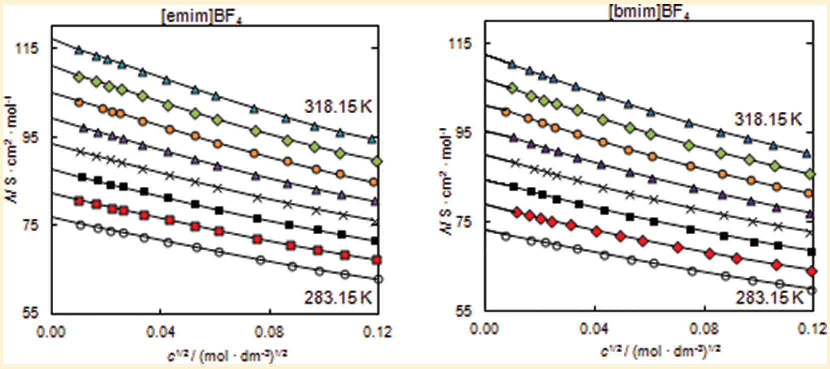
JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

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

Agnieszka Boruń and Adam Bald*

Department of Physical Chemistry of Solutions, University of Łódź, 90-236 Łódź, Pomorska 163, Poland



ABSTRACT: 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 *N*,*N*-dimethylformamide have been measured over the temperature range from (283.15 to 318.15) K. The ionic association constant, K_A, limiting molar conductivities, Λ_o, and distance parameters, *R*, were obtained using the Fuoss–Justice equation for the investigated systems. Slight ion association effect was found for the ionic liquids in DMF at all experimental temperatures. 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 free energy, entropy, and enthalpy for the process of ion pair formation were calculated from the temperature dependence of the ion association constants.

■ INTRODUCTION

In our previous works, we investigated the conductivity properties of several electrolytes in *N*,*N*-dimethylformamide.[1−5] Now, we decided to extend these studies to a new class of electrolytes such as ionic liquids.

Ionic liquids (ILs) are a promising class of new materials with a bright technological future. Current interest in ILs stems primarily from the utility of ionic liquids as solvents or catalysts for a variety of reactions.[6−9] Ionic liquids offer a great opportunity to be used in reactions involving inorganic and bio catalysis and separations including distillations, extraction, liquid–liquid partitioning, gas separations, liquid crystals, etc. They are used as heat transfer fluids, for processing biomass and as electrically conductive liquids in electrochemistry (batteries and solar cells).[10−12] ILs are liquid at ambient temperatures, have high electrolytic conductivity and very low vapor pressure at room temperature,[13] they show selective solubility of water and organics and have stable liquid range of over 300 K. Therefore, they can replace many volatile organic solvents in chemical processes.

The physical and chemical properties of ionic liquids are determined by the choice of the cations and anions selected, for example, the anion shows a primary effect on water miscibility.[14,15] ILs are miscible with liquids of medium to high dielectric constant and immiscible with liquids with low-dielectric constant.[14] Most commonly used ILs are those with 1,3-dialkylimidazolium, *N*-alkylpyridinium, or tetraalkylammonium cations and anions including halide ions, tetrafluoroborate, tetrachloroaluminate, hexafluorophosphate, or trifluoromethylsulfonate.

A survey of literature indicates that physical properties of pure ionic liquids have been studied extensively, but the thermophysical and thermodynamic properties of ILs, and in particular, their aqueous or organic mixtures have not been studied in a systematic way so far. Some studies report the specific conductivity data for pure ionic liquids[16−18] or binary or ternary mixtures of IL with various solvents.[15,16,19−28] Often, however, the temperature ranges and concentration regions measured have been rather limited, but only a few conductivity studies concerned the ionic association in IL solutions.[29−37]

Received: October 4, 2011
Accepted: January 9, 2012
Published: January 27, 2012

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.

In this article, we present precise conductometric studies of dilute solutions of [emim]BF_4 and [bmim]BF_4 in *N,N*-dimethylformamide at T = (283.15 to 318.15) K. From the experimental data, the values of the limiting molar conductivities, Λ_o, and the association constants, K_A, have been obtained for the investigated mixtures. The Gibbs free 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, $\Delta H^{\ddagger}_{\lambda}$, have been evaluated.

EXPERIMENTAL SECTION

Data on the reagents used are summarized in Table 1.

Table 1. Specification of Chemical Samples

chemical name	source	initial mass fraction purity	purification method	final water mass fraction
DMF[a]	Aldrich	0.998	none	0.00005[d]
[emim][BF_4][b]	Fluka	0.990	none	< 0.0002[d]
				< 0.00015[e]
[bmim][BF_4][c]	Fluka	0.985	none	< 0.0005[d]
				< 0.0004[e]

[a] DMF = *N,N*-dimethylmethanamide (*N,N*-dimethylformamide). [b] [emim][BF_4] = 1-ethyl-3-methylimidazolium tetrafluoroborate. [c] [bmim][BF_4] = 1-butyl-3-methylimidazolium tetrafluoroborate. [d] Manufacturer's analysis. [e] Our analysis (Karl Fischer coulometric titration).

