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# Thermophysical properties of ionic liquid, 1-hexyl-3-methylimidazolum bromide + N-N'bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) Schiff base + N,N-dimethylformamide solutions

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# ABSTRACT

Effect of *N*-*N*'bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) Schiff base on thermodynamic properties of ionic liquid, 1-hexyl-3-methylimidazolium bromide ([HMIm]Br) in *N*,*N*-dimethylformamide (DMF) solutions were determined at *T* = 298.15–313.15 K. The standard partial molar volumes,  $V_{\phi}^{0}$ , partial molar volumes of transfer,  $\Delta_{tr}V_{\phi}^{0}$  have been calculated using the measured density data. The cosphere overlap model was used to interpretate the partial molar volumes of transfer,  $\Delta_{tr}V_{\phi}^{0}$ . The calculated Hepler's constants,  $\partial^{2}V_{\phi}^{0}/\partial^{2}T$ , indicate that the BPIE and ionic liquid have structure-breaking (chaotropic) tendency. Ion association constants,  $K_{a}$ , and limiting molar conductivities,  $\Lambda_{0}$ , viscosity *B*-coefficients and molar refractions,  $R_{D}$ , have been used to confirm the conclusions obtained from the volumetric properties. The results were interpreted in terms of various solute–solvent interactions between the BPIE Schiff base and the ionic liquid with increasing BPIE concentration.

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# 1. Introduction

Schiff bases can be prepared from the condensation of aldehydes, ketones, or  $\beta$ -diketones reacting with primary amines and related derivatives and formation imine functional groups. These compounds are considered a class of very important ligands in the coordination chemistry [1–3]. Schiff-bases are widely studied and used in the fields of organic synthesis and metal ion complexation for a number of reasons [4,5]: their physiological and pharmacological activities [6,7], use in ion-selective electrodes [8–14] and in the determination of heavy metal ions in environmental samples [15]. On the other hand, the thermodynamic properties of Schiff bases in solutions can provide valuable information regarding the molecular intractions, their solubility, biological properties and the activity of catalyst.

It is very well known that the medium, and specifically the solvent, plays a dramatic influence on the outcome of chemical reactions. In recent years, there has been an increasing interest in exploiting the potential of ionic liquids as reaction media aimed to develop green chemistry, avoiding the use of volatile organic solvents. The use of ionic liquids as reaction media for processes involving Schiff bases and their metal complexes is promising in view of their successful application in separation, extraction and catalytic processes. To optimize and control processes involving Schiff bases by ionic liquids, the knowledge of their thermophysical and thermodynamic properties is required and their developments demand on reliable reference data on the thermodynamic and thermophysical properties of their mixtures with other compounds. However, there is very limited thermodynamic studies of Schiff bases [16,17] and our literature survey shows that there are no reports on the thermodynamic properties of Schiff bases in the presence ionic liquids.

In the present study, experiments have been performed to measure the density at 298.15–313.15 K, viscosity, electrical conductivity and refractive indices at 298.15 K of 1-hexyl-3-methylimidazolium bromide in the presence of *N*-*N*bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) Schiff base in *N*,*N*-dimethylformamide (DMF) solutions. The apparent molar volumes  $(V_{\phi})$ , standard partial molar volumes  $(V_{\phi}^{0})$ , partial molar volumes  $(V_{\phi})$ , standard partial molar isobaric expansibilities  $(E_{\phi}^{0})$  and Hepler's constant  $(\partial^2 V_{\phi}^0/\partial^2 T)$  have been computed from the experimental densities (*d*) at 298.15–313.15 K. Molar conductivities have been used to obtain the ion association constants (*K*<sub>a</sub>), and limiting molar conductivities ( $\Lambda_0$ ) of the investigated ionic liquid using low concentration Chemical model (IcCM). The viscosity B-coefficients were calculated by using the Jones–Dole equation [18].



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**Table 1** Densities (*d*), viscosities ( $\eta$ ) and refractive indices ( $n_D$ ) of pure compounds at T = 298.15 K.

Compound	$d (g  cm^{-3})$	η (mPa s)	n <sub>D</sub>
DMF	0.94409 0.94406 [16] 0.94380 [19]	0.861 0.803 [22] 0.8605 [23]	1.4285 1.4276 [16]
[HMIm]Br	1.2221 1.2235 [21]	3986 [21]	

The experimental refractive indices and density data were used for the calculation of molar refractions. All these parameters were used to interpret the present solute–solute and solute–solvent interactions and effect of temperature on the solvation properties of ionic liquid in the presence of BPIE Schiff base.

# 2. Experimental

#### 2.1. Materials

The chemicals used in this work were *N*-methylimidazole (>99%), 1-bromohexane (>99%), *N*,*N*-dimethylformamide (GR, >99.8%), ethyl acetate (>99%), pyridine-2-aldehyde (>99.8%) and ethylenediamine (>99.9%) which purchased from Merck. *N*-methylimidazole was freshly distilled at reduced pressure and other reagents were used without further purification. During the course of the experiments, the purity of *N*,*N*-dimethylformamide was checked by density and viscosity and refractive index measurement. The physical properties of the pure compounds are given in Table 1 which compared with the literature values [16,19–22].

#### 2.2. Synthesis of ionic liquid and Schiff base

The ionic liquid, 1-hexyl-3-methylimidazolium bromide, [HMIm]Br was synthesized as described in the literature [23,24]. Briefly, [HMIm]Br was synthesized by direct alkylation of Nmethylimidazole which it was freshly distilled at reduced pressure and with an excess amount of 1-bromohexane in a round bottom flask at 353 K for 72 h under a nitrogen atmosphere. The crude product was separated from unreacted reagents and then washed three times with fresh ethyl acetate. The removal of residual volatile compounds from the ionic liquid was made in high vacuum at 333 K using a rotary evaporator for at least 4 h in 0.7 kPa. The obtained ionic liquid has purity greater than 0.99 in mass fraction, which was used after vacuum desiccated for at least 48 h to remove trace amount of moisture. Water contents found by Karl Fischer method in the ionic liquid was less than 0.05% in mass. [HMIm]Br was analyzed by <sup>1</sup>H NMR (Brucker Av-300) and FTIR (PerkinElmer, Spectrum RXI) to confirm the absence of any major impurities which were found to be in good agreement with those reported in the literature [25,26]. N-N'bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) Schiff base was synthesized according to literature method [27]. 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 h 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 sold orange product was obtained and recrystallized from diethylether. The estimated purity for BPIE is greater than 99.3%. <sup>1</sup>H NMR (CDCl<sub>3</sub> versus TMS):  $\delta$  = 4.06 (s, 4H, =NCH<sub>2</sub>CH<sub>2</sub>N=), 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).

