

## Research Article

# Physiochemical Properties of Hydrodenitrification and Hydrodesulphurization Inhibiting Compounds with 1-Ethyl-3-Methylimidazolium Ethylsulphate at $T = (298.15 \text{ to } 323.15) \text{ K}$ and $p = 1 \text{ Bar}$

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Received 25 November 2010; Accepted 28 February 2011

Academic Editor: Dominique Richon

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This work investigates the ability of 1-ethyl-3-methylimidazolium ethylsulphate ( $[\text{emim}][\text{EtSO}_4]$ ) as a green and tuneable solvent for denitrification and desulphurization of diesel oil. Experimental density, surface tension, and refractive index data have been measured for the following systems:  $[\text{emim}][\text{EtSO}_4](1) + \text{pyridine}(2)$ ,  $[\text{emim}][\text{EtSO}_4](1) + \text{pyrrole}(2)$ ,  $[\text{emim}][\text{EtSO}_4](1) + \text{quinoline}(2)$ ,  $[\text{emim}][\text{EtSO}_4](1) + \text{indoline}(2)$ ,  $[\text{emim}][\text{EtSO}_4](1) + \text{thiophene}(2)$ , and  $[\text{emim}][\text{EtSO}_4](1) + \text{water}(2)$  over the entire mole fraction of  $[\text{emim}][\text{EtSO}_4]$  at temperatures of  $(298.15 \text{ to } 323.15) \text{ K}$  and at atmospheric pressure. Further, from experimental density values, coefficient of thermal expansivity and excess molar volume were also calculated. It was found that the heteroaromatic nitrogen/sulphur compounds and water are completely miscible in the  $[\text{emim}][\text{EtSO}_4]$  ionic liquid. The surface tension values were found to increase while the refractive index decrease with increasing mole fraction of  $[\text{emim}][\text{EtSO}_4]$ . On the other hand, dissimilar molecule such as water showed mobility of ions on mixing resulting in lower surface tension. The experimental values of surface tension increased in the order: thiophene > pyridine > pyrrole > indoline > quinoline and for refractive index: quinoline > indoline > pyrrole > pyridine > thiophene > water. It was found that the composition of  $[\text{emim}][\text{EtSO}_4]$  has a greater influence than temperature in deciding the densities, surface, optical, and thermodynamic properties.

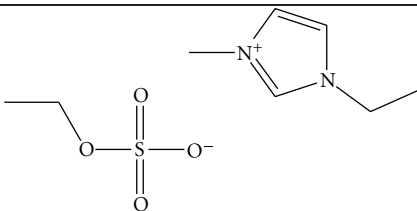
## 1. Introduction

Aromatic nitrogen, sulphur, and its derivatives in diesel oil cause severe environmental problems. Nitrogen and sulphur are present in diesel oil exhaust in the form of  $\text{NO}_x$  [1],  $\text{SO}_x$  [2], and particulate matter (PM) [1]. These are the major contributors for air pollution and also reduce the efficiency of the pollution control equipment in vehicles [2]. Therefore, the removal of aromatic nitrogen, sulphur, and its derivatives from diesel oil has become a challenge for petroleum industries. The growing environmental regulations and strict regulatory environments compel the industries to reduce nitrogen and sulphur level in diesel oil to less than 0.1 ppm [3] and 10 ppm [4, 5], respectively. The separation of aromatic nitrogen species and sulphur

from diesel oil is not feasible via conventional hydrodesulphurization (HDS) process, due to the presence of aromatic nitrogen species. Aromatic nitrogen species strongly act as inhibitors for HDS process in the form of catalyst poisoning or deactivation. Additionally, HDS cannot meet current environmental regulation in aromatic nitrogen and sulphur level in diesel oil. On the other hand, HDS process requires high active catalyst at high operating temperature or pressure [6]. It also requires high reactor volume for the removal of limited amount of saturated nitrogen and sulphur species from diesel oil.

