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Conductometric study of ionic liquids in the presence of N,N'-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) Schiff base in acetonitrile solutions at 298.15 K

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Abstract

In recent years, Schiff bases and their metal complexes in the presence of ionic liquids (ILs) have been used in synthesis of various chemical compounds. To better understanding of ionic liquid influence on these processes, it is required to obtain information about the ion association behavior of the ionic liquids. Therefore, in this work, the molar conductivities of the ILs [RMIm]X (R= propyl, pentyl, and hexyl; X= Br⁻ and Cl⁻) in different concentrations of N,N'-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) Schiff base + acetonitrile solutions were determined at 298.15 K. The obtained conductivity data were analyzed by low concentration Chemical Model (lcCM) conductivity equation to calculate the limiting molar conductivities (Λ_0) and ion association constants (K_A). The results show that BPIE, alkyl chain length of cation, and anion type have effect on the ionic association process of the ILs. The Λ_0 and K_A values

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decrease as the Schiff base concentration, alkyl chain length of cation, and anion size increase in the solution. The association constants were also used to calculate the standard Gibbs energy (ΔG_A^0) of ion-pairing association. The resulted ΔG_A^0 values are negative and become more negative as the alkyl chain length of the cation and the size of anion increase. The large negative values of the standard Gibbs energy obtained for [HMIm]Br indicates the more spontaneity and the more feasibility of the association process for this ionic liquid.

Keywords: Ionic liquids; BPIE Schiff base; Molar conductivity; Low concentration Chemical Model (lcCM).

1. Introduction

The oxidation of alcohols to the corresponding aldehydes, ketones, and carboxylic acids is one of the most important reactions in organic chemistry, especially in industrial synthetic chemistry [1]. From the past, this transformation is performed with toxic, expensive inorganic oxidizing agents in organic solvents. The selective oxidation of alkenes is another important process to reach fine chemicals [2]. Enantiomerically pure epoxides obtained from the oxidation of alkenes have shown a good potential as key molecules, useful intermediates, and building blocks in the synthesis of optically active compounds. The industrial importance of these processes and environmental concerns made chemists develop effective, greener catalytic systems that use inexpensive oxidants. Schiff bases and their transition metal complexes are attractive oxidation catalysts because of their cheap, ease of preparation, and chemical and thermal stability [3-7]. They are considered as an appropriate catalyst to oxidize alcohols and alkenes to the relative products [8-10]. However, the practical use of selective catalytic system faces the

fundamental problem of the separation of products from the reaction mixture, and the recovery of catalysts often becomes difficulty. The fascinating possibilities of two-phase catalysis motivated large research efforts devoted to the use of ionic liquids as solvents for the transition-metal catalysts. These systems are able to separate the reaction products from the catalytic solution by simple decantation of the insoluble liquid phases. It has also been reported that ionic liquids enhances the activity of catalyst in the mixture. The IL/Schiff base systems, therefore, provide a means to develop reusable catalysts with high activity. Moreover, the addition of co-solvents has been found to strongly affect various physico-chemical properties of ionic liquids. The mixed organic solvents and ionic liquids can be used advantageously to achieve homogeneous systems in which the reactants and catalysts have the best solubility. The efficiency of these systems is strongly dependent on the various molecular interactions between ionic liquid and mixed solvent. Thermodynamic properties of ionic liquids in Schiff base solutions are very useful tools to discuss different interactions of the system. One natural difference between ionic liquids and conventional molecular solvents is that ionic liquids exhibit high electrolytic conductivity and wide electro-chemical window, which is a measure for their electrochemical stability against oxidation and reduction processes. When selecting an ionic liquid for electrochemical usages, electrical conductivity is of great importance. Since ILs are entirely composed of ions, the formation of ion pairs is expected to be one essential feature for describing both solvation in ILs and solvation of ILs in other media. The phenomenon of ion-pair formation is by itself of fundamental importance to the chemical field, as it influences reaction rates or may be exploited in numerous chemical applications. Conductometry is an electrochemical technique, which provides most