#### 2.3. Apparatus and procedure

The solutions were prepared in glass vials and in molal base concentration by weighing using an analytical balance (Sartrious, AG TE214S, Switzerland) with an uncertainty  $\pm 1 \times 10^{-4}$  g and closed tightly. The uncertainty for molalities of the solutions is less than  $2.0 \times 10^{-4}$  mol kg<sup>-1</sup>. The sample densities were measured with a vibrating tube densimeter (Anton Paar, DMA 4500M, Austria). The apparatus was calibrated with doubly distilled deionized and degassed water, and dry air 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 accuracy of apparatus performance was also tested with the density of a known molality of aqueous NaCl using the data given by Pitzer et al. [28]. The uncertainty of density measurements was better than  $\pm 4.0 \times 10^{-5}$  g cm<sup>-3</sup>.

Electrical conductance measurements were carried out on a digital conductivity meter (Metrohm model 712, Switzerland) with a sensitivity of 0.7% and a dipping-type conductivity cell with platinized electrodes with a cell constant of 0.913 cm<sup>-1</sup> under nitrogen atmosphere and at a frequency of 1 MHz. The cell constant was calibrated with aqueous KC1 (0.01 M) solution. About 50 ml of solvent was placed in the conductivity cell and the cell was closed. Weighed pure ionic liquid was added with a syringe to the cell containing solvent. Circulating water from a thermostatically was regulated bath around the sample holder with double wall. The conductivity cell was purged with nitrogen during each run. The temperature was kept constant using thermostat bath (Julabo NP, Germany) with temperature stability of  $\pm$ 0.01 K.

The viscosities were measured using an Ubbelohde-type viscometer, which has a flow time of about 200 s for water at 298.15 K. The viscometer was calibrated with doubly distilled deionized water. Viscosity of the solution ( $\eta$ ) 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 and L and K are the viscometer constants. A digital stopwatch with a resolution of 0.01 s has been used for the measurement of flow time measurement. The estimated uncertainly of the experimental viscosity was  $\pm 0.005$  mPa s.

Refractive indices of the studied solutions were determined using a digital refractometer (ATAGO-DRA1, Japan) with an uncertainty of  $\pm 3 \times 10^{-4}$ . The instrument was calibrated with doubly distilled water before each series of measurements. A procedure called "zero setting" was always performed before the actual measurements of the sample's refractive index, to ensure that the refractometer is working properly. Calibration was checked with pure liquids of known refractive index. The temperature was controlled using a circulating bath thermostat (Julabo NP, Germany) with a thermal stability of  $\pm 0.01$  K.

# 3. Results and discussion

# 3.1. Volumetric properties

The apparent molar volumes  $(V_{\phi})$  of the [HMIm]Br in the presence of different concentrations of *N*-*N*'bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) Schiff base in DMF solutions [29] were calculated using density data through the following equation:

$$V_{\phi} = \frac{M}{d} - \left[\frac{1000(d-d_0)}{mdd_0}\right] \tag{2}$$

Densities (d) and apparent molar volumes ( $V_{\phi}$ ) of [HMIm]Br in Schiff base (BPIE) + DMF solutions at T = 298.15–313.15 K.

