

it follows that entropic effects seem to dominate over the enthalpic effects because the Gibbs-free energy, ΔG_A^0 , is negative, and thus the ion pair formation is spontaneous in both cases. Furthermore, earlier studies [4–7, 19] confirm that in the case of other solvents, spontaneity of ionic association process results mainly from changes of the entropy.

Conclusions

Molar conductivities of very dilute solutions of 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium tetrafluoroborate in dichloromethane have been reported for the first time at $T=278.15$ to 303.15 K. Conductivity data were analyzed using the Barthel's low concentration Chemical Model (lcCM). The examined ionic liquids act like very weak electrolytes ($K_A \approx 60 \cdot 10^4 \text{ mol}^{-1} \text{ dm}^3$ for [emim][BF₄] and $\approx 48 \cdot 10^4 \text{ mol}^{-1} \text{ dm}^3$ for [bmim][BF₄], respectively) in the low-permittivity solvent DCM at used temperature range. With increasing temperature, the tendency to form the ion pairs increases. [Emim][BF₄] is more associated electrolyte than [bmim][BF₄]. K_A values depend significantly on the adopted model of ion pairs, (CIP) or (SSIP). The values of Λ for ionic liquids in DCM are smaller than in DMF [6], water [4], and 1-propanol [5] and change very slightly with a change of temperature. In turn, Λ_0 values are much higher than corresponding values determined in 1-propanol, DMF, and water. The evaluated values of thermodynamic functions of association suggest the spontaneity of the association process. The values of ΔH_A^0 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 DCM is spontaneous in both cases.

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