precise data and valuable information regarding ion association and ion solvation behavior and character of the ion pair in electrolyte solutions. Most of the papers presenting conductometric studies of the ILs analyze the conductance data using different conductivity equations in terms of the ionic association constant and the limiting molar conductivity. It is shown that the alkyl chain length of the cations and type of anion affect the ionic association constants and limiting molar conductivities of the ILs. A large portion of the conductivity data reported in literatures are related to pure ionic liquids or their binary mixtures in water or in molecular solvent for both dilute region and the whole composition range of ionic liquids solutions [11-20]. However, the number of works performed for ternary solutions of ionic liquids is very limited. Hence, in this communication, the conductivities of a number of imidazolium based ionic liquids [PMIm]Br, [PnMIm]Br, [HMIm]Br, and [HMIm]Cl in BPIE + MeCN solutions were measured at 298.15 K. The obtained data were analyzed using low concentration Chemical Model (lcCM) conductivity equation, and the values of limiting molar conductivity (Λ_0) and ion association constant (K_A) were calculated. The K_A values were used to estimate the standard Gibbs energy (ΔG_A^0) of ion association process. All the parameters were discussed based on the ion-solvent interactions that occur in the system. It was also attempted to study the effects of the alkyl chain length of the cations and the type of anion on the solvation behavior of the ILs.

2. Experimental

2.1. Chemicals

The chemicals used to synthesize the ionic liquids were *N*-methylimidazole (>99%), 1-bromopropane (>99%), 1-bromopentan (>99%), 1-bromohexane (>99%), 1-

chlorohexane (>99%), and ethyl acetate (GR, >99.8%) that were bought from Merck company. Pyridine-2-aldehyde (>99.8%), ethylenediamine (>99.9%), and acetonitrile (>99.9%) were also purchased from Merck. All the materials were used without any further purification.

2.2. Synthesis of the ionic liquids

1-Alkyl-3-methylimidazolium halide (C_n MImBr, n = 3, 5, 6 and C_6 MImCl) was synthesized according to the procedure described in literatures [21-23] by direct alkylation of *N*-methylimidazole with an excess amount of 1-haloalkane in a round bottom flask mixed by a magnetic stirrer under a nitrogen atmosphere. The mixing of the chemicals was done at first under ice-cooling, but after the temperature was risen to room temperature. The temperature was then gradually increased over a period of several hours to a final reaction temperature of about 50 $^{\circ}$ C and kept constant until the end of the reaction. The reaction mixture was stirred for one week. Finally, the crude product was separated from reagents and then washed three times with fresh ethylacetate. The removal of residual volatile compounds from the ionic liquid was done in high vacuum at 60 $^{\circ}$ C using a rotary evaporator for at least 4 hours at reduced pressure. The obtained ionic liquid has purity about 98% verified by ¹H NMR spectroscopy. The ionic liquid was used after vacuum desiccated for at least 48 hours to remove trace amount of moisture. Water content found by Karl Fischer method in the ionic liquid was less than 0.2%.

2.3. Synthesis of the Schiff base

N,N'-Bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) was synthesized according to literature method [24]. The pyridine-2-aldehyde (0.6 mol) was added slowly to the ethylenediamine (0.3 mol) in ethanol solution. After stirring the mixture gently for

1 hour and the removal of the ethanol by rotary evaporation, an orange-yellow residual liquid product was obtained. The product was extracted with hot hexane in several times. After cooling, a solid orange product was obtained and recrystallized from diethyl ether. Yield, 36%. ¹H NMR (CDCl₃ versus TMS): $\delta = 4.06$ (s, 4H, =NCH₂CH₂N=), 7.30 (m, 2H, -N=CH-py), 7.73 (m, 2H, py), 7.98 (m, 2H, py), 8.42 (m, 2H, py), 8.63 (m, 2H, py). Fig. 1 shows the structure of *N*,*N*'-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) Schiff base.