$m_{IL}$ (mol k g <sup>-1</sup> )	298.15 K		303.15 K		308.15 K		313.15 K	
	d (g cm <sup>-3</sup> )	$V_{\phi}$ (cm <sup>3</sup> mol <sup>-1</sup> )	$d(g \operatorname{cm}^{-3})$	$V_{\phi}$ (cm <sup>3</sup> mol <sup>-1</sup> )	$d(\mathrm{gcm^{-3}})$	$V_{\phi}$ (cm <sup>3</sup> mol <sup>-1</sup> )	$d(g \operatorname{cm}^{-3})$	$V_{\phi}$ (cm <sup>3</sup> mol <sup>-1</sup> )
$m_{\rm BPIE} = 0.0000  {\rm mol  k}$	(g <sup>-1</sup>							
0.0000	0.94409		0.94082		0.93579		0.93063	
0.0233	0.94560	188.7	0.94235	188.1	0.93730	187.4	0.93221	186.8
0.0435	0.94689	189.1	0.94365	188.7	0.93859	187.8	0.93356	187.3
0.0658	0.94829	189.4	0.94507	188.9	0.93999	188.1	0.93502	187.7
0.0824	0.94931	189.7	0.94610	189.2	0.94101	188.4	0.93608	188.1
0.1049	0.95067	190.1	0.94748	189.6	0.94238	188.7	0.93752	188.3
0.1228	0.95173	190.3	0.94858	189.8	0.94344	189.2	0.93865	188.6
0.1428	0.95291	190.7	0.94977	190.1	0.94462	189.4	0.93988	188.9
0.1583	0.95383	190.8	0.95067	190.4	0.94553	189.6	0.94081	189.3
0.1869	0.95545	191.3	0.95233	190.8	0.94716	190.1	0.94251	189.8
0.2051	0.95647	191.6	0.95336	191.1	0.94817	190.4	0.94357	190.1
$m_{\rm BPIE} = 0.0402  {\rm mol}  {\rm I}$	(g <sup>-1</sup>							
0.0000	0.94546	107.0	0.94150	107.2	0.93679	100.4	0.93189	105 5
0.0204	0.94680	187.8	0.94286	187.2	0.93813	186.4	0.93330	185.5
0.0428	0.94824	188.2	0.94432	187.7	0.93958	186.6	0.93482	185.8
0.0640	0.94958	188.6	0.94568	188.0	0.94091	187.2	0.93622	186.4
0.0817	0.95068	188.9	0.94680	188.3	0.94201	187.6	0.93738	186.8
0.1034	0.95200	189.4	0.94814	188.8	0.94334	188.0	0.93877	187.3
0.1199	0.95299	189.7	0.94914	189.1	0.94431	188.5	0.93980	187.7
0.1470	0.95458	190.2	0.95076	189.6	0.94590	189.0	0.94147	188.3
0.1614	0.95542	190.4	0.95160	189.9	0.94673	189.3	0.94232	188.7
0.1828	0.95663	190.8	0.95283	190.3	0.94795	189.6	0.94359	189.2
0.2011	0.95765	191.2	0.95386	190.7	0.94896	190.0	0.94465	189.6
$m_{\rm BPIE} = 0.0764  {\rm mol  k}$	(g <sup>-1</sup>							
0.0000	0.94676		0.94272		0.93792		0.93339	
0.0242	0.94837	186.7	0.94435	186.2	0.93958	185.4	0.93507	184.5
0.0429	0.94959	186.9	0.94559	186.4	0.94084	185.6	0.93634	185.0
0.0601	0.95070	187.2	0.94670	186.9	0.94198	185.9	0.9375	185.3
0.0818	0.95206	187.7	0.94809	187.2	0.94340	186.3	0.93892	185.7
0.1015	0.95328	188.1	0.94932	187.7	0.94466	186.7	0.94019	186.1
0.1208	0.95444	188.6	0.95051	188.1	0.94590	186.8	0.94142	186.2
0.1419	0.95572	188.8	0.95177	188.6	0.94719	187.4	0.94272	186.6
0.1634	0.95698	189.3	0.95305	189.0	0.94850	187.8	0.94402	187.1
0.1809	0.95798	189.6	0.95406	189.4	0.94958	187.9	0.94508	187.4
0.2013	0.95913	190.0	0.95522	189.8	0.95079	188.3	0.94627	187.9
$m_{\rm BPIE} = 0.1208  {\rm mol}  {\rm I}$	(g <sup>-1</sup>							
0.0000	0.94807		0.94395		0.93919		0.93492	
0.0205	0.94945	185.6	0.94535	185.0	0.94057	184.2	0.93637	183.2
0.0439	0.95100	185.9	0.94691	185.6	0.94211	184.8	0.93800	183.6
0.0629	0.95223	186.3	0.94815	186.1	0.94335	185.0	0.93929	184.1
0.0843	0.95358	186.9	0.94952	186.6	0.94472	185.3	0.94072	184.5
0.1029	0.95474	187.3	0.95068	187.1	0.94589	185.6	0.94194	184.9
0.1183	0.95567	187.7	0.95164	187.4	0.94684	185.9	0.94295	185.1
0.1437	0.95720	188.2	0.95322	187.6	0.94837	186.5	0.94454	185.9
0.1606	0.95819	188.6	0.95424	187.9	0.94937	186.9	0.94559	186.3
0.1806	0.95932	189.1	0.95539	188.5	0.95055	187.2	0.94680	186.8
0.2005	0.96045	189.6	0.95655	188.8	0.95170	187.6	0.94799	187.2
$m_{\rm BPIE} = 0.1644  {\rm mol}  {\rm k}$	⟨g <sup>−1</sup>							
0.0000	0.94929		0.94472		0.94014		0.93616	
0.0259	0.95104	185.2	0.94649	184.9	0.94194	184.1	0.93799	183.2
0.0413	0.95206	185.4	0.94753	184.8	0.94298	184.5	0.93904	183.9
0.0654	0.95363	185.9	0.94910	185.8	0.94458	185.2	0.94067	184.5
0.0813	0.95463	186.4	0.95013	186.0	0.94562	185.6	0.94171	185.0
0.1019	0.95591	187.0	0.95143	186.6	0.94694	186.1	0.94304	185.7
0.1214	0.95711	187.3	0.95261	187.2	0.94814	186.8	0.94427	186.2
0.1416	0.95833	187.8	0.95385	187.6	0.94938	187.3	0.94553	186.7
0.1618	0.95950	188.3	0.95505	188.1	0.95060	187.7	0.94675	187.2
0.1776	0.96040	188.7	0.95597	188.4	0.95152	188.1	0.94767	187.8
0.2054	0.96197	189.4	0.95753	189.2	0.95313	188.8	0.94927	188.6

m<sub>IL</sub> is the molality of ionic liquid in reference solvent (BPIE + DMF). m<sub>BPIE</sub> is the molality of N,N-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) in DMF.

where *M* is the molar mass of ionic liquid, *d* and  $d_0$  denote the densities of the solution and reference solvent (BPIE + DMF), respectively and *m* shows that the molality of the ionic liquid. The  $V_{\phi}$  values along with density data of the investigated solutions are given in Table 2. Fig. 1 shows the values of  $V_{\phi}$  for the ionic liquid in the different molalities (0.00, 0.04, 0.08, 0.12 and 0.16 mol kg<sup>-1</sup>) of Schiff base (BPIE) in DMF solutions at 298.15–313.15 K. As can be seen

from this figure, the apparent molar volumes decrease with increasing the BPIE molality. The values of  $V_{\phi}$  in a fixed concentration of BPIE (0.08 mol kg<sup>-1</sup>) at 298.15, 303.15, 308.15 and 313.15 K are also compared together in Fig. 2. This figure also shows that the apparent molar volumes decrease with increasing temperature.

At infinite dilution, the solute-solute interaction is negligible. Therefore, the limiting partial molar volume which equals



**Fig. 1.** Apparent molar volumes of [HMIm]Br in (BPIE + DMF) solutions versus molality of ionic liquid at 298.15 K at several concentration of BPIE: (♦) 0.0000; (▲) 0.0402; (■) 0.0767; (◊) 0.1208; (□) 0.1644.