Currently, ionic liquids (ILs) are getting more attraction for aromatic/aliphatic [7], thiophene [8–11], and nitrogen [12] compound separation. Liquid-liquid extraction (LLE) is a well-established process; it can operate at moderate

TABLE 1: Name and structure of the studied ionic liquid.

S. no	Name	Structure	Acronym	Mole. for	Mol-wt (g/mole)	CASRN <sup>a</sup>	Density (g/cm <sup>3</sup> )	Appearance
01	1-Ethyl-3-methylimidazolium ethylsulphate		[emim] [EtSO <sub>4</sub> ]	C <sub>8</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> S	236.29	342573-75-5	1.24	liquid

<sup>a</sup>CASRN: Chemical Abstracts Service Registry Number.

temperature and atmospheric pressure without the requirement of extensive energy. Further, it does not change the chemical structure of the components due to their unique feature as tunable or designer solvents [12, 13]. Having negligible vapor pressure, they do not evaporate like volatile organic component (VOC) to the environment. They possess high chemical and thermal stability and have a good solubility for organic, inorganic, and polymeric compounds. These properties justify them as a solvent for HDS and hydrodenitritication (HDN) process.

To design new desulphurization and denitrification process involving ionic liquid on an industrial scale, it is necessary to know the physiochemical properties with aromatic sulphur and nitrogen compounds. There are limited literature data with experimental data involving binary systems consisting of ionic liquid and aromatic sulphur/nitrogen compound. The physiochemical properties are very important for process optimization. This further helps in regeneration and subsequent recycling of the ILs. The presence of water and other impurities like residual halide in ILs has an important role in tailoring their physiochemical properties [14, 15]. The fluorinated anion-based ILs are harmful since they produce HF, when in contact with water [16] even at 100 ppm [15]. Thus, ILs with halide anion are corrosive in nature and, therefore, cannot be used for industrial applications. On the other hand, alkylsulphates, organoborates, and alkylsulfonates [16] anions are easily available at low cost with required physical properties which include low viscosity and low melting point [14].

One of the most important ionic liquid is based on the ethylsulphate anion, that is, 1-ethyl-3-methylimidazolium ethylsulphate ([emim][EtSO<sub>4</sub>]). The solubility of aliphatic and aromatic hydrocarbons in the ionic liquid, [emim][EtSO<sub>4</sub>], is already available [17]. The physical properties including density, viscosity, refractive index and speed of sound were measured in several alcohols [15, 17, 18], water [18], and in 2-ethoxy-2-methylpropane [15]. Excess molar volume, deviation of refractive index, dynamic viscosity, and speed of sound were also studied at several temperatures and at atmospheric pressure [15, 17, 18]. Heat capacity and excess enthalpy of 1-ethyl-3-methylimidazolium based ionic liquid with water has been recently reported by Ficke et al. [19]. Pereiro et al. [20] has used the alkylsulfate-based ionic liquids to separate azeotropic mixtures such as hexane or heptane from ethanol via liquid-liquid extraction [20]. However, till

date the thermophysical properties of ethyl sulphate based ionic liquid with aromatic nitrogen and sulphur components are not available in the literature, so a systematic study needs to be carried out.

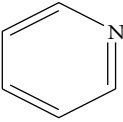
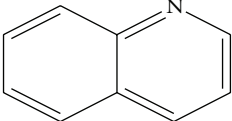
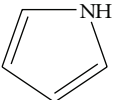
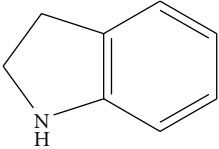
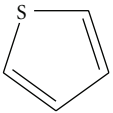
The aim of this work is to measure the physiochemical properties including density, refractive index and surface tension for pure 1-ethyl-3-methylimidazolium ethylsulphate ([emim][EtSO<sub>4</sub>]) (Table 1), Pyridine (PY), Quinoline (QU), Pyrrole (PYRR), Indoline (INDO), Thiophene (TS) and binary mixtures with IL such as: [emim][EtSO<sub>4</sub>](1) + PY(2), [emim][EtSO<sub>4</sub>](1) + PYRR(2), [emim][EtSO<sub>4</sub>](1) + QU(2), and [emim][EtSO<sub>4</sub>](1) + INDO(2) over the entire mole fraction of [emim][EtSO<sub>4</sub>](1) at  $T = (298.15 \text{ to } 323.15) \text{ K}$  and atmospheric pressure (Table 2). Further excess molar volume are calculated from experimental data. Thus, the binary mixture data will be helpful for the simultaneous desulphurization and denitrification of diesel oil as well as the regeneration of [emim][EtSO<sub>4</sub>].