All the solutions were prepared by mass using an analytical balance (Sartorius RC 210D) with a precision of ± $1\cdot10^{-5}$ g.

The measurement procedure was based on the method described by Bešter-Rogač et al.[37,38] Conductivity measurements were performed with a three-electrode cell with the use of a Precise Component Analyzer type 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 Ultra UB 20F with Through-flow cooler DLK 25, Lauda, Germany). The cell was calibrated with aqueous KCl solutions.[39] All measured conductance values, $\lambda = 1/R_\infty$, were the results of an extrapolation of the cell resistance, $R(\nu)$, to infinite frequency, $R_\infty = \lim_{\nu\to\infty} R(\nu)$ using the empirical function $R(\nu) = R_\infty + A/\nu$, where parameter A is specific to the cell. All data were corrected with the specific conductance of the solvent.

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.

Viscosities were measured with a AVS 350 viscosimeter (Schott Geräte, Germany). The viscosimeter filled with the liquid was placed vertically in a glass-sided water thermostat. 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 Julabo F32 (Julabo Labortechnik GmbH, Germany). The accuracy of temperature control was 0.01 K.

RESULTS AND DISCUSSION

The densities, viscosities, and relative permittivities of DMF as a function of temperature are listed in Table 2. The values of relative permittivities were taken from the literature.[40]

Table 2. Densities, ρ_o, Viscosities, η, and Relative Permittivities, ε_r, of *N,N*-Dimethylformamide as a Function of Temperature, T, at Pressure p = 0.1 MPa[a]

T/K	ρ_o/g·cm^{-3}	η/mPa·s	ε_r^{35}
283.15	0.958096	1.0158	39.61
288.15	0.953346	0.9545	38.68
293.15	0.948584	0.8985	37.75
298.15	0.943817	0.8455	36.81
303.15	0.939042	0.7990	35.88
308.15	0.934255	0.7553	34.95
313.15	0.929458	0.7172	34.01
318.15	0.924650	0.6826	33.07

[a] Standard uncertainties u are $u(T)$ = 0.01 K, $u(p)$ = 0.05p, and the combined expanded uncertainties U_c are $U_c(\rho_o) = 2\cdot10^{-5}$ g·cm^{-3}, and $U_c(\eta)$ = 0.0030 mPa·s (level of confidence = 0.95).

To convert molonity, $\tilde{m}$ (moles of electrolyte per kilogram of solution), into molarity, c, the values of density gradients, b, were determined from the equation

$$c/\tilde{m} = \rho = \rho_o + b\tilde{m} \tag{1}$$

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 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 3.

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

The conductivity data were analyzed by means of the Fuoss–Justice equation[41,42] in the form

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

together with

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

and

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

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.[43−45] The values of Λ_o, K_A, and R were obtained using the well-known procedure given by Fuoss[42] and are collected in Table 4.

As seen from Table 4, the association constants are practically negligible and one can assume that these electrolytes exist essentially as free ions in the DMF. Only a small part of these electrolytes exist in the undissociated form, and this tendency is slightly higher in the case of [emim][BF_4]. With increasing temperature, the association constants increase

Table 3. Molar Conductances, Λ, Corresponding Molalities, *m*, and Density Gradients, *b*, for Solutions of [emim][BF_4] and [bmim][BF_4] in DMF over the Temperature Range from (283.15 to 318.15) K at Pressure *p* = 0.1 MPa[a]