**Fig.2.** Apparent molar volumes of [HMIm]Br in (BPIE +DMF) solutions with molality 0.04 of BPIE: at (♦)298.15 K; (▲)303.15 K; (◊) 308.15 K; (□) 313.15 K.

to standard partial molar volume  $(V_{\phi}^{0})$  and its temperaturedependency provide valuable information of the solute-solvent interactions [30–32]. The standard partial molar volume is often obtained from the extrapolation of the apparent molar volume,  $V_{\phi}$ to an infinite dilution using the following equation:

$$V_{\phi} = V_{\phi}^{0} + S_{\nu} m_{IL} \tag{3}$$

where  $m_{IL}$  is the concentration of ionic liquid and  $S_{\nu}$  is the slope indicating solute–solute interactions [33,34]. The values of  $V_{\phi}^{0}$  and  $S_{\nu}$  along with their standard errors of parameters are listed in

Table 3. From a look at this table it is observed that the  $V_{\phi}^{0}$  decreases with an increase in concentration of BPIE Schiff base and temperature which indicating the presence of solute-solvent interactions in studied solutions and these types of interactions are weakened with an increase in concentration of Schiff base and temperature. The values of  $S_v$  for all the studied solutions are positive and increase with an increase in Schiff base concentration. This indicates the presence of solute ([HMIm]Br)-cosolute (BPIE) interactions which are strengthened at high concentrations of Schiff base (BPIE).

The temperature dependence of  $V_{\phi}^{0}$  values for the studied ionic liquid can be expressed by the equation:

$$V_{\phi}^{\ 0} = A + BT + CT^2 \tag{4}$$

where A, B and C have been estimated by the least-square fitting of standard partial molar volumes at different temperatures. Differentiation of Eq. (4) with respect to temperature was done to calculate partial molar isobaric expansions:

$$E_{\phi}^{0} = \left(\frac{\partial V_{\phi}^{0}}{\partial T}\right)_{p} = B + 2CT$$
(5)

The calculated values of partial molar isobaric expansions  $(E_{\phi}^{0})$  are given in Table 4. It can be seen from this table, the  $E_{\phi}^{0}$  values are decreasing with increase in temperature. The values of partial molar isobaric expansions  $(E_{\phi}^{0})$  are an important indicator of solute-solvent interactions and also employed in interpretation of the structure-making or breaking properties of various solutes [35]. This behavior is also characteristic of solvation and electrostriction (the contraction of the solvent around the ion) of organic electrolytes in solutions. This trend of partial molar isobaric expansion implies that the loosely attached DMF molecules around the ions of ionic liquid would slowly pass into solution.

The general thermodynamic expression is as follows:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V_{\phi}^0}{\partial T^2}\right) = -2cT \tag{6}$$

The sign of second derivatives of the standard partial molar volume with respect to the temperature  $(\partial^2 V_{\phi}{}^0/\partial T^2)_p$  reflect the structure making and breaking ability of a solute in the solution [36]. The  $(C_p)$  is the heat capacity of the solute at infinite dilution. In this expression,  $(\partial C_p/\partial p)_T$  values should be positive for structure-breaking and negative for structure-making solute. Therefore, if the sign of  $(\partial^2 V_{\phi}{}^0/\partial T^2)_p$  is negative, the solute is a structure breaker; otherwise, it is a structure maker. The values of  $(\partial^2 V_{\phi}{}^0/\partial T^2)_p$  for the [HMIm]Br in different concentration of BPIE Schiff base (Table 3) have negative values for studied systems. Therefore, the ionic liquid under study is predominantly a structure breaker and this tendency is strengthening with increasing BPIE concentration.

The partial molar volumes of transfer  $(\Delta_{tr}V_{\phi}^{0})$  of the solute (ionic liquid) from DMF to BPIE + DMF solutions were calculated as follows:

$$\Delta_{tr} V_{\phi}^{0} = V_{\phi}^{0} (\text{in BPIE} + \text{DMF solutions}) - V_{\phi}^{0} (\text{in DMF})$$
(8)

Table 3

Standard partial molar volumes ( $V_{A}^{0}$ ) and experimental slopes ( $S_{v}$ ), for the [HMIm]Br in BPIE Schiff base + DMF solutions at T = 298.15–313.15 K.

$m_{ m BPIE}$ (mol kg <sup>-1</sup> )	) $V_{\phi}^{0}$ (cm <sup>3</sup> mol <sup>-1</sup> )				$S_{\nu} ({\rm cm}^3 {\rm L}^{1/2} { m mol}^{-3/2})$			
	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
0.0000	$188.39\pm0.71$	$187.88 \pm 0.76$	$187.05 \pm 0.28$	$186.51 \pm 0.41$	$15.79\pm0.09$	$15.84\pm0.06$	$16.40\pm0.04$	$17.47\pm0.05$
0.0402	$187.42\pm0.02$	$186.77 \pm 0.02$	$185.90\pm0.06$	$184.92 \pm 0.03$	$18.69\pm0.18$	$19.46\pm0.19$	$20.69\pm0.46$	$23.13\pm0.29$
0.0764	$186.12\pm0.44$	$185.59 \pm 0.43$	$184.90\pm0.31$	$184.30 \pm 0.63$	$19.38\pm0.05$	$20.86\pm0.05$	$21.05\pm0.04$	$21.21\pm0.08$
0.1208	$185.01\pm0.05$	$184.78\pm0.10$	$183.80\pm0.06$	$182.64 \pm 0.05$	$22.67\pm0.41$	$20.44\pm0.81$	$18.72\pm0.52$	$25.50\pm0.61$
0.1644	$184.48\pm0.06$	$184.05 \pm 0.09$	$183.47\pm0.04$	$182.60\pm0.06$	$23.79\pm0.49$	$24.99\pm0.75$	$26.24\pm0.38$	$29.15\pm0.44$

*m*<sub>BPIE</sub> is the molality of *N*,*N*-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) in DMF.

