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Triple Ion Formation in Solutions of [emim][BF_4] and [bmim][BF_4] in Dichloromethane at Various Temperatures. A New Method of Analysis of Conductivity Data

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Detailed conductometric studies of solutions of the imidazolium-based ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF_4] and 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] in the low-permittivity solvent dichloromethane have been carried out from ($6 \cdot 10^{-4}$ to $1 \cdot 10^{-2}$) mol dm^{-3} in the temperature interval of (278.15 - 303.15) K. A new method of analysis of conductivity data based on the low concentration Chemical Model (lcCM) has been developed and successfully applied to the solutions containing free ions, ion pairs, and triple ions in order to obtain the triple ion formation constants K_T and the limiting molar conductances of triple ions $\Lambda_{o,T}$. The values of limiting molar conductances at various temperatures were used to calculate the Eyring's activation enthalpy of charge transport. The thermodynamic parameters of triple ion formation such as standard Gibbs energy, enthalpy, and entropy were also calculated from the temperature dependence of the triple ion formation constants.

Keywords: conductance, ion association, triple ions, dichloromethane.

1. INTRODUCTION

In low permittivity solvents ($\varepsilon_r < 10$) such as tetrahydrofuran, chloroform, dichloromethane, ethyl acetate, aniline, o-toluidine, o-xylene, chlorobenzene, or 1,3-dioxolane salts exist as free ions, ion pairs or higher aggregates even at low concentrations [1-3]. A major role in the association of ions play the electrostatic interactions between the ions. Ionic association of electrolytes has a significant influence on ionic solvation, which depends on the solvent property. The viscosity and relative permittivity of the solvent should be taken into account for the purpose of determining the extend of association or solvent-solvent interactions [4]. Conductometric measurements, which are a subject of our interest for many years, provide relevant information on ionic association, interactions between ions and solvent and solvent structure. Most frequently, if the minima were observed in the conductometric curves (Λ versus $c^{1/2}$), the corresponding conductance data was analyzed using the Fuoss-Kraus theory of triple ions [5-8] or the Fuoss-Hsia equations [3, 9-12]. Hojo et al. [13-18] developed an analytical method based on the Onsager's limiting law to a system, in which not only ion pairs, but also triple ions and quadrupoles (dimers of ion pairs) exist in a solution.

In our earlier work [19], we have reported the conductance data of very dilute solutions (c = (0.4 to 4 · 10^{-4}) mol dm^{-3}) of the ionic liquids (ILs) [emim][BF_4] and [bmim][BF_4] in dichloromethane. The data was analyzed assuming the presence of contact (CIP) and solvent- separated (SSIP) ion pairs in the solution in order to calculate the limiting molar conductances and the ionic association constants. As it was expected, both ILs are highly associated in dichloromethane over the whole temperature range from (278.15 to 303.15) K.

The dielectric spectra measurements in [bmim][BF_4] + DCM system [20] also confirm strongly association with CIPs as the dominant species at $x_{IL} \leq 0.03$. However, with an increase of the ionic liquid content, ion-ion pair interactions lead to their breakup and/or replacement by other charged species such as triple ions [20].

Therefore, extending our studies on the conductometric properties of the ionic liquids in dichloromethane, in the present paper, precise electrical conductance measurements of [emim][BF_4] and [bmim][BF_4] in DCM have been carried out at different temperatures 278.15 K, 283.15 K, 288.15 K, 293.15 K, 298.15 K, and 303.15 K and at higher concentrations than previously [19]. The experimental data was analyzed using the lcCM model to calculate the limiting molar conductances of triple ions $\Lambda_{o,T}$ and the triple ion formation constants K_T. The final part of our work presents the thermodynamic properties of the examined ILs in DCM, i.e. ΔG_T^o, ΔH_T^o, and ΔS_T^o of triple ions formation.

2. EXPERIMENTAL

2.1. Reagents and chemicals

[Emim][BF_4] (purity > 99%) and [bmim][BF_4] (purity > 98.5%) were obtained from Fluka and were used as received. The final water mass fraction as determined by Karl-Fischer titration was less than 0.015% in [emim][BF_4] and 0.05% in [bmim][BF_4], respectively. Dichloromethane with purity of minimum mass fraction 0.998, and water content < 0.02% was purchased from POCH Gliwice (Poland) and was used without any purification. Gas chromatography was used for analyzing the actual purity of DCM estimated to be 99.97%. The specific conductance κ of the solvent was in the range of 2 - 2.5 · 10^{-9} S · cm^{-1} at 278.15-303.15 K, which is in good agreement with available data [21, 22].