$m\cdot10^4$	Λ	$m\cdot10^4$	Λ	$m\cdot10^4$	Λ	$m\cdot10^4$	Λ
$\text{mol}\cdot\text{kg}^{-1}$	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$
[emim][BF_4]							
T = 283.15 K		T = 288.15 K		T = 293.15 K		T = 298.15 K	
b = 0.0646 $\text{kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$		b = 0.0649 $\text{kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$		b = 0.0653 $\text{kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$		b = 0.0656 $\text{kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$	
1.0214	75.24	0.91589	80.75	1.2250	86.04	1.1325	91.67
2.8942	74.40	2.6952	79.83	2.9309	85.16	2.7045	90.77
4.6170	73.87	5.0978	79.01	4.9066	84.42	4.7297	89.93
7.0705	73.26	6.9319	78.51	7.2551	83.72	6.7192	89.26
11.577	72.38	11.678	77.46	11.772	82.63	11.511	87.98
18.765	71.28	19.153	76.19	18.922	81.30	19.323	86.39
29.085	70.01	28.865	74.89	29.108	79.81	29.096	84.86
39.104	68.99	39.337	73.74	39.320	78.60	38.824	83.61
60.465	67.24	59.141	71.99	59.790	76.68	59.571	81.52
80.432	65.96	79.753	70.57	79.788	75.20	79.120	79.96
100.22	64.92	99.370	69.44	99.546	73.98	99.610	78.59
120.09	64.03	120.50	68.40	119.28	72.92	119.98	77.42
149.05	62.86	148.72	67.15	148.02	71.55	148.54	75.98
T = 303.15 K		T = 308.15 K		T = 313.15 K		T = 318.15 K	
b = 0.0660 $\text{kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$		b = 0.0663 $\text{kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$		b = 0.0667 $\text{kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$		b = 0.0671 $\text{kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$	
1.4329	97.09	1.0256	103.10	0.95186	108.95	1.0021	114.75
2.9762	96.22	3.6413	101.55	2.7747	107.72	2.7221	113.57
5.0695	95.32	5.0158	100.95	4.7200	106.77	4.2937	112.75
7.1357	94.60	6.6635	100.33	6.8358	105.92	6.8527	111.65
11.723	93.30	11.468	98.84	11.589	104.38	11.730	110.00
18.936	91.72	19.471	96.97	19.479	102.42	18.992	108.08
29.128	89.99	28.944	95.25	29.094	100.57	29.468	105.93
39.259	88.61	38.829	93.79	39.343	98.97	39.087	104.33
58.789	86.49	58.395	91.49	59.555	96.47	59.411	101.63
79.563	84.71	79.908	89.48	79.640	94.49	79.355	99.52
99.241	83.30	99.796	87.92	99.048	92.89	99.988	97.70
120.18	82.00	119.20	86.61	119.24	91.47	120.00	96.23
148.89	80.50	148.58	84.94	152.04	89.68	149.36	94.58
[bmim][BF_4]							
T = 283.15 K		T = 288.15 K		T = 293.15 K		T = 298.15 K	
b = 0.0549 $\text{kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$		b = 0.0536 $\text{kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$		b = 0.0540 $\text{kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$		b = 0.0560 $\text{kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$	
0.55421	72.04	1.2892	77.13	1.1103	82.80	1.2462	88.22
2.9150	70.90	2.6276	76.44	2.9431	81.72	3.1993	87.00
4.8948	70.31	4.2705	75.81	4.4831	81.08	5.2696	86.12
6.9417	69.81	6.0693	75.26	6.9398	80.27	6.9097	85.55
11.534	68.93	10.218	74.27	12.175	78.99	11.746	84.24
19.379	67.77	16.973	73.06	19.957	77.59	19.262	82.73
29.273	66.62	25.458	71.88	29.351	76.28	29.295	81.21
38.877	65.70	34.542	70.86	39.369	75.15	39.557	79.96
59.031	64.15	51.791	69.29	59.164	73.36	59.535	78.02
80.045	62.88	70.431	67.94	79.333	71.90	80.437	76.40
99.644	61.89	87.721	66.89	100.95	70.59	99.994	75.12
120.04	61.00	118.59	65.33	120.08	69.60	120.48	73.97
148.52	59.90	149.18	64.08	149.48	68.33	148.99	72.65
T = 303.15 K		T = 308.15 K		T = 313.15 K		T = 318.15 K	
b = 0.0598 $\text{kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$		b = 0.0653 $\text{kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$		b = 0.0725 $\text{kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$		b = 0.0814 $\text{kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$	
1.0366	93.90	0.57631	99.91	0.90630	104.96	0.94008	110.33
2.8140	92.62	2.4474	98.26	2.9522	103.37	2.7908	108.87
4.9403	91.60	4.4950	97.16	4.8676	102.38	4.5255	107.94
7.4074	90.69	6.8215	96.21	7.0148	101.50	6.4681	107.09
11.925	89.40	11.834	94.67	11.773	99.97	11.440	105.40
18.862	87.90	19.332	92.95	19.509	98.11	18.965	103.47
29.126	86.21	29.112	91.24	29.460	96.26	29.001	101.47
39.124	84.89	39.190	89.81	39.057	94.82	38.919	99.88
61.074	82.61	59.269	87.56	59.119	92.42	59.171	97.30

Table 3. continued

$m\cdot10^4$	Λ	$m\cdot10^4$	Λ	$m\cdot10^4$	Λ	$m\cdot10^4$	Λ
$\text{mol}\cdot\text{kg}^{-1}$	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$
			[bmim][BF_4]				
79.744	81.07	80.077	85.73	79.247	90.53	79.797	95.27
99.932	79.66	99.970	84.26	99.596	88.95	99.455	93.68
119.46	78.49	120.12	82.98	119.91	87.59	119.46	92.27
149.22	76.99	149.00	81.40	151.06	85.74	148.80	90.38

[a] Standard uncertainties u are $u(T) = 0.01$ K, $u(p) = 0.05p$, $u(m) = 10^{-5}m$, and the combined expanded uncertainty U_c is $U_c(\Lambda) = 0.02 - 0.1$ $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ (level of confidence = 0.95).