## 2. Experimental Section

**2.1. Chemicals.** 1-ethyl-3-methylimidazolium ethylsulphate [emim][EtSO<sub>4</sub>] (C<sub>8</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>S) ionic liquid was purchased from Fluka with a purity of >99%. A water content of 0.058% in [emim][EtSO<sub>4</sub>] was assessed by Karl Fischer titration. Pyrrole (C<sub>4</sub>H<sub>5</sub>N) and indoline (C<sub>8</sub>H<sub>9</sub>N) were supplied from Spectrochem, India, with the mass fraction of 99%. Pyridine (C<sub>5</sub>H<sub>5</sub>N), quinoline (C<sub>9</sub>H<sub>7</sub>N) and thiophene (C<sub>4</sub>H<sub>4</sub>S) were received from Sigma Aldrich with mass fractions greater than 98% and were used without further purification.

**2.2. Phase Equilibria Measurement.** Samples were prepared by transferring known mass of the pure liquids into stoppered bottles via syringe. The stoppered bottles were closed with screw caps to seal and prevent evaporation. All weighing was carried out in a balance (Mettler Toledo AT 261) with an accuracy of  $\pm 10^{-4}$  gm. Previous experiments [11] showed that equilibrium was recognized after 6 hours of stirring at 100 rpm at a temperature of 298.15 K, using circulating water bath along with automatic controller. In our study, the equilibrium was attained by keeping the mixture settled for 12 hours during which good contact was obtained between two pure components (Figure 1). It is clear from Figure 1 that all the compounds form a single homogenous phase

TABLE 2: List of studied aromatic nitrogen and sulphur compound used in this work.

S.no	Name	Structure	Acronym	Properties					Appearance
01	Pyridine		PY	Mole. for $C_5H_5N$	Mol.wt $g \cdot mole^{-1}$ 79.04	B.Point K 388.2	M.Point K 231.4	Density $g \cdot cm^{-3}$ 0.9819	liquid
02	Quinoline		QU	$C_9H_7N$	129.06	511	258	1.093	liquid
03	Pyrrole		PYRR	$C_4H_5N$	67.04	402–404	250	0.967	liquid
04	Indoline		INDO	$C_8H_9N$	119.07	493–494	252	1.063	liquid
05	Thiophene		TS	$C_4H_4S$	84	357	234.5	1.05	liquid

after equilibrium. Thus, our study mainly deals with the physiochemical aspects of the mixtures. Samples from the homogeneous mixture were withdrawn using syringes for their physiochemical studies. All the samples were prepared immediately prior to performing density, surface tension, and refractive index measurements so as to prevent variation in composition due to water/air retention via the hygroscopic IL.

**2.3. Density Measurement.** Densities of the pure components and binary mixture were measured at atmospheric pressure with Anton Paar DSA-4500MA digital vibrating U-tube densimeter. The densitometer has a well-defined thermo-electric temperature control system. The uncertainty in the density measurement is  $\pm 0.0011 g \cdot cm^{-3}$ . The instrument automatically corrects the influence of the viscosity on the measured density. The apparatus was calibrated by measuring the density of Millipore quality water and ambient air.

**2.4. Surface Tension Measurement.** The surface tension of the pure components and binary mixtures were measured with a tensiometer by plate type method (Hanging drop tensiometer method, KRUS K9, Germany) with a precision of 0.01 mN/m. The apparatus was calibrated by measuring the surface tension of Millipore quality water at ambient temperature.