2.2. Apparatus

The electrical conductance measurements were carried out in a three-electrode cell with the use of a Precision Component Analyzer 6430B (Wayne-Kerr, UK) at the different frequencies ν ranging from 0.2 to 20 kHz and under argon atmosphere. The temperature was controlled with an accuracy of

0.003 K (Calibration Thermostat Ultra UB 20F with Through-flow cooler DLK 25, Lauda, Germany). The cell constant was determined by measuring the resistance of a cell filled with KCl solution of known specific conductance [23]. All the solutions were prepared by mass on a Sartorius RC 210D balance with a precision of ± $1\cdot10^{-5}$ g. First, the cell was filled with a known mass of dichloromethane and the resistances R were measured at various temperatures, then known masses of stock solution were sequentially added and the procedure was repeated. The resistance values R_∞ were derived by linear extrapolation of the dependence R = f(1/ν) to infinite frequency. Then, the measured conductance values were calculated as $\lambda = 1/R_\infty$. From the measured conductances of the pure solvent and solution and the cell constant, the specific conductivities κ were calculated and converted to molar conductances ($\Lambda = \kappa / c$). The uncertainty of the measured values of conductivity was estimated to be 0.15%.

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 apparatus was calibrated with extra pure water, previously degassed ultrasonically. The estimated uncertainty of the density is ± $1\cdot10^{-5}$ g · cm^{-3}.

3. RESULTS AND DISCUSSION

The physical properties of dichloromethane such as densities, viscosities, and relative permittivities at all temperatures tested were given in our previous paper [19].

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

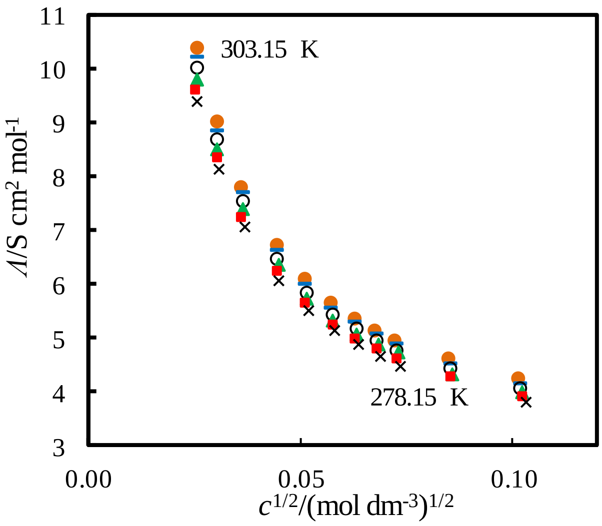

Figure 1. Molar conductance Λ of [emim][BF$_4$] solutions in DCM versus $c^{1/2}$ as a function of temperature; ×, 278.15 K; ■, 283.15 K; ▲, 288.15 K; ○, 293.15 K; - , 298.15 K; ●, 303.15 K

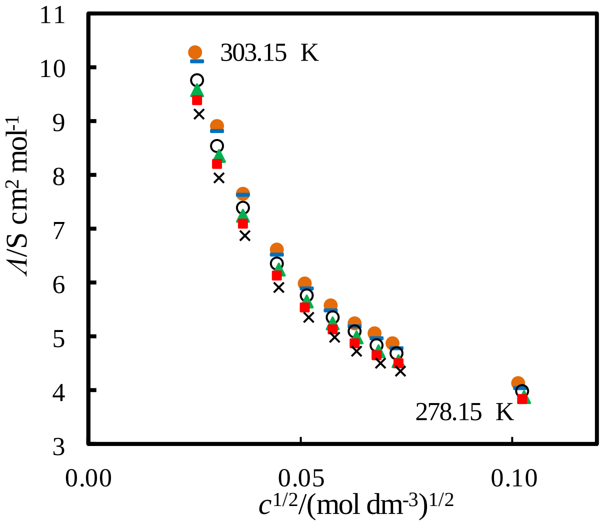

Figure 2. Molar conductance Λ of [bmim][BF_4] solutions in DCM versus $c^{1/2}$ as a function of temperature; ×, 278.15 K; ■, 283.15 K; ▲, 288.15 K; ○, 293.15 K; - , 298.15 K; ●, 303.15 K