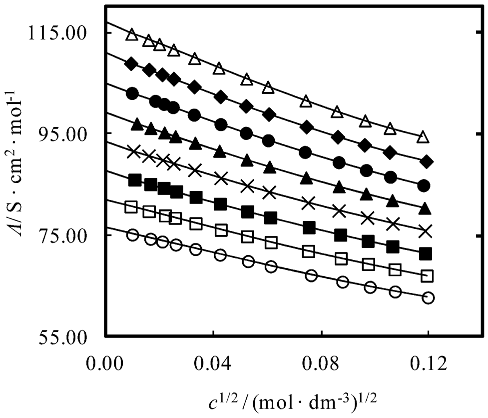


Figure 1. Molar conductance, Λ, of [emim]BF_4 solutions in DMF versus $c^{1/2}$ at experimental temperature: ○, 283.15 K; □, 288.15 K; ■, 293.15 K; ×, 298.15 K; ▲, 303.15 K; ●, 308.15 K; ◆, 313.15 K; △, 318.15 K. Lines were generated using the Fuoss–Justice equation.

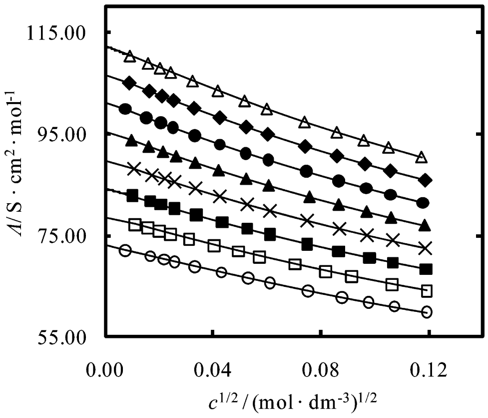


Figure 2. Molar conductance, Λ, of [bmim]BF_4 solutions in DMF versus $c^{1/2}$ at experimental temperatures: ○, 283.15 K; □, 288.15 K; ■, 293.15 K; ×, 298.15 K; ▲, 303.15 K; ●, 308.15 K; ◆, 313.15 K; △, 318.15 K. Lines were generated using the Fuoss–Justice equation.

slightly. Similarly, 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 at about 4.6–4.8 units from those values for [bmim][BF_4]. This indicates that the Λ_o values decrease with increasing alkyl chain length of the ILs. This phenomenon was also observed for [$C_n$mim]Br (n = 4, 6, 8, 10, 12) in various molecular solvents[29] for [$C_n$mim]Br (n = 4–6) in water,[33] and for [$C_n$mim]BF_4 (n = 2–4) in propylene carbonate.[34] To our knowledge, the values of K_A and Λ_o for studied ILs in DMF are not available in the literature; therefore, a direct comparison our values with literature ones is not possible.

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 DMF at Different Temperatures[a]

T/K	$\Lambda_o/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$K_A/\text{dm}^3\cdot\text{mol}^{-1}$	R/nm	$\sigma(\Lambda)$
		[emim]BF_4		
283.15	76.71 ± 0.03	10.48 ± 0.16	0.86	0.09
288.15	82.21 ± 0.03	10.75 ± 0.10	0.82	0.06
293.15	87.79 ± 0.02	11.10 ± 0.07	0.80	0.04
298.15	93.47 ± 0.02	11.30 ± 0.06	0.78	0.04
303.15	99.26 ± 0.02	11.57 ± 0.06	0.76	0.04
308.15	105.14 ± 0.03	12.06 ± 0.09	0.76	0.07
313.15	111.04 ± 0.05	12.29 ± 0.13	0.76	0.10
318.15	117.13 ± 0.06	12.72 ± 0.18	0.78	0.14
		[bmim]BF_4		
283.15	73.12 ± 0.03	9.77 ± 0.12	0.86	0.07
288.15	78.69 ± 0.01	9.95 ± 0.04	0.76	0.02
293.15	84.26 ± 0.02	10.26 ± 0.07	0.72	0.04
298.15	89.83 ± 0.03	10.57 ± 0.10	0.71	0.07
303.15	95.45 ± 0.03	10.80 ± 0.10	0.64	0.07
308.15	101.09 ± 0.03	11.18 ± 0.10	0.65	0.07
313.15	106.71 ± 0.01	11.45 ± 0.04	0.71	0.03
318.15	112.35 ± 0.02	11.96 ± 0.05	0.77	0.04

[a] In all cases, ΔR = 0.05 nm.