Partial molar isobaric expansions ( $E_{\phi}^{0}$ ), partial molar volumes of transfer ( $\Delta_{tr}V_{\phi}^{0}$ ) and Helper's constants ( $\partial^{2}V_{\phi}^{0}/\partial T^{2}$ ) for the [HMIm]Br in BPIE Schiff base + DMF solutions at T = 298.15–313.15 K.

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$m_{\rm BPIE} ({ m mol}{ m kg}^{-1})$	298.15 K	303.15 K	308.15 K	313.15 K	$\partial^2 V_{\phi}^0 / \partial^2 T (\mathrm{cm}^3 \mathrm{mol}^{-1} \mathrm{K}^{-1})$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$E_{\phi}^{0}$ (cm <sup>3</sup> mol <sup>-1</sup> K <sup>-1</sup> )					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0000	-0.126	-0.128	-0.131	-0.134	_
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0402	-0.117	-0.150	-0.183	-0.217	-0.0066
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0764	-0.096	-0.120	-0.144	-0.168	-0.0047
0.1644 $-0.058$ $-0.103$ $-0.147$ $-0.191$ $-0.0089$ $\Delta V_{\phi}^{0}$ (cm <sup>3</sup> mol <sup>-1</sup> )       -       -       -       -       -       -       -       -       -       0.0000       -       -       -       -       -       -       -       -       -       0.0402       -       0.056 ± 0.04       -       -       1.11 ± 0.02       -       1.20 ± 0.06       -       1.50 ± 0.05       - <td>0.1208</td> <td>-0.020</td> <td>-0.114</td> <td>-0.208</td> <td>-0.301</td> <td>-0.0051</td>	0.1208	-0.020	-0.114	-0.208	-0.301	-0.0051
$ \Delta V_{\phi}^{0} (\text{cm}^{3} \text{ mol}^{-1}) $ $ 0.0000 \qquad - \qquad -$	0.1644	-0.058	-0.103	-0.147	-0.191	-0.0089
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Delta V_{\phi}^0$ (cm <sup>3</sup> mol <sup>-1</sup> )					
$0.0402   -0.96 \pm 0.04   -1.11 \pm 0.02   -1.20 \pm 0.06   -1.50 \pm 0.05$	0.0000	-	_	_	-	
	0.0402	$-0.96\pm0.04$	$-1.11 \pm 0.02$	$-1.20\pm0.06$	$-1.50\pm0.05$	
$-2.26 \pm 0.06$ $-2.29 \pm 0.04$ $-2.47 \pm 0.06$ $-2.67 \pm 0.22$	0.0764	$-2.26\pm0.06$	$-2.29\pm0.04$	$-2.47\pm0.06$	$-2.67\pm0.22$	
$0.1208 \qquad -3.07 \pm 0.05 \qquad -3.12 \pm 0.05 \qquad -3.13 \pm 0.07 \qquad -3.78 \pm 0.06$	0.1208	$-3.07\pm0.05$	$-3.12\pm0.05$	$-3.13 \pm 0.07$	$-3.78\pm0.06$	
$0.1644 \qquad -3.91 \pm 0.05 \qquad -3.83 \pm 0.06 \qquad -3.89 \pm 0.05 \qquad -4.00 \pm 0.58$	0.1644	$-3.91\pm0.05$	$-3.83\pm0.06$	$-3.89\pm0.05$	$-4.00\pm0.58$	

 $m_{\text{BPIE}}$  is the molality of *N*,*N*-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) in DMF.

The types of interaction present in the studied solutions are as following:

- (a) Polar–ionic group interactions between the N groups of BPIE Schiff base, and the ions of [HMIm]Br.
- (b) Polar–polar group interactions between the polar groups of BPIE Schiff base, and the imidazolium ring of [HMIm]Br through the hydrogen bonding.
- (c) Polar–nonpolar group interactions between the N group of BPIE Schiff base and the nonpolar groups of [HMIm]Br.
- (d) Nonpolar-nonpolar groups interactions between the nonpolar groups of BPIE and alkyl group attached to imidazolium ring of [HMIm]Br.

Taking the cosphere overlap model [37] as a guideline, the (a) and (b) types of interactions should lead to positive  $\Delta_t V_{\phi}^0$  values since there is a reduction in the electrostriction effect. Interactions of types (c) and (d) should lead to negative  $\Delta_{tr}V_{\phi}^0$ . An increase in the concentration of Schiff base (BPIE), results in more negative  $\Delta_{tr}V_{\phi}^0$  (Table 3) indicating an enhancement in the nonpolar–nonpolar interactions between the BPIE Schiff base and the ionic liquid.

### 3.2. Conductometric results

The calculated molar conductivities ( $\Lambda$ ) of ternary solutions of [HMIm]Br + BPIE + DMF solutions are given in Table 5. The calculated molar conductivity ( $\Lambda$ ) has uncertainty better than 0.01. The dependency of the molar conductivities ( $\Lambda$ ) on the molar concentration (c) of the ionic liquid ([HMIm]Br) at several molalities of BPIE Schiff base have been shown in Fig. 3. It is seen that the molar conductivities ( $\Lambda$ ) decrease with increasing ionic liquids concentration. Increasing in ionic liquids concentration causes the formation of ion-pair in dilute region and the stronger ion association in solvent.



**Fig.3.** The molar conductivities of [HMIm]Br in (BPIE +DMF) solutions with different molalities of BPIE: ( $\blacklozenge$ ) 0.0000; ( $\blacktriangle$ ) 0.0380; ( $\Box$ ) 0.0707; ( $\diamondsuit$ ) 0.1183 at 298.15 K.

This figure also represents that the molar conductivity ( $\Lambda$ ) values of ionic liquid decrease with increasing BPIE concentration. Increasing Schiff base concentration causes stronger interaction between alkyl chain of ionic liquid and pyridyl group of Schiff base, thus leads to decrease in molar conductivity of [HMIm]Br.