The molarity of solutions *c* necessary to use the conductance equation, was determined from solution molonity $\tilde{m}$ (moles of electrolyte per kilogram of solution) and solution density ρ

$c = \tilde{m}\,\rho$ (1a)

In this purpose density measurements for the pure solvent ρ_o and the binary solution of ILs at different temperatures were performed and the density gradients *b* were determined from the equation

$b = \rho - \rho_o / \tilde{m}$ (1b)

In the next step, density values for all examined molonity were calculated and converted into molarity. The concentrations of ILs solutions expressed in molality *m* (moles of electrolyte per kilogram of solvent) as well as the molar conductances Λ and the density gradients *b* as a function of temperature are listed in Table 1. The following relationship exist between *m*, $\tilde{m}$, and *c*

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

where *M* is the molar mass of electrolyte.

Table 1. Molar conductances Λ as a function of IL molality *m* and temperature *T*, and density gradients *b* for solutions of [emim][BF_4] and [bmim][BF_4] in DCM

	T/K					
	278.15	283.15	288.15	293.15	298.15	303.15
	[emim][BF_4]					
	b/ kg^2 dm^{-3} mol^{-1}					
	0.0067	0.0082	0.0100	0.0116	0.0134	0.0150
10^3 *m*/mol kg^{-1}	Λ/ S cm^2 mol^{-1}					
0.4973	9.405	9.605	9.814	10.031	10.229	10.391
0.7024	8.158	8.329	8.512	8.689	8.859	9.024

1.0034	7.075	7.233	7.391	7.537	7.685	7.823
1.5024	6.086	6.219	6.356	6.484	6.610	6.724
1.9929	5.522	5.626	5.750	5.868	5.987	6.100
2.5030	5.129	5.234	5.349	5.457	5.564	5.666
3.0028	4.869	4.970	5.080	5.183	5.285	5.382
3.5115	4.658	4.765	4.874	4.971	5.061	5.158
4.0015	4.485	4.590	4.732	4.790	4.879	4.965
5.5176	4.144	4.241	4.331	4.442	4.526	4.614
7.8551	3.804	3.895	3.994	4.089	4.161	4.260
11.018[a]	3.582	3.676	3.766	3.850	3.929	4.002
11.996[a]	3.559	3.654	3.742	3.826	3.906	3.978
19.915[a]	3.552	3.649	3.741	3.829	3.910	3.980
[bmim][BF$_4$]						
b/ kg^2 dm^{-3} mol^{-1}						
	-0.0183	-0.0159	-0.0136	-0.0112	-0.0080	-0.0062
0.50100	9.139	9.375	9.590	9.791	10.106	10.303
0.70352	7.956	8.194	8.370	8.546	8.815	8.909
1.00628	6.895	7.081	7.265	7.388	7.630	7.658
1.50263	5.941	6.106	6.242	6.373	6.514	6.621
1.99512	5.367	5.519	5.662	5.774	5.889	6.003
2.50312	5.008	5.128	5.244	5.353	5.461	5.590
2.98196	4.743	4.866	4.989	5.094	5.184	5.269
3.50289	4.533	4.640	4.748	4.849	4.949	5.060
4.01440	4.359	4.462	4.567	4.686	4.762	4.880
8.37073	3.697	3.800	3.887	3.981	4.053	4.143
16.01073[a]	3.863	3.975	4.078	4.177	4.265	4.350
18.8788[a]	3.865	3.984	4.085	4.188	4.353	4.448
27.0433[a]	3.913	4.034	4.143	4.252	4.474	4.586

[a] These concentrations were not used for calculations because in these range of concentrations may form higher ion-aggregates in the solution