**2.5. Refractive Index Measurement.** Refractive index of the pure components and binary mixtures were determined at

ambient temperature using an automatic refractometer AD-13 model (ABBEMAT-WR Dr.Kernchen), with an uncertainty of  $\pm 0.00004$ .

From these measurements, the coefficient of thermal expansion “ $\alpha$ ” of [EMIM][EtSO<sub>4</sub>] ionic liquid is calculated via (1)

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_P \quad (1)$$

Here,  $V$  is the molar volume of the pure fluid,  $\rho$  is the density of the pure fluid, and subscript  $P$  indicates constant pressure. The excess molar volume of the binary mixture  $V_m^E$  is calculated from the density of binary mixture  $\rho_{\text{mix}}$ , and density of the pure components  $\rho_1$  and  $\rho_2$  according to (2) [21–26]

$$V_m^E = \frac{(x_1 M_1 + x_2 M_2)}{\rho_{\text{mix}}} - x_1 \frac{M_1}{\rho_1} - x_2 \frac{M_2}{\rho_2} \quad (2)$$

$$= V_{\text{mix}} - x_1 V_1 - x_2 V_2,$$

where  $x_1$  and  $x_2$  are the mole fraction of component 1 and 2, respectively.  $M_1$ ,  $M_2$  are the molecular weight of the component 1 and 2, respectively.

### 3. Results and Discussion

**3.1. Pure Components.** Experimental densities of pure [emim][EtSO<sub>4</sub>], aromatic nitrogen, and aromatic sulphur species are measured and benchmarked at different temperatures (Tables 3 and 4). Table 3 shows the comparison of measured densities for pure [emim][EtSO<sub>4</sub>] with temperature.

