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Effect of N,N′-Bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) Schiff Base on the Thermophysical Properties of Ionic Liquids in N,N-Dimethylformamide Solutions at 298.15 K

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ABSTRACT: Various thermophysical properties, densities, electrical conductances, viscosities, and refractive indices of two ionic liquids, 1-pentyl-3-methylimidazolium bromide ([PnMIm]Br) and 1-propyl-3-methylimidazolium bromide ([PMIm]Br, in the presence of *N,N*′-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) Schiff base in *N,N*-dimethylformamide (DMF) solutions have been measured at 298.15 K. These data have been used to calculate the standard partial molar volumes, $V_\phi{}^0$, partial molar volumes of transfer, $\Delta_{tr}V_\phi{}^0$, ion association constants, K_a, limiting molar conductivities, Λ_0, viscosity *B*-coefficients, and molar refractions, R_D, for the solutions studied. These parameters decrease with increasing BPIE concentration and increase with increasing alkyl chain length of ionic liquids. The results were interpreted in terms of cosphere overlap model and solute−solvent interactions. In general, it is concluded that there is an enhancement in the nonpolar−nonpolar interactions between the BPIE Schiff base and the ionic liquid.

■ INTRODUCTION

Schiff bases or imines, $R_2C = NR$, are the condensation products of aldehydes, ketones, and β-diketones reacting with primary amines and related derivatives and are considered an important class of ligands in coordination chemistry. They have extensive application in different fields such as the novel tetradentate N_2O_2 Schiff base as a chromogenic reagent for the determination of nickel in some natural food samples and the polydentate Schiff base compounds containing aminic nitrogens as corrosion inhibitors for mild steel in acidic media.[1−3] Schiff bases are more selective in various reactions such as oxidation, hydroxylation, aldol condensation, and epoxidation. For example, the Schiff base metal complexes of pyridyl bis(imide) and pyridine bis(imine) have been used as catalysts in the polymerization of ethylene and propylene.[4,5] In oxidation catalysis, the choice of a suitable ligand is often delicate because it must also be resistant toward the oxidant. The most efficient Jacobsen's and Katsuki's catalysts have evolved as standard reagents for asymmetric epoxidation reactions due to the ease of the Schiff base synthetic generation.[6−8] In recent years, several works have been reported on the Schiff bases and its metal complexes in the presence of ionic liquids. It was found that the activity of these types of catalysts was increased by adding ionic liquids (ILs) to the reaction mixture.[9] ILs derived from the 1,3-dialkylimidazolium cation have been found to be convenient reaction media for green chemistry, avoiding the use of volatile organic compounds and making possible in some cases the recovery of the catalyst. These neoteric solvents have received increased attention in many fields and as new solvents for applications in organic, inorganic, and polymer chemistry due to their negligible vapor pressure, high thermal stability, and nonflammability. As a result, a better immobilized catalyst in the IL with the adequate ionic structure would permit developing a convenient experimental procedure for a suitable biphasic reusable catalytic system.[10]

The efficiency of the Schiff base catalyst/IL system is strongly dependent on the various molecular interactions of the ILs and Schiff bases. The thermophysical properties such as the volumetry, viscometry, and conductometry of these compounds in the presence of ILs can provide important information about solute−solvent and solute−solute interactions occurring in these types of systems.[11,12] However, there are no reports in literature. In our previous paper[13] the partial molar volumes of salen Schiff base in various organic solvents have been measured without using ILs at different temperatures.

In the present work, the ILs based on the imidazolium cation with a fixed anion (Br^-), 1-propyl-3-methylimidazolium bromide ([PMIm][Br]), 1-pentyl-3-methylimidazolium bromide ([PnMIm][Br]), and *N,N*′-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) Schiff base (Figure 1) were synthesized. The experimental densities, *d*, viscosities, η, molar conductivities, Λ, and refractive indices, n_D, of ILs in the BPIE + *N,N*-dimethylformamide (DMF) binary solutions have been measured to obtain various thermophysical properties at $T = 298.15$ K. The apparent molar volumes, V_ϕ, of ILs were calculated using density data and used to calculate the standard partial molar volumes, $V_\phi{}^0$, and the partial molar volumes of transfer, $\Delta_{tr}V_\phi{}^0$, of the ILs from DMF to the BPIE + DMF binary solutions. Molar conductivities have been used to obtain the ion association constants, K_a, and limiting molar conductivities, Λ_0, of the ILs. The viscosity *B*-coefficients were calculated by using the Jones−Dole equation.[15] The results are discussed in terms of

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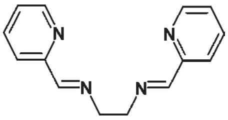

Figure 1. Chemical structure of *N*,*N*′-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) Schiff base.

Table 1. Physical Properties of Pure *N*,*N*-Dimethylformamide (DMF) at T = 298.15 K

$d/\text{g}\cdot\text{cm}^{-3}$		$10^3\ \eta/\text{Pa}\cdot\text{s}$		n_D	
exp.	lit.	exp.	lit.	exp.	lit.
0.94388	0.94380[a]	0.8608	0.8605[a]	1.4285	1.4267[a]
	0.94406[b]				1.4276[b]
	0.9445[c]				1.4275[c]
	0.94446[d]				

[a] Reference 11. [b] Reference 13. [c] Reference 32. [d] Reference 33.

various solute—solvent interactions occurring between the IL and the Schiff base.

EXPERIMENTAL SECTION

Materials. The chemicals used in this work were *N*-methylimidazole (> 99 %), 1-bromopropane (> 99 %), 1-bromopentane (> 99 %), *N*,*N*-dimethylformamide (guaranteed reagent (GR) grade, > 99.8 %), ethyl acetate (> 99 %), pyridine-2-aldehyde (> 99.8 %), and ethylenediamine (> 99.9 %), which were purchased from Merck. *N*-Methylimidazole was freshly distilled at reduced pressure, and the other reagents were used without further purification. The purity of DMF was checked by measurement of its density, viscosity, and refractive index given in Table 1 which were in agreement with those reported in literature values.