2.4. Apparatus and procedure

2.4.1. Density and viscosity measurements

The sample densities were measured with a vibrating tube densimeter (Anton Paar, DMA 4500M, Austria), which was calibrated with doubly distilled water at atmospheric pressure. Density is extremely sensitive to temperature, so it was kept constant within $\pm 1.0 \times 10^{-3}$ K using the Peltier technique built in densimeter. The uncertainty of density measurements for BPIE + DMF was better than $\pm 4.0 \times 10^{-5}$ g cm⁻³. The analytical balance was Sartrious (AG TE214S, Switzerland) with an uncertainty $\pm 1 \times 10^{-4}$ g.

The viscosities were measured using an Ubbelohde-type viscometer, which was calibrated with doubly distilled water. Viscosity of solution (η) is obtained by the following equation

$$\frac{\eta}{d} = Lt - \frac{K}{t} \tag{1}$$

where d is the density, t is the flow time of the solution, L, and K are the viscometer constants. A digital stopwatch with a resolution 0.01 s has been used for the measurement

of flow time. The estimated uncertainly of the experimental viscosity was ± 0.002 mPa s.

2.4.2. The measurement of specific conductivity

Specific conductivities were measured using a conductivity meter (Metrohm model 712, Switzerland) with accuracy $\pm 0.5\%$. The cell constant was calculated by repeated measurements of KCl solution in 0.01 mol kg⁻¹. About 50 ml of solvent was filled into the conductivity cell and the cell was closed. Weighting was performed by an analytical balance (Sartrious, AG TE214S) with precision $\pm 1\times10^{-4}$ g. After the measurement of the solvent conductivity, a weighed amount of pure ionic liquid was added with a syringe to the cell containing solvent and the measurement was repeated. To minimize the risk of the presence of concentration gradients in the cell, the solution was continuously stirred with a magnetic stirrer. The water from a thermostatically regulated bath was circled around the cell with double wall to maintain the temperature with an uncertainty ± 0.02 K.

3. Model detail

The values of molar conductivity (Λ) obtained for the ionic liquids in investigated solutions (BPIE + MeCN) have been calculated by the relation $\Lambda = 1000\kappa/c$, where κ is the specific conductivity of the ionic liquid solutions. The obtained values of molar conductivity are given in Table 1. The conductivity data were analyzed with low concentration Chemical Model (lcCM) conductivity equation using the following set of equations [25] which is the Fuoss-Onsager type equation.

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

$$K_A = \frac{1 - \alpha}{\alpha^2 c \gamma^2_{\pm}}$$

(3)

 $\kappa^2 = \frac{16000N_A z^2 e^2 \alpha c}{\varepsilon_0 \varepsilon k_B T}$

 $q = \frac{z^2 e^2}{8\pi\epsilon_0 \epsilon k_{\rm B} T}$

 $\ln \gamma_{\pm} = -\frac{\kappa q}{1+\kappa R}$

(4)

(5)

(6)

In above equations, Λ and Λ_0 are molar conductivities at molarity c and at infinite dilution, (1- α) is the fraction of oppositely charged ions acting as ion pairs, γ_{\pm} is the corresponding mean activity coefficient of the free ions, κ is the Debye parameter, e is the electronic charge, z is the ionic charge, ε_0 is the permittivity of vacuum, ε is the dielectric constant of the solvent, and the other symbols have their usual meanings. The coefficients E, J_1 , and J_2 required for calculations were taken from Ref. [25]. The parameter R represents the center-to-center distance between the ions in the ion pairs. Due to the lack of association constant for the studied solutions, the K_A was first estimated from the Arrhenius-Ostwald relation [26] and then the other parameters were determined using Eq. 2.

Three-parameter fits were used to obtain the limiting molar conductivity (Λ_0) , association constant (K_A) , and distance parameter (R) by non-linear least squares iterations. The calculation is made by finding the values Λ_0 , K_A , and R that minimized

the standard deviation $\sigma(\Lambda)$. The standard deviation of the measured molar conductivities (Λ_{exp}) and the calculated one (Λ_{cal}) was computed as follows

$$\sigma(\Lambda) = \left[\frac{\sum (\Lambda_{\exp} - \Lambda_{cal})^2}{n - p}\right]^{\frac{1}{2}}$$
(7)

where *n* and *p* show the number of experimental data and parameters, respectively. The values of K_A , Λ_0 , and *R* obtained by this procedure are given in Table 2.