Analysis of conductivity data in the framework of the lowconcentration chemical model (LcCM) uses the set of equations:

$$\Lambda = \alpha [\Lambda_0 - S(c\alpha)^{1/2} + Ec\alpha \ln(c\alpha) + J_1 c\alpha + J_2 (c\alpha)^{3/2}]$$
(9)

Table 5

Molar conductivities (  $\Lambda$  ) of ionic liquid in BPIE Schiff base + DMF solutions at 298.15 K.

	$m_{IL} (\times 10^4 { m mol}{ m kg}^{-1})$	$\Lambda$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$m_{IL} (\times 10^4 { m mol}{ m kg}^{-1})$	$\Lambda$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$m_{IL} (\times 10^4 { m mol}{ m kg}^{-1})$	$\Lambda$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$m_{IL} (\times 10^4 { m mol}{ m kg}^{-1})$	$\Lambda(\mathrm{Scm^2mol^{-1}})$
Î	$m_{\rm BPIE}$ = 0.0000 mol kg <sup>-</sup>	-1	$m_{\rm BPIE} = 0.0380  {\rm mol  kg}$	-1	$m_{\rm BPIE} = 0.0707  {\rm mol  kg^{-1}}$	1	$m_{\rm BPIE} = 0.1183  {\rm mol  kg^{-1}}$	
	6.1117	104.56	7.0554	95.15	8.0757	90.87	8.8763	86.65
	11.7478	97.73	15.1897	88.56	15.7964	85.65	17.2272	82.66
	18.8404	93.72	20.9545	84.88	22.4425	82.46	24.2215	77.95
	26.0780	87.90	28.0099	82.38	31.0222	78.56	34.0008	73.93
	31.1623	85.86	35.2980	79.65	33.7377	77.72	38.3682	71.76
	37.0304	83.88	42.2793	77.60	42.1694	72.65	45.7317	68.75
	41.6168	80.88	51.1858	75.20	49.1008	70.83	56.9457	63.78
	49.3597	78.89	62.4617	71.53	60.8292	67.39	69.2780	61.21
	56.5942	76.10	68.4487	69.85	74.9033	63.24	84.4797	59.17
	62.3246	75.12	75.4300	68.15	87.4136	59.27	89.4379	58.43

m<sub>IL</sub> is the molality of ionic liquid in reference solvent (BPIE+DMF). m<sub>BPIE</sub> is the molality of N,N-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) in DMF.

Ion association constants ( $K_a$ ), limiting molar conductivities ( $\Lambda_0$ ), Walden products ( $\Lambda_0\eta_0$ ), distance parameters (R) and standard deviations ( $\sigma(\Lambda)$ ) of [HMIm]Br in BPIE + DMF solutions, m at 298.15 K.

$m_{ m BPIE}$ (mol kg <sup>-1</sup> )	$K_a$ (dm <sup>3</sup> mol <sup>-1</sup> )	$\Lambda_0 (\mathrm{Scm^2mol^{-1}})$	$R(\times 10^{10}\mathrm{m})$	$\Lambda_0\eta_0~({ m Scm^2mol^{-1}mPas})$	$\sigma(\Lambda)$
0.0000	135.57	111.56	13.10	96.05	0.69
0.0380	107.54	101.03	10.42	88.73	0.61
0.0707	86.53	97.96	26.18	87.47	0.57
0.1183	70.43	92.37	27.16	83.96	1.20

#### Table 7

Viscosities ( $\eta$ ) of BPIE + DMF + [HMIm]Br ternary solutions at 298.15 K.

$m_{IL}$ (mol kg <sup>-1</sup> )	$\eta$ (mPa s)	$m_{IL}$ (mol kg <sup>-1</sup> )	$\eta$ (mPas)	$m_{IL}$ (mol kg <sup>-1</sup> )	$\eta$ (mPa s)	$m_{IL}$ (mol kg <sup>-1</sup> )	$\eta$ (mPa s)	$m_{IL}$ (mol kg <sup>-1</sup> )	$\eta$ (mPa s)	
$m_{\rm BPIE} = 0.0000  ({ m m}$	ol kg <sup>-1</sup> )	m <sub>BPIE</sub> = 0.0402 (m	ol kg <sup>-1</sup> )	$m_{\rm BPIE} = 0.0764 (m_{\rm BPIE})$	$n_{\rm BPIE} = 0.0764 ({\rm mol}{\rm kg}^{-1})$		$m_{\rm BPIE} = 0.1208 ({\rm mol  kg^{-1}})$		$m_{\rm BPIE} = 0.1644 ({\rm mol}{\rm kg}^{-1})$	
0.0000	0.861	0.0000	0.878	0.0000	0.893	0.0000	0.909	0.0000	0.926	
0.0230	0.897	0.0200	0.906	0.0211	0.911	0.0261	0.945	0.0240	0.955	
0.0441	0.913	0.0431	0.922	0.0442	0.926	0.0412	0.957	0.0430	0.969	
0.0663	0.929	0.0643	0.935	0.0634	0.942	0.0654	0.965	0.0601	0.991	
0.0825	0.938	0.0825	0.950	0.0846	0.951	0.0816	0.981	0.0822	1.005	
0.1057	0.952	0.1037	0.962	0.1039	0.962	0.1028	0.993	0.1014	1.018	
0.1240	0.969	0.1210	0.976	0.1191	0.982	0.1221	1.011	0.1216	1.029	
0.1443	0.985	0.1484	0.994	0.1455	0.996	0.1435	1.029	0.1429	1.043	
0.1596	0.997	0.1627	1.000	0.1629	1.013	0.1639	1.043	0.1643	1.054	
0.1892	1.014	0.1852	1.020	0.1833	1.023	0.1802	1.055	0.1826	1.064	
0.2077	1.022	0.2036	1.036	0.2038	1.036	0.2079	1.062	0.2030	1.076	

m<sub>IL</sub> is the molality of ionic liquid in reference solvent (BPIE + DMF). m<sub>BPIE</sub> is the molality of N,N-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) in DMF.