Synthesis of ILs and the BPIE Schiff Base. The ILs, 1-propyl-3-methylimidazolium bromide ([PMIm][Br]) and 1-pentyl-3-methylimidazolium bromide ([PnMIm][Br]), were prepared and purified by using the procedure previously described in the literature.[14,15] Briefly, ILs were synthesized by direct alkylation of *N*-methylimidazole with an excess of 1-bromoalkane in a round-bottom flask at 353 K for 48 h under a nitrogen atmosphere. The crude product was separated from reagents and then washed three times with fresh ethyl acetate. The removal of residual volatile unreacted reagents from synthesized ILs was accomplished using a rotary evaporator for at least 4 h at reduced pressure at 333 K. The obtained IL has a purity greater than 0.99 in mass fraction. The IL was used after vacuum desiccated for at least 48 h to remove a trace amount of moisture. The water content found by the Karl Fischer method in the ILs was less than 0.05 %. These synthesized ILs were analyzed by ^{1}H NMR (Bruker Av-300) and FT-IR (Perkin-Elmer, Spectrum RXI) to confirm the absence of any major impurities, and they were found to be in good agreement with those reported in the literature.[16−18] *N*,*N*′-Bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) was synthesized according to literature.[19] 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 several times. After cooling, an orange product was obtained and recrystallized from diethyl ether. Yield, 36 %. ^{1}H NMR (CDCl$_3$ versus TMS): δ = 4.06 (s, 4H, =NCH$_2$CH$_2$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).

Apparatus and Procedure. The solutions were prepared in glass vials and in molal base concentrations by weighing using an analytical balance (Sartorius, AG TE214S, Switzerland) with an uncertainty of $\pm\,1\cdot10^{-4}$ g and closed tightly. The uncertainty for molalities of the solutions is less than $2.0\cdot10^{-4}$ mol kg^{-1}. 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. The density is extremely sensitive to temperature, so it was kept constant within $\pm\,1.0\cdot10^{-3}$ 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.[20] The uncertainty of density measurements of the solutions was better than $\pm\,4.0\cdot10^{-4}$ g·cm^{-3} and for the other solutions studied was $\pm\,4.0\cdot10^{-5}$ g·cm^{-3}.

Conductance measurements were carried out on a digital conductivity meter (Metrohm model 712, Switzerland) with a sensitivity of 0.1 % and a dipping-type conductivity cell with platinized electrodes with a cell constant of 0.824 cm^{-1} under nitrogen atmosphere and at a frequency of 1 MHz. The cell constant was calibrated with aqueous KCl (0.01 M) solution. About 50 mL of solvent was placed in the conductivity cell, and the cell was closed. Weighed pure IL was added with a syringe to the cell containing solvent. To maintain temperature in a stable state, water was circulated from a thermostat bath around the sample holder with a double wall. The conductivity cell was purged with nitrogen during each run. The temperature was kept constant using a thermostat bath (Julabo NP, Germany) with a temperature stability of ± 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. The viscosity of the solution, η, is obtained by the following equation:

$$\frac{\eta}{d} = Lt - \frac{K}{t} \qquad (1)$$

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. The estimated uncertainty of the experimental viscosity was ± 0.002 mPa·s.

Refractive indices of the studied solutions were determined using a digital refractometer (ATAGO-DRA1, Japan) with an uncertainty of $\pm\,1\cdot10^{-4}$. 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. The calibration was checked with pure liquids of a known refractive index. The temperature was controlled using a circulating bath thermostat (Julabo NP, Germany) with a temperature stability of ± 0.01 K.

RESULTS AND DISCUSSION

Volumetric Properties. The measured densities of IL + DMF binary solutions and BPIE + IL + DMF ternary solutions at

Table 2. Densities, d, and Apparent Molar Volumes, V_ϕ, of ILs in (BPIE + DMF) Solutions at 298.15 K