4. Results and discussion

4.1. Limiting molar conductivities

It is shown that the molar conductivity (Λ) decreases with increasing the ionic liquids concentration due to ionic atmosphere effects, and in more concentrated solutions, ion paring is responsible for the observed reduction in molar conductivities. Moreover, the molar conductivity (Λ) values of ionic liquids decrease at higher concentrations of BPIE solution. Increasing Schiff base concentration causes stronger interaction between the alkyl chain of ionic liquid and the pyridinyl group of Schiff base, which leads to a reduction in the molar conductivity of ILs. The effect of Schiff base concentration on the Λ values of [PnMIm]Br is depicted by Fig. 2.

Table 2 shows that the limiting molar conductivities of the studied ionic liquids in pure acetonitrile are greater than those in BPIE + MeCN solutions. It is also clear that the Λ_0 values for each ionic liquid decrease with increasing the concentration of BPIE in the solutions (see Fig. 4). This reduction is due to the fact that the viscosity of medium increases as BPIE is added to the solution. Moreover, the solvated radii of the ions get larger due to the interactions with the Schiff base. Both of theses reasons make the ionic

mobility decrease, and consequently the molar conductivity of the ILs reduces. To eliminate the effect of viscosity on the ionic mobility, Walden products ($\Lambda_0 \eta$) were calculated and given in Table 2. Walden product is a useful tool to discuss ion-solvent interactions. The conductivity of an ion at infinite dilution depends only on its speed. Therefore, it is expected that the product of ion conductivity by the viscosity of the medium is independent of the solvent nature. A constant Walden product for solutions with different concentrations indicates that the radius of the ions remains unchanged. Table 2 shows that the $\Lambda_0 \eta$ values of all the ionic liquids change with the concentration of BPIE. This suggests that the ions do not have the same effective radius in different solvent compositions and provides evidence for the solvation of ions in the solutions.

It is also obvious from Figs. 3 and 4 that the ionic liquid with a longer alkyl chain has larger Λ_0 values in both pure solvent and solution. Accordingly, the limiting molar conductivities of the ionic liquids increase with the alkyl chain length of the cation in the order propyl < pentyl < hexyl. The reason of the observed trend could be related to the solute–solvent interactions between the ionic liquid and MeCN. Acetonitrile is a relatively polar solvent and its interaction with ionic liquids must decrease as the nonpolarity of ILs enhances. Therefore, [HMIm]Br with a long non-polar alkyl chain is less solvated by the solvent molecules and has greater ionic mobility. The comparison between the Λ_0 values of [HMIm]Br and [HMIm]Cl reveals the effect of anion size of ionic liquid on its conductivity. In the studied solutions, the Λ_0 values increase as the anion size gets larger (Cl⁻ < Br⁻). We observed this result in our previous paper [27], where we studied the conductivities of these two ionic liquids in aqueous saccharide solutions. A good reason for this observation is the reduction of the surface electrical

charge density resulted by a rise in the anion size that increases the mobility of the anion inside a medium with free ions.

4.2. Ion association constants

The values of ion association constant (K_A) of the ionic liquids in BPIE + MeCN solutions are given in Table 2. Clearly, the K_A values of each ionic liquid decrease at higher concentrations of BPIE solution. This is due to the strong ion–Schiff base interactions in the concentrated solutions that reduce the ion-pair formation. At a fixed molality of BPIE, the values of ion association constant increase with the alkyl chain length of the cations in the sequence propyl < pentyl < hexyl. As stated above, the cation with hexyl alkyl chain is less solvated by the solvent (MeCN) molecules and consequently forms more ion-pairs relative to the two other cations.