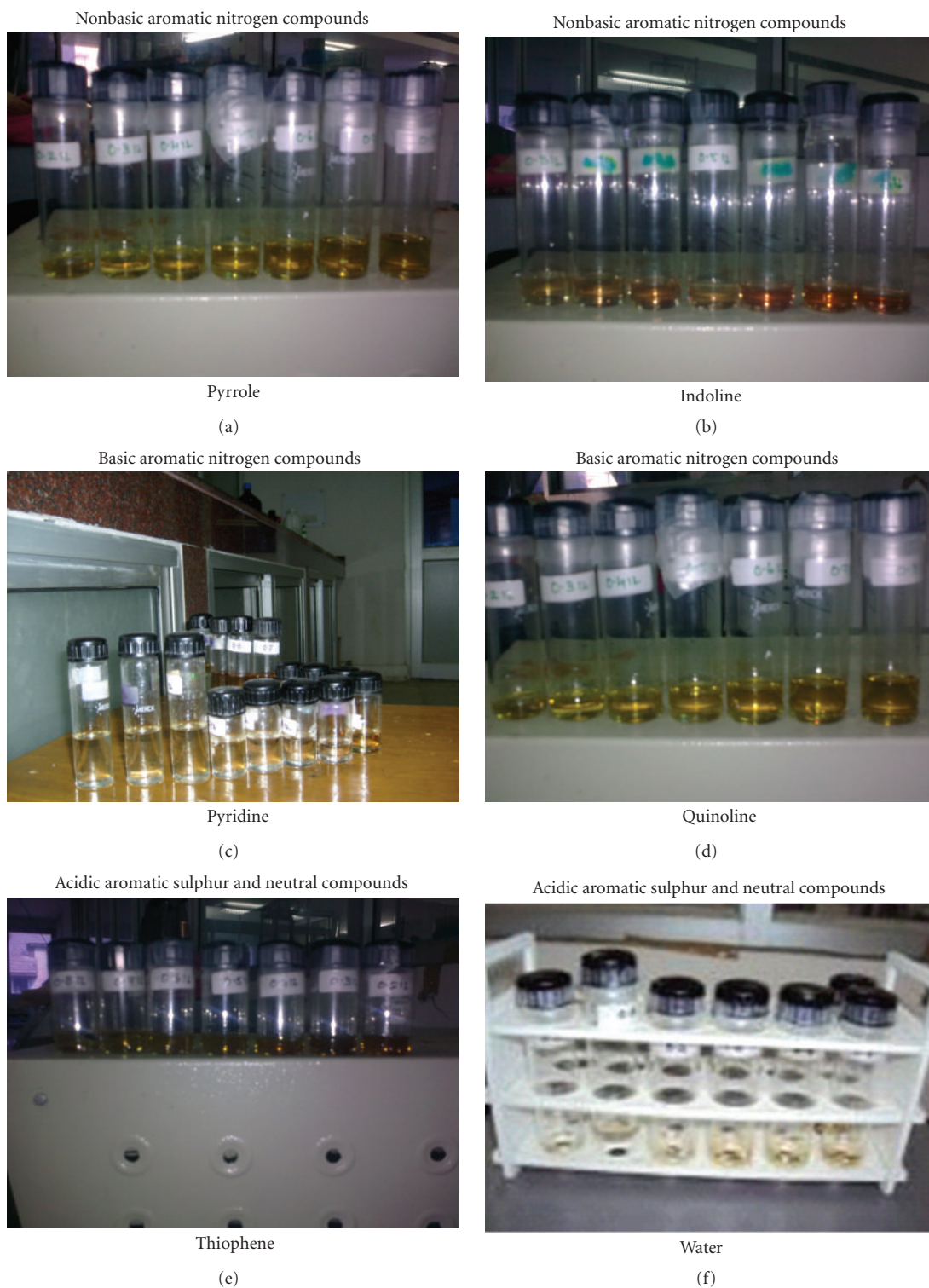


FIGURE 1: 1-ethyl-3-methylimidazolium ethyl sulphate ( $[\text{emim}][\text{EtSO}_4]$ ) is completely miscible with heteroaromatic nitrogen/sulphur and with water molecules.

Beside the effect of temperature and experimental method, the presence of trace amount of impurities such as water or ions can have a remarkable effect on thermodynamic properties [29]. Due to this very reason, the % deviation in the

density values is 6% when compared to the literature values. Table 4 also shows the comparison between experimental and literature data of the pure aromatic nitrogen/sulphur and water at 298.15 K. The density  $\rho$  of pure ionic liquid



TABLE 3: Comparison of measured density  $\rho$  of Pure [emim][EtSO<sub>4</sub>] data with literature data at the temperatures (298.15 to 323.15) K.

T/K	Experimental	$\rho/\text{g}\cdot\text{cm}^{-3}$	Literature value	% Deviation*
298.15	1.2345		1.2423 <sup>a</sup>	6.22
303.15	1.2313		1.2388 <sup>a</sup>	6.05
308.15	1.2279		1.2354 <sup>a</sup>	6.07
313.15	1.2246		1.2319 <sup>a</sup>	5.92
318.15	1.2213		1.2285 <sup>a</sup>	5.86
323.15	1.2179		1.2251 <sup>a</sup>	5.87

<sup>a</sup> Reference [27]; \* (literature value – experimental value)/experimental value  $\times$  100.

TABLE 4: Comparison of measured density  $\rho$  as a function of temperature with literature data for of pure compounds.

	T/K					
	298.15	303.15	308.15	313.15	318.15	323.15
	$\rho/\text{g}\cdot\text{cm}^{-3}$					
Pyridine (PY)						
Measured	0.9783	0.9732	0.9682	0.9631	0.9581	0.9581
Reported	0.9780 <sup>b</sup>	NA	NA	NA	NA	NA
Pyrrole (PYRR)						
Measured	0.9655	0.9611	0.9568	0.9524	0.9479	0.9436
Reported	0.9733 <sup>b</sup>	NA	NA	NA	NA	NA
Quinoline (Qu)						
Measured	1.0883	1.0843	1.0804	1.0764	1.0724	1.0685
Reported	1.0929 <sup>b</sup>	NA	NA	NA	NA	NA
Indoline (INDO)						
Measured	1.0883	1.0843	1.0804	1.0764	1.0724	1.0685
Reported	NA	NA	NA	NA	NA	NA
Thiophene (TS)						
Measured	1.0584	1.0525	1.0465	1.0405	1.0344	1.0284
Reported	1.0585 <sup>c</sup>	NA	NA	NA	NA	NA
Water						
Measured	0.9971	0.9957	0.9939	0.9918	0.9879	0.9849
Reported	0.9971 <sup>d</sup>	NA	NA	NA	NA	NA