where ion association constant,  $K_a$ 

$$K_a = \frac{1 - \alpha}{\alpha^2 c \gamma_{\pm}^2} \tag{10}$$

and

$$\ln \gamma_{\pm} = \frac{\kappa q}{1 + \kappa R} \tag{11}$$

$$\kappa^2 = \frac{16,000N_A z^2 e^2 \alpha c}{\varepsilon_0 \varepsilon K_B T} \tag{12}$$

and

$$q = \frac{z_c z_a e^2}{8\pi\varepsilon_0 \varepsilon KT} \tag{13}$$

where  $\Lambda$  and  $\Lambda_0$  are the molar conductivity and limiting molar conductivity, respectively at molarity c,  $1 - \alpha$  is the fraction of oppositely charged ions acting as ion pairs,  $K_a$  is the ion association constant of [HMIm]Br, R is distance parameter,  $\gamma_{\pm}$  is the corresponding mean activity coefficient of the free ions. The coefficients E,  $J_1$ , and  $J_2$  required for calculations were taken from Ref. [33]. Three-parameter fits of molar conductivity data yields the association constant ( $K_a$ ), the limiting molar conductivity ( $\Lambda_0$ ) and distance parameter (R) by non-linear least-squares iteration. The calculated  $K_a$ ,  $\Lambda_0$ , and R parameters are summarized in Table 6.

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

$$\sigma(\Lambda) = \left(\frac{\sum \left[\Lambda(\exp.) - \Lambda(\operatorname{calc.})\right]^2}{(n-p)}\right)^{1/2}$$
(14)

where *n* and *p* show the number of the experimental data and parameters, respectively. The limiting molar conductivity  $\Lambda_0$  values decrease with increase in the concentration of Schiff base in BPIE+[HMIm]Br+DMF ternary solutions. This can be ascribed to the facts that (i) with the increasing concentration of BPIE, the dielectric constant of solution decrease and electrostatic attraction between the ions increases, and hence the ions in the free state decrease; (ii) with the increase in microscopic viscosity of solutions, the mobility of ions decrease.

To eliminate the influence of viscosity on the ionic mobility, the Walden products of the solutions were determined using the method reported in the literature [38]. The values of the Walden product  $(\Lambda_0 \eta_0)$  were calculated and included in Table 6. An increase in viscosity leads to a decrease in conductivity. This effect was formulated quantitatively by the Walden rule [39] which states that the product  $\Lambda_0\eta_0$  should be approximately constant for a given electrolyte, irrespective of the nature of the solvent, provided that the radius of the ion remains unchanged. As seen in Table 6, the absolute values of the Walden product decrease slowly with increasing BPIE concentration. This suggests that these ions do not have the same effective radius in different solvent compositions and consequently provides evidence for the desolvation of the ions in solution. This behavior seems to be caused by the preferential solvation of ions of ionic liquid by BPIE molecules. This result supports the conclusion obtained at by considering volumetric results.

# 3.3. Viscosity B-coefficients

The Jones–Dole empirical equation (Eq. (15)) describes the relative viscosities of electrolyte solutions as functions of their concentrations

$$\frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc \tag{15}$$

The *A*-coefficient (also called Falkenhagen coefficient [40], reflecting solute–solute interactions) can be calculated theoretically but are usually small (negligible for nonelectrolytes) [41]. Generally, viscosity *B*-coefficients reflect the solute–solvent

The values of viscosity B-coefficients, standard deviations $(\sigma(\eta))$ and solvation num
pers $(B/V_{\phi}^{0})$ for BPIE+DMF+[HMIm]Br ternary solutions at 298.15 K.

$m_{ m BPIE} ( m molkg^{-1})$	$B (\mathrm{dm^3  mol^{-1}})$	$B/V_{\phi}^{0}$	$\sigma(\eta)(\times 10^3)$
0.0000	$0.835\pm2.14{\times}10^{-3}$	4.43	3.06
0.0402	$0.825\pm1.55\times10^{-3}$	4.40	2.24
0.0764	$0.806\pm2.74{\times}10^{-3}$	4.33	3.94
0.1208	$0.790\pm3.14{\times}10^{-3}$	4.27	4.49
0.1644	$0.741\pm3.69{\times}10^{-3}$	4.02	5.26

Refractive indices  $(n_D)$  and molar refractions  $(R_D)$  of BPIE + [RMIm]Br + DMF ternary solutions at 298.15 K.

$m_{lL}$ (mol k g <sup>-1</sup> )	n <sub>D</sub>	$R_D$ (cm <sup>3</sup> mol <sup>-1</sup> )	$m_{lL}$ (mol k g <sup>-1</sup> )	n <sub>D</sub>	$R_D$ (cm <sup>3</sup> mol <sup>-1</sup> )	$m_{lL}$ (mol k g <sup>-1</sup> )	n <sub>D</sub>	$R_D(\mathrm{cm}^3\mathrm{mol}^{-1})$	
$m_{\rm BPIE} = 0.0000  {\rm mol  k}$	$g^{-1}$		$m_{\rm BPIE} = 0.0402  {\rm mol  k}$	$g^{-1}$		$m_{\rm BPIE} = 0.0764  {\rm mol}  {\rm kg}^{-1}$			
0.0233	1.4303	20.06	0.0204	1.4316	20.08	0.0242	1.4329	20.11	
0.0435	1.4306	20.11	0.0428	1.4325	20.16	0.0429	1.4333	20.17	
0.0658	1.4311	20.18	0.0640	1.4329	20.22	0.0601	1.4345	20.25	
0.0824	1.4316	20.24	0.0817	1.4335	20.28	0.0818	1.4348	20.31	
0.1049	1.4320	20.30	0.1034	1.4342	20.36	0.1015	1.4352	20.38	
0.1228	1.4325	20.36	0.1199	1.4344	20.40	0.1208	1.4356	20.42	
0.1428	1.4330	20.42	0.1470	1.4346	20.47	0.1419	1.4363	20.50	
0.1583	1.4336	20.48	0.1614	1.4354	20.53	0.1634	1.4366	20.56	
0.1869	1.4344	20.58	0.1828	1.4357	20.59	0.1809	1.4368	20.61	
0.2051	1.4347	20.63	0.2011	1.4361	20.65	0.2013	1.4371	20.66	
$m_{\rm BPIE}$ = 0.1208 mol k	g-1		$m_{\rm BPIE} = 0.1644  {\rm mol  kg^{-1}}$						
0.0205	1.4347	20.15	0.0259	1.4352	20.15				
0.0439	1.4350	20.22	0.0413	1.4359	20.23				
0.0629	1.4362	20.28	0.0654	1.4366	20.29				
0.0843	1.4365	20.36	0.0813	1.4370	20.34				
0.1029	1.4374	20.43	0.1019	1.4376	20.41				
0.1183	1.4376	20.47	0.1214	1.4383	20.48				
0.1437	1.4379	20.54	0.1416	1.4389	20.56				
0.1606	1.4385	20.61	0.1618	1.4394	20.62				
0.1806	1.4388	20.67	0.1776	1.4403	20.69				
0.2050	1.4392	20.73	0.2054	1.4410	20.79				