In our previous paper [19], we determined the values of limiting molar conductances Λ_o and association constants K_A for [emim][BF$_4$] and [bmim][BF$_4$] in dichloromethane in the temperature range from (278.15 to 303.15) K. Analysis of the results was based on the assumption that only free ions and ion pairs are present in the investigated solutions. According to Fuoss [24], this assumption may not be true, if the maximum concentration of the electrolyte exceeds $c_{max} = 3.2 \cdot 10^{-7} \cdot \varepsilon_r^3$ mol dm^{-3} (in DCM $c_{max} = 2.3 \cdot 10^{-4}$ mol dm^{-3}). Indeed, it turned out that for concentrations greater than the c_{max}, the calculated values of molar conductances Λ_{calc} were lower than the experimental ones (Λ_{exp}) [19]. This suggests that with increasing concentration of the ionic liquid, above the concentration c_{max}, in the solution appear chemical individuals having a charge. Obviously, the simplest explanation for the discrepancy between the values of Λ_{calc} and Λ_{exp} is the triple ion formation. As the concentration of a solution increases, the differences between calculated and experimental values of Λ increase, which is shown in the Figures 3a and 3b. The values of Λ_{exp} for [emim][BF$_4$] and [bmim][BF$_4$] given in our previous paper [19] and Λ_{exp} obtained in this paper at 298.15 K were used for comparison. Whereas, the values of Λ_{calc} were obtained on the basis of Λ_o and K_A determined in the paper [19], assuming the formation of contact ion pairs.

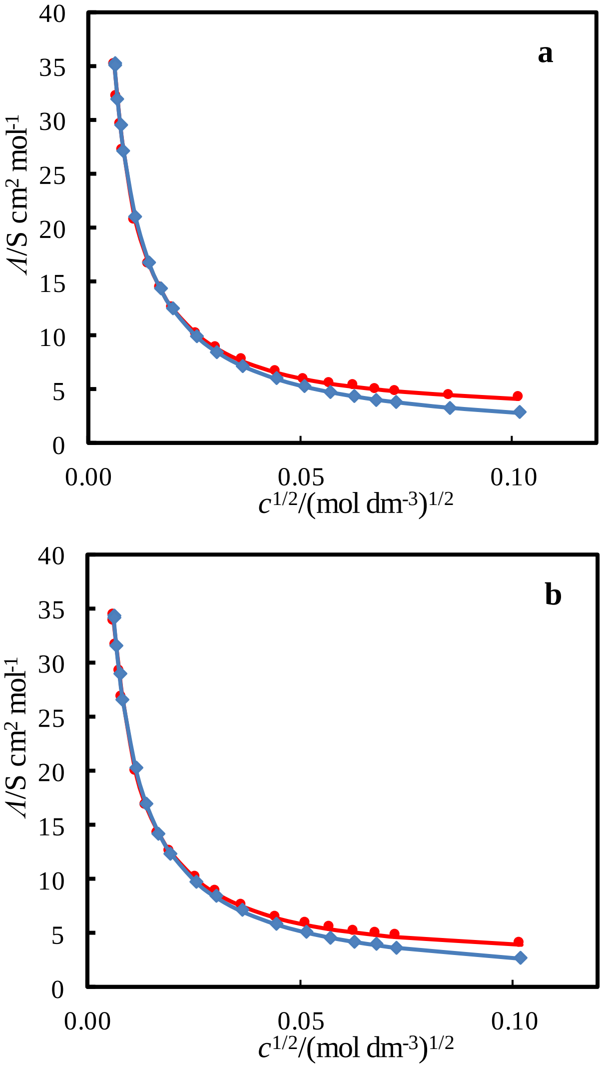

Figure 3a and 3b. Comparison of ●, experimental and ♦, calculated molar conductances for **a.** [emim][BF$_4$] and **b.** [bmim][BF$_4$] in DCM.

As you can see in Figures 3a and 3b, with increasing electrolyte concentration, the difference of molar conductances (Λ_{exp} - Λ_{calc}) increases, reaching at $c \approx 0.01$ mol·dm^{-3} about 35% (for [bmim][BF$_4$]) and about 30% (for [emim][BF$_4$]) of the experimental value (Λ_{exp}). The differences (Λ_{exp} - Λ_{calc}) are very significant and show that at higher concentrations, the analysis of the molar conductances must take into account the phenomenon of triple ion formation in solutions of [emim][BF$_4$] and [bmim][BF$_4$] in dichloromethane.