<sup>b</sup> Reference [28]. <sup>c</sup> Reference [6]. <sup>d</sup> Reference [18]. NA: not available.

is higher than that of water and aromatic nitrogen/sulphur compounds. Table 5 show a comparison of surface tension  $\sigma$  and refractive index  $n_D$  of pure components with literature data at 298.15 K. As compared to densities, the deviation in surface tension and refractive index for [emim][EtSO<sub>4</sub>] was equal to 3% and 0.15%, respectively. Thus, a small impurity such as water or other ions has marked difference in density when compared to surface tension or refractive index.

**3.2. Binary Mixtures.** Experimental densities over the entire composition range for [emim][EtSO<sub>4</sub>](1) + PY(2) (Table 6), [emim][EtSO<sub>4</sub>](1) + PYRR(2) (Table 7), [emim][EtSO<sub>4</sub>](1) + QU(2) (Table 8), [emim][EtSO<sub>4</sub>](1) + INDO(2) (Table 9), [emim][EtSO<sub>4</sub>](1) + TS(2) (Table 10), and [emim][EtSO<sub>4</sub>](1) + water(2) (Table 11) have been determined at temperature of (298.15 to 323.15) K and at

atmospheric pressure. As expected, the density was found to decrease with increasing temperature. In order to compare the properties such as refractive index and surface tension, we will concentrate our study at room temperature, that is,  $T = 298.15$  K. Thereafter the surface tension  $\sigma$  and refractive index  $n_D$  of the pure component and its binary mixtures, that is, [emim][EtSO<sub>4</sub>](1) + PY(2), [emim][EtSO<sub>4</sub>](1) + PYRR(2), [emim][EtSO<sub>4</sub>](1) + QU(2), [emim][EtSO<sub>4</sub>](1) + INDO(2), and [emim][EtSO<sub>4</sub>](1) + TS(2) were determined at  $T = 298.15$  K over the entire composition range of [emim][EtSO<sub>4</sub>](1). The refractive index was found to decrease, while the surface tension increased with increasing mole fraction of [emim][EtSO<sub>4</sub>]. Further, measurements of the physiochemical properties of mixtures: [emim][EtSO<sub>4</sub>](1) + water(2) were also carried out, which is helpful for the purification and regeneration of [emim][EtSO<sub>4</sub>] [24].

TABLE 5: Surface tension  $\sigma$  and refractive index  $nD$  for pure compounds of the binary system studied in this work at 298.15 K and atmospheric pressure.

	$\sigma/\text{mN}\cdot\text{m}^{-1}$		$nD$	
	Present study	Literature value	Present study	Literature value
[emim][EtSO <sub>4</sub> ]	48.4	46.96 <sup>d</sup>	1.4771	1.4794 <sup>d</sup>
Pyridine (PY)	37.5	NA	1.5013	NA
Pyrrole (PYRR)	41.7	NA	1.4884	NA
Quinoline (QU)	46.5	NA	1.4997	NA
Indoline (INDO)	32.6	NA	1.5867	NA
Thiophene (TS)	31.7	NA	1.5271	1.5255 <sup>e,f</sup>
Water	72.1	71.1 <sup>d</sup>	1.3357	NA

<sup>d</sup>Reference [18]. <sup>e</sup>Reference [30]. <sup>f</sup>Reference [31]. NA: not available.TABLE 6: Experimental density  $\rho$  and excess molar volume  $V_m^E$  for the binary system [emim][EtSO<sub>4</sub>](1) + Pyridine(2).