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

$$\ln \Lambda_o + 2/3 \ln \rho_o = -\frac{\Delta H_\lambda^\ddagger}{RT} + B \tag{5}$$

where B is an empirical constant. From the slope of the linear function of ln Λ_o + 2/3 ln ρ_o versus the inverse of the temperature ($1/T$), which is shown in Figure 3, we obtained $\Delta H_\lambda^\ddagger$values. $\Delta H_\lambda^\ddagger$ values are 8541 $\text{J}\cdot\text{mol}^{-1}$ and 8669 $\text{J}\cdot\text{mol}^{-1}$ for [emim][BF_4] and [bmim][BF_4], respectively. For [bmim]-[BF_4], the value of $\Delta H_\lambda^\ddagger$ is thus higher by about 130 units. It is the result of the presence of a larger substituent in the [bmim]$^+$ cation compared to [emim]$^+$.

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

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

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

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

The values of parameters A_o, A_1, and A_2 of eq 7 and correlation coefficients, r^2, are summarized in Table 5.

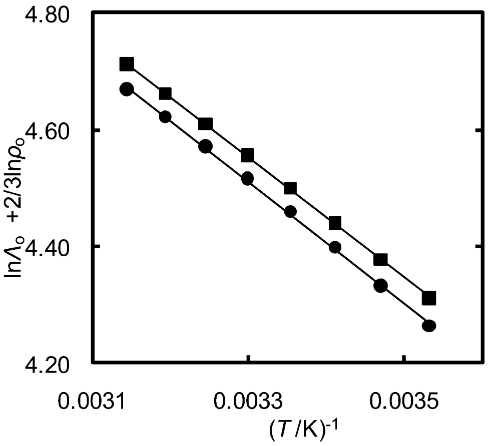


Figure 3. Plot of ln Λ_o + 2/3 ln ρ_o as a function of $1/T$ for ■, [emim]BF$_4$, and ●, [bmim]BF$_4$ in DMF.

Table 5. Coefficients of Eq 7 and Correlation Coefficients, r^2, for [emim][BF$_4$] and [bmim][BF$_4$] in DMF

	A_o/kJ·mol^{-1}	A_1/J·mol^{-1}·K^{-1}	A_2/J·mol^{-1}·K^{-2}	r^2
[emim][BF$_4$]	−4.103	20.71	−0.091	0.99924
[bmim][BF$_4$]	−7.940	47.47	−0.136	0.99945

Entropy and enthalpy of ion association are defined as

$$\Delta S_A^o = -\left(\frac{\partial \Delta G_A^o}{\partial T}\right)_p = -A_1 - 2A_2T \tag{8}$$

$$\Delta H_A^o = \Delta G_A^o + T\Delta S_A^o = A_o - A_2T^2 \tag{9}$$

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

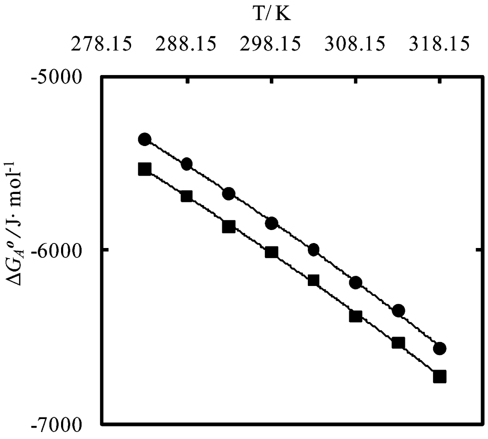


Figure 4. Variation of Gibbs free energy, ΔG_A^o, as a function of temperature T of ■, [emim]BF$_4$, and ●, [bmim]BF$_4$ in DMF.

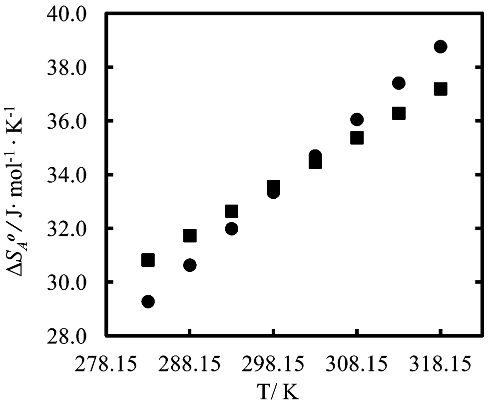


Figure 5. Variation of association entropies, ΔS_A^o, as a function of temperature of ■, [emim]BF$_4$, and ●, [bmim]BF$_4$ in DMF.

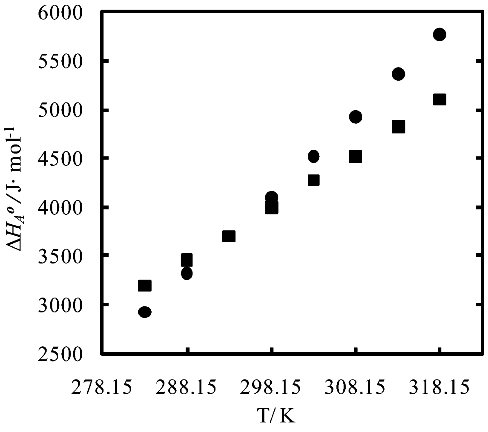


Figure 6. Variation of enthalpies,ΔH_A^o, as a function of temperature of ■, [emim]BF$_4$, and ●, [bmim]BF$_4$ in DMF.