The association constants were used to calculate the standard Gibbs energy (ΔG_A^0) of ion-association process using the following equation

$$\Delta G_A^0 = -RT \ln K_A \tag{8}$$

The obtained values of the standard Gibbs energy are given in Table 2. The ΔG_A^0 values are negative and become more negative as the size of cation and anion increases. The large negative values of the standard Gibbs energy obtained for [HMIm]Br indicates the more spontaneity and the more feasibility of the association process for this ionic liquid.

5. Conclusions

The effect of cation and anion size on the conductivity of the ionic liquids 1propyl-3-methylimidazolium bromide ([PMIm]Br), 1-pentyl-3-methylimidazolium

bromide ([PnMIm]Br), 1-hexyl-3-methylimidazolium bromide ([HMIm]Br), and 1-hexyl-3-methylimidazolium chloride ([HMIm]Cl) in *N,N'*-bis(2-pyridylmethylidene)-1,2diiminoethane (BPIE) Schiff base + acetonitrile solutions was studied at 298.15 K. For this purpose, limiting molar conductivities (Λ_0) and ion association constants (K_A) were calculated using low concentration Chemical Model (lcCM) conductivity equation. The results show that the Λ_0 values decrease as BPIE concentration increases in the solution. Moreover, the limiting molar conductivities increase with the alkyl chain length of the cation in the order propyl < pentyl < hexyl and also increase with the anion size in the order Cl⁻ < Br⁻. The K_A values reduce with the increase of BPIE concentration but increase as the size of cation and anion gets larger. The association constants were used to calculate the standard Gibbs energy (ΔG_A^0) of ion-pairing association. The obtained ΔG_A^0 values are negative and become more negative as the alkyl chain length of the cation and the size of anion increase. The large negative values of the standard Gibbs energy obtained for [HMIm]Br indicates the more spontaneity and the more feasibility of the association process for this ionic liquid.

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Figure captions

Fig. 1. The structure of N,N'-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) Schiff base.

Fig. 2 Molar conductivities (Λ) of [PnMIm]Br in MeCN and in MeCN + BPIE solutions with several molalities of BPIE at 298.15 K. Symbols: \blacklozenge , 0.0000; \blacktriangle , 0.0452; \Box , 0.0991; and Δ , 0.1210 mol kg⁻¹.

Fig. 3. Comparison of molar conductivities (Λ) of [RMIm]Br in BPIE +MeCN solution with 0.04 mol kg⁻¹ molality of BPIE at 298.15 K. Symbols: •, [PMIm]Br; \blacktriangle , [PnMIm]Br; and \Box , [HMIm]Br.

Fig. 4. Limiting molar conductivities (Λ_0) of the ionic liquids against the molality of BPIE Schiff base at 298.15 K. Symbols: \blacktriangle , [PMIm]Br; \blacksquare , [PnMIm]Br; \circ , [HMIm]Br; and \times , [HMIm]Cl.

Table 1

The molar conductivities (Λ) of the ionic liquids [PMIm]Br, [PnMIm]Br, [HMIm]Br, and [HMIm]Cl in BPIE + MeCN solutions as a function of IL concentration (c) at 298.15 K.