The electrolyte solution containing the cations C^+ and anions A^- as well as the ion pairs CA and the triple ions C_2A^+ and CA_2^- can be considered as a solution consisting of the following components:

- completely dissociated into ions C^+ and A^-
- completely dissociated into ions (triple ions) C_2A^+ and CA_2^-
- undissiociated part, i.e., the ion pairs CA.

In the solution, the equilibria described by the equations (2) and (3) are established

$$C^+ + A^- \rightleftharpoons CA \tag{2}$$

$$CA + C^+ \rightleftharpoons C_2A^+ \tag{3a}$$

$$CA + A^- \rightleftharpoons CA_2^- \tag{3b}$$

The amounts of individual ions result from the total electrolyte concentration *c* and the values of equilibrium constants described by the equations (4), (5a) and (5b)

$$K_A = [CA] y_{CA} / [C^+]\, y_{C^+}\, [A^-]\, y_{A^-} = [CA] / [C^+]\, [A^-]\, y_{+}^{2} \tag{4}$$

$$K_{T_1} = [C_2A^+] y_{C_2A^+} / [CA]\, [C^+]\, y_{C^+} = [C_2A^+] / [CA]\, [C^+] \tag{5a}$$

$$K_{T_2} = [CA_2^-] y_{CA_2^-} / [CA]\, [A^-]\, y_{A^-} = [CA_2^-] / [CA]\, [A^-] \tag{5b}$$

where K_A and K_T are the ion pair and triple ion formation constants, respectively.
In the equations (4), (5a) and (5b) it was assumed that $y_{CA} = 1$, $y_{C^+} y_{A^-} = y_\pm^2$, $y_{C_2A^+} = y_{C^+}$ and $y_{CA_2^-} = y_{A^-}$.

Assuming symmetric triple ion formation, $K_{T_1} = K_{T_2} = K_T$, and $[C^+] = [A^-]$ [15, 25]. The concentrations of individual ions can be written as

$$[C^+] = [A^-] = \beta_1 c \tag{6}$$

$$[C_2A^+] = [CA_2^-] = \beta_T c \tag{7}$$

$$[CA] = (1 - \beta_1 - 3\beta_T)\, c \tag{8}$$

From equations (4)-(8) result that

$$\beta_1 = [-1 + (1 + 4K_A c\, y_\pm^2 (1 - 3\beta_T))^{1/2}] / (2K_A\, c\, y_\pm^2) \tag{9}$$

$$\beta_T = K_T c\, \beta_1 (1 - \beta_1) / (1 + 3K_T \beta_1 c) \tag{10}$$

where the activity coefficient $y_\pm$ and the ionic strength *I* of the solution are described by the equations

$$\ln y_\pm = -A\sqrt{I} / (1 + BR\sqrt{I}) \tag{11}$$

$$I = (\beta_1 + \beta_T) c \tag{12}$$

R is the distance parameter of ions, *A* and *B* are the Debye – Hückel coefficients.

For specific values of K_A and K_T, the values of β_1 and β_T coefficients for any concentration *c* were calculated from equations (9) - (12) using the numerical methods of successive approximations. Similar methods for determining the concentration of ions on the basis of equilibrium constants we used in our previous papers [26-29]. Other authors [15] calculate the values of $\beta_1 = [A^-] / c$ and $\beta_T = [C_2A^+] / c = [CA_2^-] / c = K_T [A^-]^3 / c$ using Newton's method to determine the value of $[A^-]$ for specified values of K_1 and K_T and the electrolyte concentration *c*.

If triple ions exist in a solution, molar conductance can be described as follows [15, 30]

$$\Lambda = \beta_1 \Lambda_1 + \beta_T \Lambda_T \tag{13}$$

where Λ_1 is the conductance of electrolyte in the form of ions C^+ and A^-, Λ_T is the conductance of electrolyte consisting of the ions C_2A^+ and CA_2^-.

In the case of extremely low electrolyte concentrations to describe the values of Λ_1 and Λ_T, the limiting molar conductances of Λ_o and $\Lambda_{o,T}$ were used, respectively [5, 30]. At higher concentrations, some authors [13-18] use the Onsager limiting law [30-32] to describe the Λ_1 and Λ_T conductances. It should be noted, however, that the Onsager limiting law applies only to very low concentrations.