m_{IL}[a]	d	V_ϕ	m_{IL}	d	V_ϕ	m_{IL}	d	V_ϕ	m_{IL}	d	V_ϕ	m_{IL}	d	V_ϕ
$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$
[PnMIm]Br														
$m_{BPIE} = 0.0000\ mol \cdot kg^{-1}$[b]			$m_{BPIE} = 0.0401\ mol \cdot kg^{-1}$			$m_{BPIE} = 0.0728\ mol \cdot kg^{-1}$			$m_{BPIE} = 0.1205\ mol \cdot kg^{-1}$			$m_{BPIE} = 0.1553\ mol \cdot kg^{-1}$		
0.0000	0.94388		0.0000	0.94531		0.0000	0.94633		0.0000	0.94734		0.0000	0.94912	
0.0201	0.94520	172.92	0.0233	0.94686	171.99	0.0244	0.94797	170.87	0.0237	0.94895	170.26	0.0231	0.95070	169.539
0.0409	0.94655	173.16	0.0408	0.94800	172.31	0.0428	0.94918	171.50	0.0482	0.95056	171.04	0.0405	0.95186	170.226
0.0618	0.94788	173.64	0.0602	0.94924	172.88	0.0628	0.95046	172.19	0.0602	0.95134	171.31	0.0613	0.95321	170.849
0.0853	0.94936	173.91	0.0814	0.95059	173.09	0.0812	0.95165	172.25	0.0853	0.95294	171.94	0.0858	0.95477	171.572
0.1009	0.95032	174.25	0.0999	0.95174	173.43	0.1001	0.95283	172.67	0.0990	0.95378	172.44	0.0994	0.95563	171.791
0.1186	0.95139	174.52	0.1205	0.95301	173.74	0.1223	0.95419	173.16	0.1253	0.95541	172.90	0.1228	0.95706	172.457
0.1433	0.95290	174.69	0.1386	0.95409	174.11	0.1405	0.95528	173.62	0.1441	0.95649	173.69	0.1410	0.95817	172.745
0.1610	0.95393	175.09	0.1603	0.95535	174.68	0.1617	0.95652	174.15	0.1617	0.95755	173.86	0.1618	0.95935	173.45
0.1798	0.95502	175.40	0.1820	0.95663	174.96	0.1793	0.95753	174.57	0.1843	0.95882	174.60	0.1848	0.96066	174.214
0.2050	0.95648	175.67	0.1966	0.95744	175.36	0.2000	0.95873	174.85	0.2034	0.95989	175.03	0.1953	0.96127	174.367
[PMIm]Br														
$m_{BPIE} = 0.0000\ mol \cdot kg^{-1}$			$m_{BPIE} = 0.0484\ mol \cdot kg^{-1}$			$m_{BPIE} = 0.0941\ mol \cdot kg^{-1}$			$m_{BPIE} = 0.1508\ mol \cdot kg^{-1}$			$m_{BPIE} = 0.1820\ mol \cdot kg^{-1}$		
0.0000	0.94399		0.0000	0.94537		0.0000	0.94667		0.0000	0.94827		0.0000	0.94925	
0.0268	0.94594	135.42	0.0271	0.94735	134.81	0.0282	0.94877	134.01	0.0283	0.95037	133.41	0.0228	0.95095	133.07
0.0444	0.9472	135.72	0.0417	0.94841	134.92	0.0431	0.94985	134.43	0.0433	0.95145	134.07	0.0437	0.95247	133.70
0.0628	0.94849	136.17	0.0599	0.94970	135.46	0.0603	0.95108	134.99	0.0618	0.95277	134.60	0.0617	0.95374	134.67
0.0851	0.95004	136.64	0.0842	0.95141	135.80	0.0850	0.95283	135.50	0.0865	0.95452	135.09	0.0834	0.95526	135.24
0.1030	0.95126	137.02	0.1015	0.95261	136.06	0.1029	0.95407	136.02	0.1043	0.95572	135.77	0.1031	0.95659	136.03
0.1256	0.95276	137.45	0.1251	0.95421	136.58	0.1263	0.95565	136.67	0.1221	0.95691	136.37	0.1262	0.95814	136.59
0.1396	0.95370	137.81	0.1403	0.95521	137.07	0.1439	0.95685	136.98	0.1447	0.95835	136.81	0.1442	0.95933	137.01
0.1656	0.95541	138.14	0.1558	0.95623	137.39	0.1639	0.95807	137.52	0.1603	0.95943	137.22	0.1620	0.96046	137.66
0.1826	0.95649	138.54	0.1800	0.95780	137.86	0.1829	0.95924	137.79	0.1864	0.96114	137.64	0.1830	0.96182	138.03
0.2057	0.95793	139.15	0.2033	0.95928	138.35	0.2017	0.96057	138.32	0.2104	0.96261	138.39	0.2024	0.96298	138.78

[a] m_{IL} is the molality of IL where the solvent is (DMF + BPIE). [b] m_{BPIE} is the molality of BPIE where the solvent is DMF.

Table 3. Standard Partial Molar Volumes, $V_\phi{}^0$, and Slopes, S_v, Partial Molar Volumes of Transfer, $\Delta_{tr}V_\phi{}^0$, Correlation Coefficients, R^2, and Standard Deviations, $\sigma(V_\phi)$, for the ILs in BPIE Schiff Base + DMF Solutions at 298.15 K

	m_{BPIE}	$10^6\ V_\phi{}^0$	$10^6\ S_v$			$\Delta_{tr}V_\phi{}^0$
system	$mol \cdot kg^{-1}$	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-2} \cdot kg$	R^2	$\sigma(V_\phi)$	$m^3 \cdot mol^{-1}$
[PnMIm]Br + DMF	0.0000	172.64 ± 0.41	15.10 ± 0.05	0.9941	0.07	
[PnMIm]Br + DMF + BPIE	0.0410	171.57 ± 0.50	18.89 ± 0.06	0.9944	0.09	−1.07
[PnMIm]Br + DMF + BPIE	0.0728	170.51 ± 0.75	22.18 ± 0.09	0.9909	0.13	−2.12
[PnMIm]Br + DMF + BPIE	0.1205	169.72 ± 0.57	26.29 ± 0.07	0.9962	0.10	−2.91
[PnMIm]Br + DMF + BPIE	0.1553	169.08 ± 0.65	27.28 ± 0.08	0.9960	0.12	−3.56
[PMIm]Br + DMF	0.0000	134.90 ± 0.04	20.49 ± 0.05	0.9970	0.07	
[PMIm]Br + DMF + BPIE	0.0484	134.13 ± 0.56	20.59 ± 0.07	0.9940	0.10	−0.77
[PMIm]Br + DMF + BPIE	0.0941	133.41 ± 0.31	24.75 ± 0.04	0.9969	0.09	−1.42
[PMIm]Br + DMF + BPIE	0.1508	132.90 ± 0.89	26.52 ± 0.11	0.9910	0.16	−2.00
[PMIm]Br + DMF + BPIE	0.1820	132.56 ± 1.01	31.06 ± 0.13	0.9916	0.18	−2.34

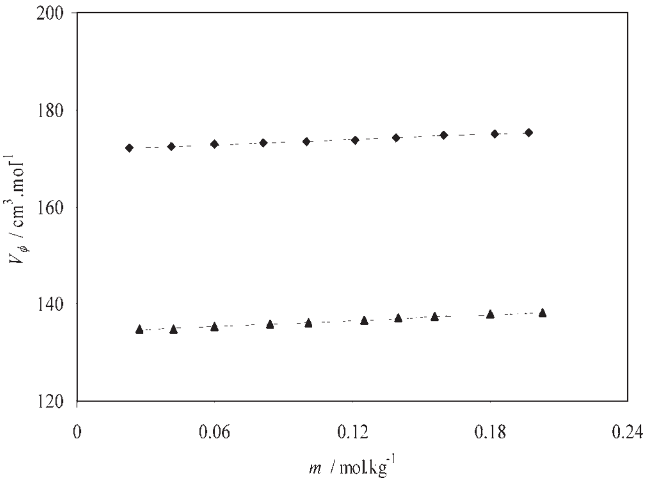

Figure 2. Comparison of apparent molar volumes of [RMIm]Br in (BPIE +DMF) solutions with a molality of 0.04 of BPIE: ◆, [PnMIm]Br; ▲, [PMIm]Br at 298.15 K.