0	4	C	Λ	C	1	C	4	
$C_{m_{2}1,,-3}$		C		C		C_{ma1}		
mol m ²	$S \text{ cm}^2 \text{ mol}^{-1}$	mol m ²	$S cm^2 mol^{-1}$	mol m ³	$S \text{ cm}^2 \text{ mol}^{-1}$	mol m *	$S \text{ cm}^2 \text{ mol}^{-1}$	
	1		[PMIm]Br +E	BPIE + MeCN	1		1	
$m_{\rm BPIE} = 0.00$	100 mol kg^{-1}	$m_{\rm BPIE} = 0.03$	$m_{\rm BPIE} = 0.0346 \text{ mol kg}^{-1}$ $m_{\rm BPIE} = 0.0655 \text{ mol kg}^{-1}$		55 mol kg ⁻¹	$m_{\rm BPIE} = 0.0959 \text{ mol kg}^{-1}$		
0.4699	144.10	0.9785	115.98	1.2034	101.47	1.2519	99.69	
1.4373	141.03	2.2515	111.69	2.6583	95.82	2.9710	95.96	
2.2205	139.16	3.3440	107.35	4.0773	90.97	4.4168	91.60	
3.1419	136.48	4.5031	105.30	5.3975	88.02	5.8098	89.00	
4.0448	133.93	5.6241	103.64	6.9063	84.03	7.1851	86.28	
4.8004	132.53	6.9351	101.37	8.5408	81.00	8.7719	83.63	
5.6480	130.08	8.0276	99.75	9.9508	78.62	10.2618	79.41	
6.5141	128.48	9.0821	98.06	11.5674	75.72	11.9104	75.94	
7.3250	126.21	10.2982	95.81	13.1121	71.76	13.6560	74.19	
8.1818	125.34	11.4097	94.02	14.4233	69.03	15.1724	72.44	
9.1216	124.27	12.5022	92.76	15.7435	68.70	16.8210	72.30	
[PnMIm]Br +BPIE + MeCN								
$m_{\rm BPIE} = 0.00$	100 mol kg^{-1}	$m_{\rm BPIE} = 0.04$	452 mol kg ⁻¹	$m_{\rm BPIE} = 0.09$	991 mol kg ⁻¹	$m_{\rm BPIE} = 0.12$	210 mol kg ⁻¹	
0.3857	163.49	0.7691	143.11	1.0198	131.08	1.1148	120.15	
0.9316	158.56	1.5632	134.51	1.9846	128.38	1.9433	114.47	
1.4876	155.16	2.3991	129.57	3.0504	123.29	2.8698	109.05	
2.0335	150.04	3.1431	126.20	4.0335	118.11	3.9318	103.42	
2.5494	148.00	4.0460	121.10	5.0901	113.43	5.0842	98.49	
3.0853	144.82	4.8903	117.80	6.0088	110.30	6.0710	95.59	
3.6312	140.09	5.7011	114.78	7.0838	105.83	6.8769	93.57	
4.1471	136.99	6.6457	110.88	8.0302	103.58	7.9164	90.83	
4.7381	133.85	7.4566	109.04	9.1051	101.38	9.0387	88.39	
5.3291	131.15	8.2006	107.43	10.125	99.08	10.0555	86.78	
5.9202	128.58	9.0198	105.66	11.0529	97.10	11.1176	84.88	
6.5012	126.78	9.8725	103.73	11.9625	96.07	11.9386	84.47	
			[HMIm]Br +I	3PIE + MeCN	1		1	
$m_{\rm BPIE} = 0.0000 {\rm mol \ kg^{-1}}$		$m_{\rm BPIE} = 0.03$	378 mol kg^{-1}	$m_{\rm BPIE} = 0.08$	352 mol kg ⁻¹	$m_{\rm BPIE} = 0.11$	30 mol kg^{-1}	
0.3186	178.54	0.6941	177.96	0.7978	137.85	0.8867	124.60	
0.8151	171.21	1.3425	169.11	1.5026	131.76	1.8660	121.59	
1.3338	166.93	1.9527	158.82	2.2406	124.29	2.7989	119.11	
1.8376	161.59	2.6545	149.79	2.9786	119.24	3.5069	116.68	
2.3637	156.17	3.2037	142.13	3.6834	117.01	4.2216	114.50	
2.8750	152.57	3.9131	136.16	4.4014	113.50	5.2670	112.18	
3.3493	149.45	4.6072	130.47	5.1328	111.18	6.0015	110.59	
3:7939	147.59	5.4616	124.62	5.9107	109.51	6.7889	108.69	
4.3274	143.75	6.2244	120.34	6.6088	108.28	7.4771	107.39	
4.9053	140.00	6.9032	116.95	7.3069	107.14	8.3505	105.08	
5.7056	136.01	7.7499	114.46	7.9984	106.22	9.0784	102.86	
6.4836	132.49			8.6167	104.98	9.8856	100.81	
						10.7195	99.69	
						11.5551	91.95	
$[HMIm]C] \perp RDIF \perp MaCN$								
$m_{} = 0.00$	$00 \text{ mol } ka^{-1}$	$m_{} = 0.03$	1000000000000000000000000000000000000	$m_{} = 0.0^{\circ}$	$140 \text{ mol } k a^{-1}$	$m_{} = 0.11$	$107 \text{ mol } k a^{-1}$	
$m_{\rm BPIE} = 0.00$	JOO HIOI Kg	$m_{\rm BPIE} = 0.03$	op i mor kg	$m_{\rm BPIE} - 0.07$	+0 mor kg	$m_{\rm BPIE} = 0.11$. 07 mor kg	