This paper is definitely the first attempt to use the low concentration Chemical Model (lcCM) [33] for analysis of molar conductances of Λ_1 and Λ_T. The lcCM applies to a much wider range of concentrations than the Onsager limiting law and it was previously used by us for the analysis of the results of conductometric studies of various electrolyte solutions [34-42], including ionic liquids [43-46]. The lcCM model we used also in the paper on very dilute solutions of [emim][BF$_4$] and [bmim][BF$_4$] in dichloromethane [19]. According to the low concentration Chemical Model, the conductances of Λ_1 and Λ_T can be described by the equations

$$\Lambda_1 = \Lambda_o - S_{(1)}\sqrt{I} + E_{(1)}I\ln I + J_{1(1)}I + J_{2(1)}I^{3/2} \qquad (14)$$

$$\Lambda_T = \Lambda_{o,T} - S_{(T)}\sqrt{I} + E_{(T)}I\ln I + J_{1(T)}I + J_{2(T)}I^{3/2} \qquad (15)$$

The expressions for the parameters S, E, J_1, and J_2 were presented by Barthel previously [33].

In the case of triple ions in the solutions, the analysis of the relationship between Λ and c requires determining the values of four parameters: Λ_o, $\Lambda_{o,T}$, K_A, and K_T. The simultaneous determination of values of four parameters, which seem to be reliable, is an extremely difficult tusk. Therefore, usually it assumes a specified quotient of the limiting molar conductances value of $\Lambda_{o,T} / \Lambda_o$ [5, 13, 14, 15, 17, 18, 30, 47]. Most often, it is assumed that $\Lambda_{o,T} / \Lambda_o$ is equal to 1/3 [5, 17, 30] or 2/3 [47] or $(1/3)^{1/3}$= 0.693 [13-15]. In the paper of Hojo et al. [18] were also considered the other values of the quotient $\Lambda_{o,T} / \Lambda_o$.

In this paper, we used the values of Λ_o and K_A determined in our previous paper [19]. In this case, we need only determine the values of $\Lambda_{o,T}$ and K_T, or only one parameter of K_T, if we use the specified value of $\Lambda_{o,T} / \Lambda_o$. However, in this study, we also made an attempt to simultaneously determine the values of $\Lambda_{o,T}$ and K_T in a wide range of temperatures from (278.15 to 303.15) K. Furthermore, we tried to assess, what is the most real value of the quotient of $\Lambda_{o,T} / \Lambda_o$. On the basis of $\Lambda_{o,T}$ and K_T we can calculate the thermodynamic functions of triple ion formation as well as the activation enthalpy of charge transport $\Delta H_\lambda^\ddagger$ for the electrolyte built of cation and anion being triple ions. A survey of literature shows that such research based on the results of conductivity measurements over a wide temperature range have not yet been taken.

The calculated values of $\Lambda_{o,T}$ and K_T are collected in Table 2. In part (a) of the Table 2 are collected the values of $\Lambda_{o,T} = \Lambda_o /3$ and the optimized K_T values. In part (b) of the Table 2 are collected the results of the simultaneous optimization of $\Lambda_{o,T}$ and K_T values. All the calculations were performed using the parameter of the closest approach of the ions R, corresponding to the contact ion pairs. For [emim][BF$_4$] and [bmim][BF$_4$] the values of $R = a_+ + a_-$ are assumed to be 0.537 nm and 0.558 nm, respectively. The details concerning the calculation of these values we reported in paper [19].

As seen from Table 2, the values of $\Lambda_{o,T}$ obtained by the optimization method (part (b) of the Table 2) are surprisingly close to the values resulting from the assumption of $\Lambda_{o,T} = \Lambda_o / 3$. We can conclude that this assumption used for a long time by many authors [5, 17, 30], can be successfully used in the studied systems.