different molalities of BPIE are presented in Table 2. The apparent molar volumes V_ϕ were calculated by the following equation

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

where M is the molar mass of IL, d and d_0 are densities of the solutions (BPIE + IL + DMF) and reference solvent (desired molality of BPIE in DMF), respectively, and m denotes the molality of the IL in reference solvent (BPIE + DMF). The calculated apparent molar volumes V_ϕ for the solutions of [PnMIm]Br and [PMIm]Br at different molal concentrations of BPIE Schiff base in DMF solutions are also given in Table 2. The data in Table 2 shows that the apparent molar volumes of [PnMIm]Br in DMF slightly decreased by increasing the BPIE molality approximately from m_{BPIE} = (0.0, 0.04, 0.08, 0.12, and 0.16) mol·kg^{-1} at 298.15 K. As can be seen from this table, there is a linear correlation between apparent molar volumes and molality of IL at T = 298.15 K. Therefore, the infinite dilution apparent molar volume, $V_\phi{}^0$, was obtained by least-squares fitting to Masson's equation:

$$V_\phi = V_\phi{}^0 + S_v m \tag{3}$$

where $V_\phi{}^0$ is the partial molar volume at infinite dilution that equals the standard partial molar volume.[21] The values of $V_\phi{}^0$ and S_v along with their standard errors are listed in Table 3. The $V_\phi{}^0$ values reflect the presence of solute−solvent interactions, while S_v values show that the nature of the solute−solute interactions.[22,23] The apparent molar volumes of [PMIm]Br and [PnMIm]Br at 0.04 molality of BPIE Schiff base in DMF solutions have been compared in Figure 2 which have the following order: [PMIm]Br < [PnMIm]Br.

It can be also seen that the standard partial molar volumes, $V_\phi{}^0$, for the ILs decrease with an increase concentration of BPIE due to the stronger intractions of BPIE and IL. The values of S_v for all studied solutions are positive, which indicates the presence of solute−solute interactions in the investigated systems. The values of S_v increase with increasing molality of the BPIE Schiff base in solutions containing ILs, which indicates that the strength of solute−cosolute interactions (Schiff base−IL) is increasing at higher concentrations of BPIE.

Standard thermodynamic properties of transfer yield qualitative and quantitative information regarding the interactions of a cosolvent and a solute without having to take into account the effects of solute−solute interactions as at infinite dilution which the interactions between solute molecules are negligible. The partial molar volumes of transfer, $\Delta_{tr}V_\phi{}^0$, for the ILs from DMF to BPIE + DMF solutions were calculated as follows:

$$\Delta_{tr}V_\phi{}^0 = V_\phi{}^0(\text{BPIE} + \text{DMF}) - V_\phi{}^0(\text{DMF}) \tag{4}$$

The values of $\Delta_{tr}V_\phi{}^0$ are given in Table 3. As shown in this table, the $\Delta_{tr}V_\phi{}^0$ values have negative values for IL + Schiff base + DMF ternary solutions and decrease with increasing concentration of BPIE.

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

(a) Polar−ionic group interactions between the N groups of BPIE Schiff base and the ions of [RMIm]Br.
(b) Polar−polar group interactions between the polar groups of BPIE Schiff base and the imidazolium ring of [RMIm]Br through the hydrogen bonding.

Table 4. Molar Conductivities, Λ, of ILs in BPIE Schiff Base + DMF Solutions at Different Molalities of ILs, m_{IL}, at 298.15 K

$10^3\, m_{IL}$[a]	$10^4\, \Lambda$	$10^3\, m_{IL}$	$10^4\, \Lambda$	$10^3\, m_{IL}$	$10^4\, \Lambda$	$10^3\, m_{IL}$	$10^4\, \Lambda$
$mol \cdot kg^{-1}$	$S \cdot m^2 \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$S \cdot m^2 \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$S \cdot m^2 \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$S \cdot m^2 \cdot mol^{-1}$
[PnMIm]Br							
m_{BPIE}[b] = 0.0000 $mol \cdot kg^{-1}$		m_{BPIE} = 0.0362 $mol \cdot kg^{-1}$		m_{BPIE} = 0.0725 $mol \cdot kg^{-1}$		m_{BPIE} = 0.1157 $mol \cdot kg^{-1}$	
0.7182	98.08	0.8197	85.38	0.9252	75.86	0.9912	71.15
1.5506	87.89	1.7019	79.91	1.9288	73.69	1.7947	70.04
2.3422	82.93	2.4749	76.61	2.8462	71.36	2.9436	68.92
3.1991	79.26	3.4351	74.08	3.7478	69.58	3.8823	67.96
3.8436	77.27	4.3329	71.66	4.5555	68.43	4.7158	66.99
4.6436	75.59	5.3947	68.00	5.4258	67.23	5.5793	66.42
5.4026	73.84	6.4018	66.07	6.1079	66.76	6.2702	65.53
6.2922	71.25	7.3543	63.97	6.8292	66.33	6.9835	64.98
7.1735	69.49	8.2053	61.73	7.5506	65.71	7.7344	64.29
8.0223	67.83	8.9860	60.52	8.8835	64.97	9.0711	63.51
[PMIm]Br							
m_{BPIE} = 0.0000 $mol \cdot kg^{-1}$		m_{BPIE} = 0.0362 $mol \cdot kg^{-1}$		m_{BPIE} = 0.0766 $mol \cdot kg^{-1}$		m_{BPIE} = 0.1197 $mol \cdot kg^{-1}$	
1.0796	83.29	1.0826	69.33	1.4018	62.41	1.7652	57.98
2.3726	77.03	2.3604	67.04	2.9541	61.43	3.5596	57.33
3.5946	71.56	3.5894	64.71	4.2806	60.54	5.0030	56.82
4.7691	67.89	4.9257	62.61	5.4471	59.59	6.3391	56.35
5.9436	64.99	6.0961	61.23	6.6043	58.95	7.6264	55.97
7.2960	62.17	7.6274	59.56	7.8179	58.28	8.9527	55.45
8.6010	60.22	8.7686	57.91	9.0974	57.38	10.2986	54.92
9.7992	58.74	10.1146	56.71	10.2827	56.87	11.5274	54.60
11.187	56.94	11.4607	55.23	11.4587	56.48	12.7172	54.37
13.0854	54.80	12.8457	54.43	12.6723	56.22	13.9264	54.19