m<sub>IL</sub> is the molality of ionic liquid in reference solvent (BPIE + DMF). m<sub>BPIE</sub> is the molality of N,N-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) in DMF.

interactions. In fact, when both *A*-coefficients are neglected in Eq. (15), this equation is equivalent to the following equation:

$$\frac{\eta}{\eta_0} = 1 + Bc \tag{16}$$

where  $\eta$  and  $\eta_0$  are the viscosities of (Schiff base+ionic liquid+DMF) ternary solutions and reference solvent (Schiff base+DMF), respectively, c is the molar concentration of [HMIm]Br in the ternary solution. The measured viscosities ( $\eta$ ) for ternary solutions at 298.15 K are tabulated in Table 7. The viscosity *B*-coefficients were obtained from the slope of linear plot of  $((\eta/\eta_0)-1)$  vs. *c* by the least square method. The viscosity *B*-coefficient is valuable to provide information concerning the solvation of the solutes and their effects on the structure of the solvent in the near environment of the solute molecules. The viscosity *B*-coefficient is a measure of the effective solvodynamic volume of solvated species and depends on the basis of shape, size and solute–solvent interactions [42].

The calculated viscosity *B*-coefficients decrease with increasing in concentration of BPIE. Positive values of B-coefficients suggest that the presence of solute-solvent interactions and the structuremaking effect of ionic liquid in DMF solvent. But these types of interactions are weakened with an increase of BPIE Schiff base concentration. This conclusion is in agreement with those obtained from volumetric properties. The calculated solvation number,  $(B/V_{\phi}^{0})$  of this ionic liquid in DMF+Schiff base solutions, along with *B* values are given in Table 8. A descending values of  $B/V_{\phi}^{0}$ is an indication of the removing solvent molecules from the primary salvation shell and the  $B/V_{\phi}^{0}$  ratio lies between 0 and 2.5 for unsolvated spherical species. The values  $B/V_{\phi}^{0}$  for the investigated systems are greater than 2.5 and decrease with increasing concentration of BPIE. Which indicating loosely attached DMF molecules around the ions of ionic liquid would slowly pass into solution in the presence of BPIE molecules. These results further support our earlier conclusions from the values of  $V_{\phi}^{0}$  and B.

#### 3.4. Refractometric results

Experimental refractive index data,  $n_D$  for [HMIm]Br+BPIE Schiff base+DMF ternary solutions were measured as a function of the ionic liquid concentration at 298.15 K. The molar refraction  $R_D$  is calculated using Lorentz–Lorenz equation [43] according to

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$$R_D = \left[\frac{(n_D - 1)}{(n_D^2 + 2)}\right] \left(\sum_{i=1}^3 \frac{x_i M_i}{d}\right)$$
(17)

where  $x_i$  and  $M_i$  are the mole fraction and molecular weight of components, respectively and *d* is density of [HMIm]Br + BPIE Schiff base + DMF solutions at a fixed concentration of Schiff base. The calculated molar refractions of the investigated solutions are given in Table 9. Since  $R_D$  value is directly proportional to molecular polarizability [44] under an electrical field [45]. Furthermore, when the structure of a molecule becomes more complex, its electron cloud becomes more decentralized, and the polarizability of the molecule increases. As it can be seen from this table, the  $R_D$  values increase with increasing amount of BPIE in the ternary solutions which indicating high polarizability of ionic liquid solutions in the presence of BPIE Schiff base.

# 4. Conclusions

Experimental density data were measured for the ternary solutions of ionic liquid, 1-hexyl-3-methylimidazolum bromide, +N-N'bis(2-pyridylmethylidene)-1,2-diiminoethane(BPIE) Schiff base + N.N-dimethylformamide at different temperatures. The calculated volumetric parameters such as standard partial molar volumes ( $V_{\phi}^{0}$ ), partial molar volumes of transfer ( $\Delta_{tr}V_{\phi}^{0}$ ), partial molar isobaric expansions  $(E_{\phi}^{0})$  show that an enhancement in the nonpolar-nonpolar interactions between the BPIE Schiff base and the ionic liquid. The values of Hepler's constants  $(\partial^2 V_{\phi}{}^0/\partial T^2)_p$ for the [HMIm]Br in different concentration of BPIE Schiff base have negative values. Therefore, the ionic liquid under study is predominantly a structure breaker and this tendency is strengthening with increasing BPIE concentration. Walden product values decrease slowly with increasing BPIE concentration. This suggests that these ions do not have the same effective radius in different solvent compositions and consequently provides evidence for the desolvation of the ions of ionic liquid in the presence of BPIE molecules. The values of viscosity B-coefficients are less than in high concentration of BPIE, which indicating the dominance of nonpolar-nonpolar interactions between BPIE and ionic liquid. In

general, It may be concluded that the addition of Schiff base (BPIE) to the ionic liquid solutions lead to preferential solvation of ionic liquid with Schiff base molecules and strengthening in structure breaking tendency of the ionic liquid.

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