Table 2. Limiting molar conductances $\Lambda_{o,T}$ and formation constants K_T of the triple ions and standard deviations $\sigma(\Lambda_{o,T})$ for the ILs in DCM from 278.15 to 303.15 K

T/K	$\Lambda_{o,T}$/S cm^2 mol^{-1}	K_T/dm^3 mol^{-1}	$\sigma(\Lambda_{o,T})$	$\Lambda_{o,T}$/S cm^2 mol^{-1}	K_T/dm^3 mol^{-1}	$\sigma(\Lambda_{o,T})$
	(a)			(b)		
			[emim][BF$_4$]			
278.15	49.91	197.5	0.009	48.51	205.6	0.025
283.15	52.13	198.5	0.028	51.8	200.3	0.010
288.15	54.85	200.1	0.028	54.04	204.2	0.017
293.15	57.50	200.2	0.031	58.33	196.3	0.023
298.15	60.35	199.3	0.013	58.86	205.8	0.023
303.15	63.54	199.4	0.013	63.24	200.6	0.024
			[bmim][BF$_4$]			
278.15	45.50	189.6	0.022	47.04	180.9	0.022
283.15	47.41	190.9	0.022	49.38	180.3	0.031
288.15	49.31	191.1	0.026	50.75	183.6	0.036
293.15	51.67	195.1	0.027	53.34	186.7	0.029
298.15	53.69	190.7	0.063	53.69	188.2	0.053
303.15	56.17	193.8	0.020	57.61	187.2	0.019

The values of K_T obtained using these two methods are also very similar. Because the values of $\Lambda_{o,T}$ based on the above mentioned assumption, change with temperature somewhat more regularly, they are used for the further analysis of the results. Similarly, the values of K_T obtained by adopting of $\Lambda_{o,T} = \Lambda_o / 3$ seem somewhat more reliable, also in the aspect of their temperature changes. The data collected in Table 2 also shows that the limiting molar conductances of triple ions increase regularly with increasing temperature. This fact is, of course, not surprising.

From the temperature dependence of $\Lambda_{o,T}$, the Eyring activation enthalpy of charge transport $\Delta H_{\lambda}^{\ddagger}$ was derived

$$\ln \Lambda_{o,T} + 2/3 \ln \rho_o = -\Delta H_{\lambda}^{\ddagger} / RT + D \qquad (16)$$

where ρ_0 is the density of the solvent, D is an empirical constant.

In Figure 4 are presented the dependencies of $\ln \Lambda_o + 2/3 \ln \rho_o$ versus the inverse of the temperature ($1/T$).

These dependencies have a highly linear character. The values of $\Delta H_{\lambda}^{\ddagger}$ for [emim][BF$_4$] and [bmim][BF$_4$] are equal to 6137 and 5256 J mol^{-1}, respectively. The fact that the $\Delta H_{\lambda}^{\ddagger}$ value for [emim][BF$_4$] is higher than for [bmim][BF$_4$] may be somewhat surprising, since in other solvents [43-46, 48-49] the $\Delta H_{\lambda}^{\ddagger}$ value was higher for [bmim][BF$_4$] than for [emim][BF$_4$]. Is also worth mentioning that the determined values of $\Delta H_{\lambda}^{\ddagger}$ for the electrolyte built of triple ions, associated with the $\Lambda_{o,T}$

conductance are practically the same as the values of $\Delta H_{\lambda}^{\ddagger}$ for the electrolyte built of simple ions, which are associated with the Λ_o conductance.

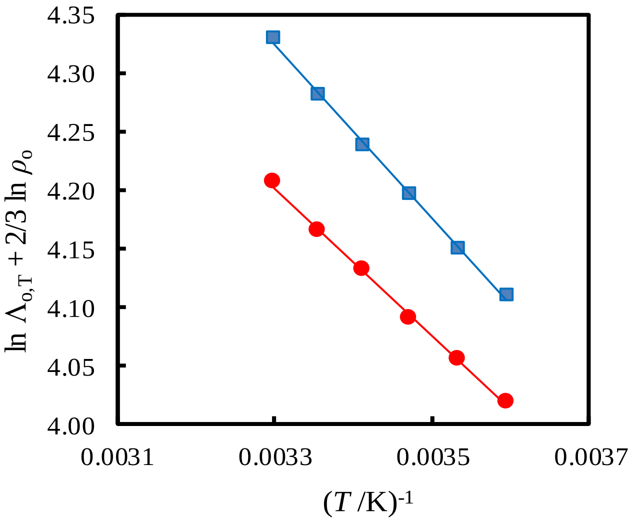

Figure 4. Plot of ln $\Lambda_{o,T}$ + 2/3 ln ρ_o as a function of 1/*T* for ■, [emim][BF_4] and ●, [bmim][BF_4] in DCM.