[a] m_{IL} is the molality of IL where the solvent is (DMF + BPIE). [b] m_{BPIE} is the molality of BPIE where the solvent is DMF.

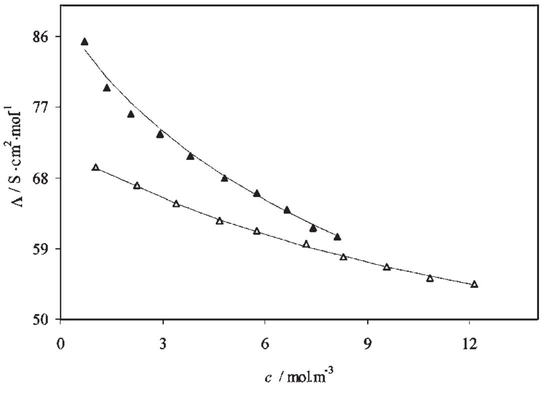

Figure 3. Comparison of molar conductivities of [RMIm]Br in (BPIE + DMF) solution with a molality of 0.04 of BPIE: ▲, [PnMIm]Br; △, [PMIm]Br at 298.15 K.

(c) Polar−nonpolar group interactions between the N group of BPIE Schiff base and the nonpolar groups (alkyl chain) of [RMIm]Br.

(d) Nonpolar−nonpolar group interactions between the nonpolar groups of BPIE and alkyl group attached to imidazolium ring of [RMIm]Br.

Taking the cosphere overlap model as a guideline, the a and b types of interactions should lead to positive $\Delta_{tr}V_{\phi}^{0}$ values, and interactions of types c and d should lead to negative $\Delta_{tr}V_{\phi}^{0}$.[24] An increase in the concentration of cosolute (BPIE) results in more negative $\Delta_{tr}V_{\phi}^{0}$, indicating an enhancement in the nonpolar−nonpolar interactions between the BPIE Schiff base and the IL. The $\Delta_{tr}V_{\phi}^{0}$ values for the [PnMIm]Br are more negative rather than [PMIm]Br solutions. This trend shows that the nonpolar−nonpolar interactions between the BPIE Schiff and [PnMIm]Br stronger than [PMIm]Br.

Conductometric Results. Conductivity measurements yield both the association constant as well as information about the relative solvating ability of solvents for the various ions.[25] Recently, the low concentration chemical model (LcCM) of the conductivity equation is widely applied for the correlation of conductance data in aqueous and nonaqueous electrolyte solution.[26] The conductivity equation of the lcCM is the Fuoss−Onsager type equation. The calculated molar conductivities Λ of ternary solutions at several concentrations of BPIE are given in Table 4. The calculated molar conductivity Λ has an uncertainty better than 1%. It is shown that the molar conductivity, Λ, decreases with increasing IL concentration. Increasing IL concentration causes the formation of ion pair in the dilute region. This table also represents that the molar conductivity, Λ, values decrease with increasing BPIE concentration. The increasing Schiff base concentration causes stronger interactions between the alkyl chain of IL and the pyridinyl group of Schiff base, thus leading to a decrease in molar conductivity of [RMIm]Br.

Table 5. Ion Association Constants, K_a, Limiting Molar Conductivities, Λ_0, Walden Products, $\Lambda_0\eta_0$, Distance Parameters, R, and Standard Deviations $\sigma(\Lambda)$ of [RMIm]Br at Several Concentrations of BPIE Schiff Base + DMF Solutions at 298.15 K

	m_{BPIE}	K_a	$10^4\ \Lambda_0$	$10^7\ \Lambda_0\eta_0$	$10^{10}\ R$	
system	$\text{mol}\cdot\text{kg}^{-1}$	$\text{dm}^3\cdot\text{mol}^{-1}$	$\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$	$\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}\cdot\text{Pa}\cdot\text{s}$	m	$\sigma(\Lambda)$
[PnMIm]Br + DMF	0.0000	96.62	100.65	86.64	18.9	1.88
[PnMIm]Br + DMF + BPIE	0.0362	82.20	89.40	76.96	18.49	0.68
[PnMIm]Br + DMF + BPIE	0.0725	24.80	76.09	65.50	16.37	0.79
[PnMIm]Br + DMF + BPIE	0.1157	19.90	72.91	62.76	9.99	0.13
[PMIm]Br + DMF	0.0000	73.05	88.20	75.92	20.07	1.02
[PMIm]Br + DMF + BPIE	0.0400	38.23	72.51	62.42	14.36	0.20
[PMIm]Br + DMF + BPIE	0.0766	13.95	64.24	55.30	0.13	0.17
[PMIm]Br + DMF + BPIE	0.1197	10.76	58.58	50.43	15.66	0.18