$x_{\text{IL}}$	$\rho$ $\text{g}\cdot\text{cm}^{-3}$	$V_m^E$ $\text{cm}^3\cdot\text{mol}^{-1}$	$x_{\text{IL}}$	$\rho$ $\text{g}\cdot\text{cm}^{-3}$	$V_m^E$ $\text{cm}^3\cdot\text{mol}^{-1}$
$T = 298.15\text{ K}$			$T = 303.15\text{ K}$		
0.2	1.0900	-1.5561	0.2	1.0860	-1.6160
0.3	1.1299	-2.2786	0.3	1.1259	-2.3311
0.4	1.1586	-2.5356	0.4	1.1549	-2.6002
0.5	1.1731	-1.7004	0.5	1.1729	-2.1481
0.6	1.1914	-1.6230	0.6	1.1878	-1.6640
0.7	1.2067	-1.5063	0.7	1.2033	-1.5300
0.8	1.2184	-1.1659	0.8	1.2149	-1.1669
$T = 308.15\text{ K}$			$T = 313.15\text{ K}$		
0.2	1.0838	-1.8536	0.2	1.0799	-1.9346
0.3	1.1220	-2.3957	0.3	1.1182	-2.4623
0.4	1.1511	-2.6546	0.4	1.1476	-2.7460
0.5	1.1703	-2.3102	0.5	1.1671	-2.4201
0.6	1.1844	-1.7185	0.6	1.1809	-1.7724
0.7	1.1998	-1.5702	0.7	1.1963	-1.6118
0.8	1.2115	-1.1903	0.8	1.2081	-1.2173
$T = 318.15\text{ K}$			$T = 323.15\text{ K}$		
0.2	1.0758	-1.9970	0.2	1.0717	-2.0625
0.3	1.11428	-2.5300	0.3	1.1104	-2.5998
0.4	1.14395	-2.8194	0.4	1.1403	-2.8958
0.5	1.16367	-2.5060	0.5	1.1527	-1.7096
0.6	1.17738	-1.8247	0.6	1.1738	-1.8797
0.7	1.19289	-1.6541	0.7	1.1894	-1.6988
0.8	1.20464	-1.2434	0.8	1.2012	-1.2717

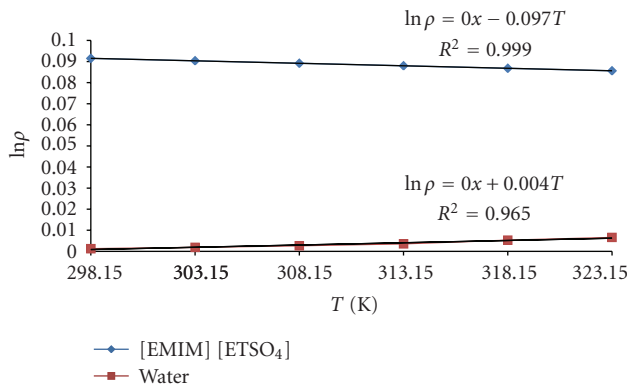
3.2.1. *The Coefficient of Thermal Expansion of the [EMIM][EtSO<sub>4</sub>]*  $\alpha$ . Figure 2 show the densities of pure [emim][EtSO<sub>4</sub>], which decrease linearly ( $R^2 = 0.999$ ) while the densities of water increase linearly ( $R^2 = 0.965$ ) with temperature. The value of  $\alpha = 0.097\text{ K}^{-1}$  ([emim][EtSO<sub>4</sub>]) and  $\alpha = 0.004\text{ K}^{-1}$  (water) was calculated from (1). The volume expansivity of [emim][EtSO<sub>4</sub>] and water was calculated using the measured density observed at different temperatures. As compared to water, the volume expansivity of [emim][EtSO<sub>4</sub>] was found to be independent of temperature (Figure 2). These observations are consistent with the observations by Rodríguez and

Brennecke [21], Wandschneider et al. [23], and Pererio et al. [32, 33].