Table 6. Thermodynamic Functions of Association of [emim]BF$_4$ and [bmim]BF$_4$ Solutions in DMF at Different Temperatures

T	ΔG_A^o	ΔS_A^o	ΔH_A^o
K	J·mol^{-1}	J·mol^{-1}·K^{-1}	J·mol^{-1}
	[emim]BF$_4$		
283.15	−5530	30.8	3200
288.15	−5690	31.7	3450
293.15	−5870	32.6	3700
298.15	−6010	33.6	3990
303.15	−6170	34.5	4280
308.15	−6380	35.4	4520
313.15	−6530	36.3	4830
318.15	−6730	37.2	5110
	[bmim]BF$_4$		
283.15	−5370	29.3	2920
288.15	−5500	30.6	3320
293.15	−5680	32.0	3700
298.15	−5850	33.3	4100
303.15	−6000	34.7	4520
308.15	−6190	36.1	4920
313.15	−6350	37.4	5370
318.15	−6560	38.8	5770

The values of ΔG_A^o presented in Table 6 and Figure 4 indicate that the spontaneity of the ion pair formation is higher in the case of salt containing the smaller cation, i.e., [emim][BF$_4$]. The increase of temperature leads to more negative ΔG_A^o values, which means shifting the equilibrium toward the formation of ion pairs. As can be seen in Figures 5 and 6, both the values of entropy and enthalpy of association increase with increasing temperature for both tested electrolytes. This increase is more pronounced in the case of salt containing the larger cation, i.e., [bmim][BF$_4$]. In both cases, the entropy values are positive, which means that as a result of association, the arrangement of the system decreases in comparison with the arrangement associated with the solvation of free ions. This process increases with increasing temperature (slightly stronger in the case of [bmim][BF_4]). The positive values of ΔH_A indicate that the ion-pairing process is endothermic. At a temperature of 283.15 K, this process is more endothermic for [emim][BF_4], while at 318.15 K, it is more endothermic for [bmim][BF_4]. From eq 10,

$$\Delta G_A^o(T) = \Delta H_A^o(T) - TS_A^o(T) \tag{10}$$

gives results that show that the entropic effects seem to dominate over the enthalpic effects because the Gibbs free energy (ΔG_A^o) is negative, and thus the ion pair formation is exoergic in both cases.

CONCLUSIONS

Molar conductivities of solutions of ionic liquids, [emim]BF_4 and [bmim]BF_4 in DMF, have been reported at T = (283.15 to 318.15) K. The conductivity data have been analyzed using the Fuoss–Justice equation. Slight ionic association was observed for the ILs in DMF at all experimental temperatures. The K_A values increase as the temperature increases (with decreasing relative permittivity of the solvent) and decrease with an increase in the alkyl chain length of the ILs. The thermodynamic functions of association such as Gibbs free energy, enthalpy, and entropy for the ion pair formation process, as well as the Eyring activation enthalpy of charge transport, have been evaluated. The values of ΔH_A 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 DMF is exoergic.

AUTHOR INFORMATION

Corresponding Author

*Tel: +48 426355846. E-mail: laurent@uni.lodz.pl.

REFERENCES

(1) Szejgis, A.; Bald, A.; Gregorowicz, J. Conductivity studies on some alkali metal iodides in aqueous *N,N*-dimethylformamide solutions at 298.15 K. *Monatsh. Chem.* **1997**, *128*, 1093–1100.

(2) Szejgis, A.; Bald, A.; Gregorowicz, J. Conductivity properties of some tetraalkylammonium iodides in the water + *N,N*-dimethylformamide mixtures at 298.15 K. *Phys. Chem. Liq.* **1997**, *35*, 165–173.

(3) Szejgis, A.; Bald, A.; Gregorowicz, J.; Kinart, C. M. Conductivity studies on LiBr, NaBr, KBr and CsBr solutions in binary mixtures of *N,N*-dimethylformamide with water at 298.15 K. *Phys. Chem. Liq.* **1997**, *34*, 189–199.

(4) Szejgis, A.; Bald, A.; Gregorowicz, J. Conductance studies of *i*-Am_3BuNI and $NaBPh_4$ and the limiting ionic conductance in Water + DMF mixtures at 298.15 K. *J. Mol. Liq.* **1998**, *75*, 237–252.