The molar conductivity values of [PMIm]Br and [PnMIm]Br in 0.04 $\text{mol}\cdot\text{kg}^{-1}$ of BPIE in DMF solutions have been compared together in Figure 3. This shows that the molar conductivity values of [PnMIm]Br in DMF + BPIE solutions are more than [PMIm]Br IL. An analysis of conductivity data in the framework of the LcCM uses the set of equations:

$$\Lambda = \alpha[\Lambda_0 - S(c\alpha)^{1/2} + Ec\alpha \ln(c\alpha) + J_1 c\alpha + J_2(c\alpha)^{3/2}] \tag{5}$$

where the ion association constant, K_a

$$K_a = \frac{1-\alpha}{\alpha^2 c \gamma_\pm{}^2} \tag{6}$$

where

$$\ln \gamma_\pm = \frac{\kappa q}{1 + \kappa R} \tag{7}$$

$$\kappa^2 = \frac{16000 N_A z^2 e^2 \alpha c}{\varepsilon_0 \varepsilon K_B T} \tag{8}$$

$$q = \frac{z_c z_a e^2}{8\pi\varepsilon_0 \varepsilon K T} \tag{9}$$

where Λ and Λ_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 [RMIm]Br, R is the distance parameter, and $\gamma_\pm$ is the corresponding mean activity coefficient of the free ions. The coefficients of eq 5 reflect the relaxation and electrophoretic effects. In eq 5, S is the coefficient of Debye–Hückel–Onsager, and E depends only on the properties of the solvent and the charge of the ions, while J_1 and J_2 depend on the same parameters and also on the distance parameter, R. The coefficients E, J_1, and J_2 required for calculations were taken from literature.[26] κ is the reciprocal Debye radius of the ion cloud, and N_A is Avogadro's number. Three-parameter fits of molar conductivity data yields the association constant, K_a, the limiting molar conductivity, Λ_0, and distance parameter, R, by nonlinear least-squares iteration. K_a, Λ_0, and R parameters are summarized in Table 5.

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

$$\sigma(\Lambda) = \left(\sum [\Lambda(\text{exp}) - \Lambda(\text{calc})]^2/(n-p)\right)^{1/2} \tag{10}$$

where n and p show the number of the experimental data and parameters, respectively.

As it is seen from Table 5, the Λ_0 values for ILs decrease with the increase concentration of BPIE Schiff base in BPIE + IL + DMF ternary solutions. This can be ascribed to the facts that (i) with the increasing concentration of Schiff base 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. This result supports the conclusion obtained by considering volumetric results. The values of K_a decrease with increasing alkyl chain length ILs and show that the interactions between the cation and the anion ILs decreased; thus, the ion association was reduced.

To eliminate the influence of viscosity on the ionic mobility, the viscosities of the solutions were determined using the method reported in the literature.[27] The values of the Walden product, $\Lambda_0\eta_0$, were calculated which are included in Table 4. An increase in viscosity leads to a decrease in conductivity. This effect was formulated quantitatively by the Walden rule 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.[28] As shown in Table 5, the absolute values of the Walden product decrease slowly with increasing BPIE concentration. According to the uncertainties in the experimental viscosity and conductivity, it can be reasonably expected that some experimental points will deviate from the linear relation, but this does not influence the decreasing tendency. 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 IL by Schiff base molecules. This indicates that the interactions of IL with the Schiff base molecules are stronger than those of DMF.

Viscometric Results. The measured viscosities η, for (IL + BPIE + DMF) ternary solutions at 298.15 K are tabulated in Table 6. This table shows that the values of η for ternary solutions of (IL + BPIE + DMF) increase with increasing the concentration of BPIE Schiff base. This phenomenon was interpreted in terms of stronger contact between the components of solution; then, the molecules of Schiff base tend to congregate together to induce the increase in the viscosity.

Experimental values of viscosity were then correlated by using the Jones–Dole equation[29] which is widely used for the description

Table 6. Viscosities, η, of Ternary ([RMIm]Br + BPIE + DMF) Solutions at 298.15 K

m_{IL}[a] mol·kg^{-1}	η mPa·s	m_{IL} mol·kg^{-1}	η mPa·s	m_{IL} mol·kg^{-1}	η mPa·s	m_{IL} mol·kg^{-1}	η mPa·s	m_{IL} mol·kg^{-1}	η mPa·s
				[PnMIm]Br + BPIE + DMF					
m_{BPIE}[b] = 0.0000 mol·kg^{-1}		m_{BPIE} = 0.0401 mol·kg^{-1}		m_{BPIE} = 0.0728 mol·kg^{-1}		m_{BPIE} = 0.1205 mol·kg^{-1}		m_{BPIE} = 0.1553 mol·kg^{-1}	
0.0201	0.877	0.0233	0.890	0.0244	0.901	0.0237	0.920	0.0231	0.945
0.0409	0.890	0.0408	0.903	0.0428	0.910	0.0482	0.928	0.0405	0.955
0.0618	0.899	0.0602	0.917	0.0628	0.928	0.0602	0.932	0.0613	0.968
0.0853	0.912	0.0814	0.927	0.0812	0.938	0.0853	0.940	0.0858	0.981
0.1009	0.925	0.0999	0.936	0.1001	0.948	0.0990	0.951	0.0994	0.986
0.1186	0.942	0.1205	0.951	0.1223	0.962	0.1253	0.962	0.1228	0.997
0.1433	0.957	0.1386	0.965	0.1405	0.978	0.1441	0.968	0.1410	1.012
0.1610	0.965	0.1603	0.979	0.1617	0.987	0.1617	0.990	0.1618	1.023
0.1798	0.982	0.1820	0.992	0.1793	0.997	0.1843	1.010	0.1848	1.035
0.2050	0.991	0.1966	1.003	0.2000	1.010	0.2034	1.018	0.1953	1.050
				[PMIm]Br + BPIE + DMF					
m_{BPIE} = 0.0000 mol·kg^{-1}		m_{BPIE} = 0.0484 mol·kg^{-1}		m_{BPIE} = 0.0941 mol·kg^{-1}		m_{BPIE} = 0.1508 mol·kg^{-1}		m_{BPIE} = 0.1820 mol·kg^{-1}	
0.0268	0.880	0.0271	0.893	0.0282	0.909	0.0283	0.935	0.0228	0.943
0.0444	0.889	0.0417	0.902	0.0431	0.922	0.0433	0.940	0.0436	0.952
0.0628	0.897	0.0599	0.915	0.0603	0.932	0.0618	0.949	0.0617	0.961
0.0851	0.905	0.0842	0.924	0.0850	0.946	0.0865	0.969	0.0834	0.972
0.1030	0.917	0.1015	0.934	0.1029	0.955	0.1043	0.979	0.1031	0.984
0.1256	0.923	0.1251	0.947	0.1263	0.968	0.1221	0.988	0.1262	0.995
0.1396	0.936	0.1403	0.959	0.1439	0.980	0.1447	0.998	0.1442	1.008
0.1656	0.956	0.1558	0.969	0.1639	0.986	0.1603	1.006	0.1620	1.018
0.1826	0.966	0.1800	0.998	0.1829	0.995	0.1864	1.016	0.1830	1.030
0.2057	0.975	0.2033	0.989	0.2017	1.013	0.2104	1.031	0.2024	1.036