This is only seemingly surprising observation. The explanation, however, you can easily find in the adoption of the assumption $\Lambda_{o,T} / \Lambda_o = 1/3$. The dependencies of ln Λ_o + 2/3 ln ρ_o = f (1/T) and ln $\Lambda_{o,T}$ + 2/3 ln ρ_o = f (1/T) have obviously the same slope and are shifted by the value equal to ln 3.

The values of triple ion formation constants K_T at various temperatures (equations 5a and 5b) were used to obtain the Gibbs free energy of triple ions ΔG_T^o

$$\Delta G_T^o = -RT \ln K_A \qquad (17)$$

The dependence of ΔG_T^o = f (*T*) is presented in Figure 5.

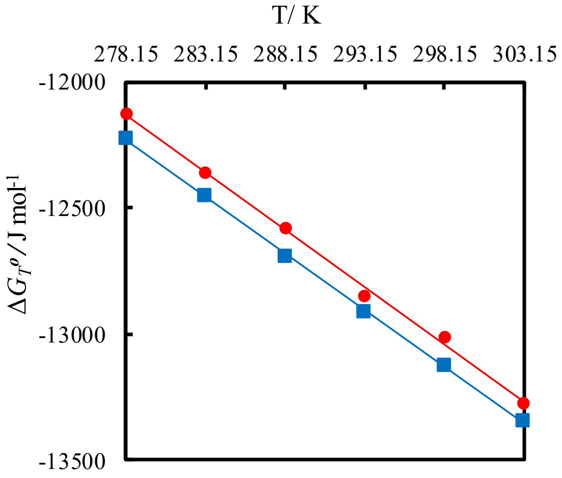

Figure 5. Gibbs free energy ΔG_T^o as a function of temperature *T* for ■, [emim][BF_4] and ●, [bmim][BF_4] in DCM.

As can be seen in Figure 5, the dependencies of ΔG_T^o = f (*T*) have practically a linear character. This means that

$$\Delta G_T^o = A + B\,T \qquad (18)$$

and the values of entropy and enthalpy in the investigated range of temperatures are practically constant, which results from the equations (19) and (20)

$$\Delta S_T^o = -(\partial \Delta G_T^o / \partial T) = -B \qquad (19)$$

$$\Delta H_T^o = \Delta G_T^o + T\Delta S_T^o = \mathrm{A} \qquad (20)$$

The values of ΔS_T^o for [emim][BF_4] and [bmim][BF_4] are equal to 44.80 J mol^{-1} K^{-1} and 45.44 J mol^{-1} K^{-1}, respectively. In turn, the values of enthalpy for the ionic liquids are equal to 236 J mol^{-1} and 505 J mol^{-1}, respectively. From equation (21)

$$\Delta G_T^o = \Delta H_T^o - T\Delta S_T^o \qquad (21)$$

results that the spontaneity of the triple ions formation is mainly entropy driven, i.e., the value of $T\Delta S_T^o$ is by far greater than the ΔH_T^o value.

4. CONCLUSIONS

The conductance behavior of [emim][BF_4] and [bmim][BF_4] solutions in dichloromethane have been studied in the concentration ranging from ($6 \cdot 10^{-4}$ to $1 \cdot 10^{-2}$) mol dm^{-3} at *T* = (278.15 to 303.15) K. The molar conductances of the solutions are considerably higher than expected from the association constants and the limiting molar conductances determined in very dilute solutions (from 0.4 to $4 \cdot 10^{-4}$ mol dm^{-3}), in which only contact ion pairs are considered in the solution. Therefore, for the first time in the analysis of the molar conductances was taken into account the phenomenon of triple ions formation in the solutions using a specially developed method based on the lcCM model. The assumption of $\Lambda_{o,T} / \Lambda_o = 1/3$ can be successfully used in the studied systems to determine the formation constants of the triple ions. The values of activation enthalpy of charge transport determined from the temperature dependence of $\Lambda_{o,T}$ for [emim][BF_4] are higher than for [bmim][BF_4] and are practically the same as for the electrolyte consisting of the simple ions. The derived values of thermodynamic functions suggest that the spontaneity of the triple ions formation is mainly entropy driven process.

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