$m_{\rm BPIE} = 0.0000 {\rm mol kg^{-1}}$

0.4831	154.77	0.9041	133.65	0.9967	126.40	1.0811	120.14
1.1507	145.43	1.8176	126.72	1.9133	120.73	2.2544	113.28
1.8711	140.11	2.7027	120.56	2.8121	114.11	3.3774	109.87
2.6353	133.44	3.5972	116.18	3.6308	111.38	4.2993	107.04
3.3381	127.46	4.4347	112.75	4.5206	107.59	5.2715	103.01
4.0320	122.93	5.4053	109.86	5.4283	104.80	6.1179	100.54
4.7523	118.37	6.1952	107.18	6.3360	102.10	7.1236	98.28
5.5429	116.34	7.0707	102.61	7.0657	99.76	7.8695	96.33
6.3599	114.41	7.9557	100.77	7.9556	97.41	8.9506	94.65
7.1592	111.42	8.8027	98.23	8.7921	95.46	9.7887	93.12

Table 2

The limiting molar conductivities (Λ_0) , Walden products $(\Lambda_0\eta)$, ion association constants (K_A) , standard Gibbs energies of ion-pairing process (ΔG_A^0) , distance parameters (R), and standard deviations $(\sigma(\Lambda))$ of the ionic liquids in BPIE + MeCN solutions at 298.15 K.

m _{BPIE} .	Λ_0	$\Lambda_0\eta_1$	K _A	ΔG_4^0	$10^{10} R$	$\sigma(\Lambda)$				
mol kg⁻¹	$S cm^2 mol^{-1}$	S cm ² mol ⁻¹ mPa s	$dm^3 mol^{-1}$	kJ mol ⁻¹	m					
[PMIm]Br + BPIE + MeCN										
0.0000	147.97	50.75	15.98	- 6.87	11.82	0.50				
0.0346	121.49	43.37	28.31	- 8.33	8.21	0.54				
0.0655	108.51	39.82	45.83	- 8.26	14.92	0.64				
0.0959	106.92	39.67	35.59	- 7.62	13.27	1.10				
[PnMIm]Br + BPIE + MeCN										
0.0000	170.73	58.56	65.50	- 10.37	16.85	0.87				
0.0452	147.15	53.12	52.68	- 9.83	16.14	1.52				
0.0991	138.96	51.69	41.54	- 9.24	16.32	1.36				
0.1210	123.44	46.29	39.68	- 9.12	17.74	2.36				
[HMIm]Br + BPIE + MeCN										
0.0000	185.33	63.59	85.66	- 11.03	15.50	0.55				
0.0378	160.47	57.45	74.29	- 10.68	18.87	1.00				
0.0852	144.57	53.49	70.68	- 10.55	8.05	1.92				
0.1130	131.72	49.13	31.21	- 8.53	12.99	0.62				
		[HMIm]Cl + BPI	F ⊥ MeCN							
0.0000	160.06	54 90	80.72	- 10.88	19.22	1.85				
0.0397	142.83/=	$-\sqrt{51.27}$	70.11	- 10 53	15.67	0.71				
0.0740	132.53	48.90	49.78	- 9 69	16.99	1 1 1				
N 0.1107	123.82	46.18	29.88	- 8.42	16.79	1.22				
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		Fig. 1	L							



Fig. 2



Fig. 3



Fig. 4