[a] m_{IL} is the molality of IL where the solvent is (DMF + BPIE). [b] m_{BPIE} is the molality of BPIE where the solvent is DMF.

Table 7. Values of Viscosity *B*-Coefficients, Standard Deviations $\sigma(\eta)$, and Solvation Number B/V_{ϕ}^{0} for BPIE + DMF + [RMIm]Br Ternary Solutions at 298.15 K

m_{BPIE} mol·kg^{-1}	$10^3\,B$ m^3·mol^{-1}	B/V_{ϕ}^{0}	$10^3\,\sigma(\eta)$
	[PnMIm]Br		
0.0000	$0.802 \pm 3.74 \cdot 10^{-3}$	4.64	5.44
0.0410	$0.770 \pm 2.30 \cdot 10^{-3}$	4.49	3.31
0.0728	$0.736 \pm 1.66 \cdot 10^{-3}$	4.32	2.37
0.1205	$0.637 \pm 4.94 \cdot 10^{-3}$	3.75	5.02
0.1553	$0.615 \pm 2.31 \cdot 10^{-3}$	3.67	3.30
	[PMIm]Br		
0.0000	$0.622 \pm 49 \cdot 10^{-3}$	4.61	3.56
0.0484	$0.616 \pm 2.65 \cdot 10^{-3}$	4.59	2.75
0.0941	$0.607 \pm 2.65 \cdot 10^{-3}$	4.49	3.74
0.1508	$0.586 \pm 2.57 \cdot 10^{-3}$	4.40	3.66
0.1820	$0.577 \pm 2.05 \cdot 10^{-3}$	4.35	2.93

of viscosity behavior in dilute electrolyte solutions;

$$\frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc \tag{11}$$

where η and η_0 are the viscosities of (Schiff base + IL + DMF) ternary solutions and reference solvent (Schiff base + DMF), respectively, and c is the molar concentration of ILs in the solution. The *A*-coefficient, whose value generally is positive, is a measure of solute−solute interactions, and the *B*-coefficient is an empirical constant which depends on solute−solvent interactions and can have positive or negative values. The calculated viscosity *B*-coefficients are given in Table 7 obtained from fitting the experimental viscosity data to the Jones−Dole equation. 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.[30] The viscosity *B*-coefficients are positive and decrease with increasing the concentration of BPIE and shortening alkyl chain length of ILs. Positive values of *B*-coefficients suggest the presence of solute−solvent interactions. But these types of interactions are weakened with an increase of Schiff base concentration. On other hand, the viscosity *B*-coefficients for [PMIm]Br are less than those values for [PnMIm]Br. It means that DMF molecules have strong interactions with [PnMIm]Br rather than other ILs. Further, the calculated solvation number, B/V_{ϕ}^{0}, in DMF + Schiff base solutions are given in Table 7. The solvation number of ILs in IL + DMF + Schiff base solutions decreases with increase in the amount of Schiff base. These results further support our earlier conclusions

Table 8. Refraction Indices, n_D, and Molar Refractions, R_D, of BPIE + [RMIm]Br + DMF Solutions at 298.15 K