(5) Szejgis, A.; Bald, A.; Gregorowicz, J.; Zurada, M. Conductance studies in mixtures of water with DMF at 298.15 K. Part VI. Lithium and sodium nitrates, sodium perchlorate and propionate, potassium picrate and thiocyanate, and limiting ionic conductance. *J. Mol. Liq.* **1999**, *79*, 123–136.

(6) Welton, T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev.* **1999**, *99*, 2071–2083.

(7) Welton, T. Ionic liquids in catalysis. *Coord. Chem. Rev.* **2004**, *148*, 2459–2477.

(8) Wasserscheid, P.; Keim, W. Ionic liquids: new "solutions" for transition metal catalysis. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772–3789.

(9) Wilkes, J. S. Properties of ionic liquid solvents for catalysis. *J. Mol. Catal. A: Chem.* **2004**, *214*, 11–17.

(10) Plechkova, N. V.; Seddon, K. R. Applications of ionic liquids in the chemical industry. *Chem. Soc. Rev.* **2008**, *37*, 123–150.

(11) Endres, F.; Zein El Abedin, S. Air and water stable ionic liquids in physical chemistry. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2101–2116.

(12) Wang, P.; Zakeeruddin, S. M.; Moser, J.-E.; Grätzel, M. A new ionic liquid electrolyte enhances the conversion efficiency of dye-sensitized solar cells. *J. Phys. Chem. B* **2003**, *107*, 13280–13285.

(13) Esperança, J. M. S. S.; Lopes, J. N. C.; Tariq, M.; Santos, L. M. N. B. F.; Magee, J. W.; Rebelo, L. P. N. Volatility of aprotic ionic liquids: A review. *J. Chem. Eng. Data* **2010**, *55*, 3–12.

(14) Seddon, K. R.; Stark, A.; Torres, M.-J. Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure Appl. Chem.* **2000**, *72*, 2275–2287.

(15) Sirieix-Plénet, J.; Gaillon, L.; Letellier, P. Behaviour of a binary solvent mixture constituted by an amphiphilic ionic liquid, 1-decyl-3-methylimidazolium bromide and water. Potentiometric and conductometric studies. *Talanta* **2004**, *63*, 979–986.

(16) Widegren, J. A.; Saurer, E. M.; Marsh, K. N.; Magee, J. W. Electrolytic conductivity of four imidazolium-based room-temperature ionic liquids and the effect of a water impurity. *J. Chem. Thermodyn.* **2005**, *37*, 569–575.

(17) Stoppa, A.; Zech, O.; Kunz, W.; Buchner, R. The conductivity of imidazolium-based ionic liquids from (−35 to 195)°C. A. Variation of cation's alkyl chain. *J. Chem. Eng. Data* **2010**, *55*, 1768–1773.

(18) Zech, O.; Stoppa, A.; Buchner, R.; Kunz, W. The conductivity of imidazolium-based ionic liquids from (248 to 468) K. B. Variation of the anion. *J. Chem. Eng. Data* **2010**, *55*, 1774–1778.

(19) Liu, W.; Zhao, T.; Zhang, Y.; Wang, H.; Yu, M. The physical properties of aqueous solutions of the ionic liquid [bmim][BF_4]. *J. Solution Chem.* **2006**, *35*, 1337–1346.

(20) Vila, J.; Ginés, P.; Rilo, E.; Cabeza, O.; Varela, L. M. Great increase of the electrical conductivity of ionic liquids in aqueous solutions. *Fluid Phase Equilib.* **2006**, *247*, 32–39.

(21) Zhu, A.; Wang, J.; Han, L.; Fan, M. Measurements and correlation of viscosities and conductivities for the mixtures of imidazolium ionic liquids with molecular solutes. *Chem. Eng. J* **2009**, *147*, 27–35.

(22) Comminges, C.; Barhdadi, R.; Laurent, M.; Troupel, M. Determination of viscosity, ionic conductivity, and diffusion coefficients in some binary systems: ionic liquids + molecular solvents. *J. Chem. Eng. Data* **2006**, *51*, 680–685.

(23) Zhang, J.; Wu, W.; Jiang, T.; Gao, H.; Liu, Z.; He, J.; Han, B. Conductivities and viscosities of the ionic liquid [bmim][PF6] + water + ethanol and [bmim][PF6] + water + acetone ternary mixtures. *J. Chem. Eng. Data* **2003**, *48*, 1315–1317.

(24) Xu, H.; Zhao, D.; Xu, P.; Liu, F.; Gao, G. Conductivity and viscosity of 1-allyl-3-methyl-imidazolium chloride + water and + ethanol from 293.15 to 333.15 K. *J. Chem. Eng. Data* **2005**, *50*, 133–135.

(25) Jarosik, A.; Krajewski, S. R.; Lewandowski, A.; Radzimski, P. Conductivity of ionic liquids in mixtures. *J. Mol. Liq.* **2006**, *123*, 43–50.