m_{IL}[a]	n_D	R_D	m_{IL}	n_D	R_D	m_{IL}	n_D	R_D	m_{IL}	n_D	R_D	m_{IL}	n_D	R_D
[PnMIm]Br														
m_{BPIE}[b] $= 0.0000\ \mathrm{mol \cdot kg^{-1}}$			$m_{BPIE} = 0.0401\ \mathrm{mol \cdot kg^{-1}}$			$m_{BPIE} = 0.0728\ \mathrm{mol \cdot kg^{-1}}$			$m_{BPIE} = 0.1205\ \mathrm{mol \cdot kg^{-1}}$			$m_{BPIE} = 0.1553\ \mathrm{mol \cdot kg^{-1}}$		
0.0201	1.4291	20.0405	0.0233	1.4307	20.0747	0.0244	1.4311	20.0825	0.0237	1.4322	20.1052	0.0231	1.4340	20.1263
0.0409	1.4297	20.1031	0.0408	1.4313	20.1222	0.0428	1.4315	20.1250	0.0482	1.4325	20.1391	0.0406	1.4346	20.1886
0.0618	1.4299	20.1540	0.0602	1.4316	20.1854	0.0628	1.4320	20.1789	0.0602	1.4328	20.198	0.0613	1.4352	20.2586
0.0853	1.4309	20.2235	0.0814	1.4319	20.2316	0.0812	1.4326	20.2383	0.0853	1.4334	20.2481	0.0858	1.4356	20.3003
0.1009	1.4312	20.2683	0.0999	1.4323	20.2865	0.1001	1.4332	20.3039	0.0990	1.4338	20.3140	0.0994	1.4359	20.3566
0.1186	1.4317	20.3339	0.1205	1.4326	20.3324	0.1223	1.4337	20.3585	0.1253	1.4342	20.3666	0.1228	1.4365	20.4155
0.1433	1.4320	20.3794	0.1386	1.4329	20.3859	0.1405	1.4344	20.4266	0.1441	1.4348	20.4239	0.1410	1.4369	20.4726
0.1610	1.4323	20.4267	0.1603	1.4333	20.4427	0.1617	1.4348	20.4769	0.1617	1.4352	20.4841	0.1615	1.4373	20.5345
0.1798	1.4329	20.498	0.1820	1.4339	20.4959	0.1793	1.4352	20.5322	0.1843	1.4356	20.5379	0.1848	1.4376	20.5673
0.2050	1.4333	20.0405	0.1966	1.4345	20.0747	0.2000	1.4355	20.0825	0.2034	1.4362	20.1052	0.1953	1.4380	20.1263
[PMIm]Br														
$m_{BPIE} = 0.0000\ \mathrm{mol \cdot kg^{-1}}$			$m_{BPIE} = 0.0484\ \mathrm{mol \cdot kg^{-1}}$			$m_{BPIE} = 0.0941\ \mathrm{mol \cdot kg^{-1}}$			$m_{BPIE} = 0.1508\ \mathrm{mol \cdot kg^{-1}}$			$m_{BPIE} = 0.1820\ \mathrm{mol \cdot kg^{-1}}$		
0.0268	1.4289	20.0338	0.0271	1.4307	20.0622	0.0282	1.4318	20.0885	0.0283	1.4334	20.1124	0.0228	1.4340	20.1367
0.0444	1.4296	20.0787	0.0417	1.4311	20.0949	0.0431	1.4324	20.1160	0.0433	1.4338	20.1499	0.0436	1.4349	20.1778
0.0628	1.4302	20.1244	0.0599	1.4314	20.1551	0.0603	1.4326	20.177	0.0618	1.4342	20.1947	0.0617	1.4354	20.2153
0.0851	1.4307	20.153	0.0842	1.4322	20.1995	0.0850	1.4336	20.2131	0.0865	1.4346	20.2437	0.0834	1.4357	20.252
0.1030	1.4309	20.1917	0.1015	1.4328	20.2391	0.1029	1.4338	20.2563	0.1043	1.4353	20.273	0.1031	1.4359	20.296
0.1256	1.4312	20.2284	0.1251	1.4331	20.2772	0.1263	1.4342	20.3129	0.1221	1.4357	20.326	0.1262	1.4362	20.34
0.1396	1.4317	20.2749	0.1403	1.4336	20.3117	0.1439	1.4351	20.3522	0.1447	1.4362	20.366	0.1442	1.4368	20.3808
0.1656	1.4321	20.3241	0.1558	1.4340	20.3602	0.1639	1.4355	20.3929	0.1603	1.4367	20.416	0.1620	1.4375	20.4255
0.1826	1.4328	20.3851	0.1800	1.4345	20.4005	0.1829	1.436	20.4254	0.1864	1.4369	20.4744	0.1830	1.438	20.4776
0.2057	1.4336	20.0338	0.2033	1.4348	20.0622	0.2017	1.4362	20.0885	0.2104	1.4379	20.1124	0.2024	1.4387	20.1367

[a] m_{IL} is the molality of IL where the solvent is (DMF + BPIE). [b] m_{BPIE} is the molality of BPIE where the solvent is DMF.

regarding the behavior of these systems (BPIE + IL + DMF) from values of V_ϕ^0 and B.

Refractometric Results. Experimental refractive index data, n_D, for [PMIm]Br or [PnMIm]Br + BPIE Schiff base + DMF ternary solutions were measured as a function of the IL concentration, and m_{IL} is the molality of IL where solvent is (DMF + BPIE) at 298.15 K. The molar refraction, R_D, is calculated using the Lorentz–Lorenz equation[31] according to

$$R_D = \left[\frac{(n_D - 1)}{(n_D^2 + 2)}\right]\left(\sum_{i=1}^{3} \frac{x_i M_i}{d}\right) \tag{12}$$

where x_i and M_i are the mole fraction and molecular weight of components, respectively, and d is the density of IL + Schiff base + DMF solutions at a fixed concentration of Schiff base. The calculated molar refractions of the investigated solutions are given in Table 8.

CONCLUSIONS

The effect of BPIE Schiff base on the thermodynamic and thermophysical properties of two ILs, 1-pentyl-3-methylimidazolium bromide and 1-propyl-3-methyl imidazolium bromide, in the *N*,*N*-dimethylformamide solutions was investigated at $T = 298.15$ K. The density, electrical conductance, viscosity, and refraction index data were measured for ternary (IL + BPIE + DMF) solutions at $T = 298.15$ K and at atmospheric pressure. The apparent molar volumes, standard partial molar volumes, and partial molar volumes of transfer have been computed from the experimental density data. It has been observed that these parameters decrease with increasing BPIE concentration and increase with increasing alkyl chain length of ILs. The variation of these parameters indicate an enhancement in the nonpolar–nonpolar interactions between the BPIE Schiff base and the IL and these types of interactions between the BPIE Schiff base and [PnMIm]Br stronger than [PMIm]Br. Electrical conductances of ILs at several concentrations of BPIE have been used for the determination of ion association constants, K_a, and limiting molar conductivities, Λ_0, using the lcCM of conductance equation. These parameters decrease with increasing the concentration of BPIE due to the dielectric constant and microscopic viscosity of the solutions studied. The values of K_a increase with increasing chain length ILs and show that ion association increases with increasing chain length alkyl of ILs. The Walden product $\Lambda_0\eta_0$ values decreased with increasing BPIE molality for both ILs, which is ascribed to the preferential solvation of the ions by BPIE molecules. The values of viscosity *B*-coefficients decrease with increasing concentration of BPIE in (BPIE + ILs + DMF) ternary solutions, which indicates the nonpolar–nonpolar interactions between BPIE and IL. The R_D values increase with an increasing amount of BPIE in the ternary solutions studied.

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