(26) Wong, C.-L.; Soriano, A. N.; Li, M.-H. Infinite dilution diffusion coefficients of [bmim]-based ionic liquids in water and its molar conductivities. *J. Taiwan Inst. Chem. Eng.* **2009**, *40*, 77–83.

(27) Soriano, A. N.; Agapito, A. M.; Lee, L. J.; Lagumbay, I.; Caparanga, A. R.; Li, M.-H. Diffusion coefficients of aqueous ionic liquid solutions at infinite dilution determined from electrolytic conductivity measurements. *J. Taiwan Inst. Chem. Eng.* **2011**, *42*, 258–264.

(28) Stoppa, A.; Hunger, J.; Buchner, R. Conductivities of binary mixtures of ionic liquids with polar solvents. *J. Chem. Eng. Data* **2009**, *54*, 472–479.

(29) Wang, H.; Wang, J.; Zhang, S.; Pei, Y.; Zhuo, K. Ionic association of the ionic liquids [C_4mim][PF6], and [$C_n$mim]Br in molecular solvents. *ChemPhysChem* **2009**, *10*, 2516–2523.

(30) Katsuta, S.; Imai, K.; Kudo, Y.; Takeda, Y.; Seki, H.; Nakakoshi, M. Ion pair formation of alkylimidazolium ionic liquids in dichloromethane. *J. Chem. Eng. Data* **2008**, *53*, 1528–1532.

(31) Katsuta, S.; Ogawa, R.; Yamaguchi, N.; Ishitani, T.; Takeda, Y. Ion Pair formation of 1-alkyl-3-methylimidazolium salts in water. *J. Chem. Eng. Data* **2007**, *52*, 248−251.

(32) Katsuta, S.; Shiozawa, Y.; Imai, K.; Kudo, Y.; Takeda, Y. Stability of ion pairs of bis(trifluoromethanesulfonyl)amide-based ionic liquids in dichloromethane. *J. Chem. Eng. Data* **2010**, *55*, 1588−1593.

(33) Shekaari, H.; Mousavi, S. S. Conductometric studies of aqueous ionic liquids, 1-alkyl-3-methylimidazolim halide, solutions at T = 298.15−328.15 K. *Fluid Phase Equilib.* **2009**, *286*, 120−126.

(34) Nishida, T.; Tashiro, Y.; Yamamoto, M. Physical and electrochemical properties of 1-alkyl-3-methylimidazolium tetrafluoroborate for electrolyte. *J. Fluorine Chem.* **2003**, *120*, 135−141.

(35) Shekaari, H.; Armanfar, E. Physical properties of aqueous solutions of ionic liquid, 1-propyl-3-methylimidazolium methyl sulfate, at T = (298.15 to 328.15) K. *J. Chem. Eng. Data* **2010**, *55*, 765−772.

(36) Bešter-Rogač, M.; Hunger, J.; Stoppa, A.; Buchner, R. Molar conductivities and association constants of 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium tetrafluoroborate in methanol and DMSO. *J. Chem. Eng. Data* **2010**, *55*, 1799−1803.

(37) Bešter-Rogač, M.; Hunger, J.; Stoppa, A.; Buchner, R. 1-Ethyl-3-methylimidazolium ethylsulfate in water, acetonitrile, and dichloromethane: Molar conductivities and association constants. *J. Chem. Eng. Data* **2011**, *56*, 1261−1267.

(38) Bešter-Rogač, M.; Habe, D. Modern advances in electrical conductivity measurements of solutions. *Acta Chim. Slov.* **2006**, *53*, 391−395.

(39) Barthel, J.; Feuerlein, F.; Neueder, R.; Wachter, R. Calibration of conductance cells at various temperatures. *J. Solution Chem.* **1980**, *9*, 209−219.

(40) Krestov, G. A., Afanas'ev, V. N., Efremova, L. S., *Fiziko-khimicheskie svoistva binarnykh rastvoritelei (Physicochemical Properties of Binary Solvents)*; Khimiya: Leningrad, Russia, 1988.

(41) Fuoss, R. M. Paired ions: Dipolar pairs as subset of diffusion pairs. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 16−20.

(42) Fuoss, R. M. Conductance-concentration function for the paired ion model. *J. Phys. Chem.* **1978**, *82*, 2427−2440.

(43) Justice, J.-C. An interpretation for the distance parameter of the Fuoss-Onsager conductance equation in the case of ionic association. *Electrochim. Acta* **1971**, *16*, 701−712.

(44) Renard, E.; Justice, J.-C. A comparison of the conductimetric behavior of cesium chloride in water−tetrahydrofuran, water−dioxane, and water−1,2-dimethoxyethane mixtures. *J. Solution Chem.* **1974**, *3*, 633−647.

(45) Fuoss, R. M.; Accascina, L. *Electrolytic Conductance*; Interscience: New York, 1959.