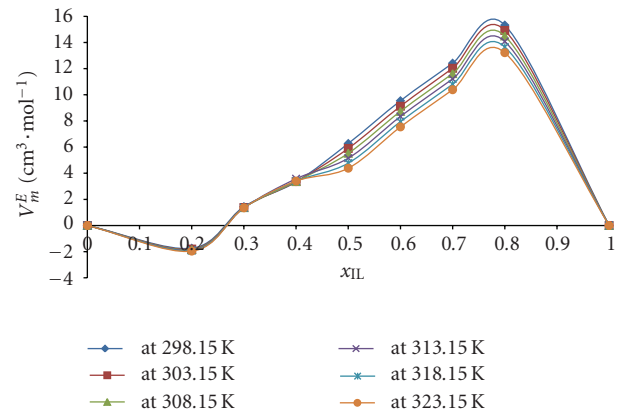
3.2.2. *Effect of Temperature on Density*. Figure 3 shows the experimental densities of pure [emim][EtSO<sub>4</sub>], aromatic nitrogen, aromatic sulphur, and water at temperatures: (298.15 to 323.15) K. It can be seen that the density of all the pure components including ionic liquid decreases linearly with temperature. Tables 6 to 11 shows the experimental densities for six binary systems studied as a function of temperature over the entire mole fraction of [emim][EtSO<sub>4</sub>]. For all the compounds with ILs, the

TABLE 7: Experimental density  $\rho$  and excess molar volume  $V_m^E$  for the binary system [emim][EtSO<sub>4</sub>](1) + Pyrrole(2).

$x_{IL}$	$\rho$ $\text{g}\cdot\text{cm}^{-3}$	$V_m^E$ $\text{cm}^3\cdot\text{mol}^{-1}$	$x_{IL}$	$\rho$ $\text{g}\cdot\text{cm}^{-3}$	$V_m^E$ $\text{cm}^3\cdot\text{mol}^{-1}$
$T = 298.15 \text{ K}$			$T = 303.15 \text{ K}$		
0.2	1.0955	-1.7383	0.2	1.0920	-1.7969
0.3	1.0963	1.4405	0.3	1.0931	1.3789
0.4	1.1085	3.3324	0.4	1.1047	3.3566
0.5	1.1095	6.2719	0.5	1.1092	5.9001
0.6	1.1080	9.5403	0.6	1.1079	9.1236
0.7	1.1094	12.414	0.7	1.1089	12.027
0.8	1.1103	15.326	0.8	1.1099	14.925
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.2	1.0883	-1.8385	0.2	1.0845	-1.8768
0.3	1.0894	1.3664	0.3	1.0856	1.3624
0.4	1.1009	3.3686	0.4	1.0955	3.5758
0.5	1.1088	5.5279	0.5	1.1085	5.1509
0.6	1.1075	8.7333	0.6	1.1072	8.3432
0.7	1.1086	11.621	0.7	1.1082	11.2132
0.8	1.1095	14.502	0.8	1.1091	14.0779
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.2	1.0807	-1.9164	0.2	1.0768	1.9547
0.3	1.0818	1.3591	0.3	1.0779	-1.3551
0.4	1.0935	3.3931	0.4	1.0898	-3.6002
0.5	1.1081	4.7705	0.5	1.1077	-4.3935
0.6	1.1068	7.9409	0.6	1.1064	-7.5508
0.7	1.1078	10.8025	0.7	1.1075	-10.3946
0.8	1.1088	13.6512	0.8	1.1084	-13.2270

FIGURE 2: Plot of experimental values of  $\ln \rho$  of the pure [emim][EtSO<sub>4</sub>] ionic liquid and water versus temperature (298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K.

densities varied linearly in the entire mole fraction with increasing temperature. This behaviour can be explained by the efficient structural interaction of [emim][EtSO<sub>4</sub>] with aromatic nitrogen/aromatic sulphur via packing effects [34, 35]. Additionally it can be a result of the smaller size of cation and anion providing better interaction with aromatic

FIGURE 3: Excess molar volume for [emim][EtSO<sub>4</sub>](1) + Pyrrole(2) as a function of [EMIM][EtSO<sub>4</sub>](1) mole fraction composition at different temperature.

nitrogen/sulphur and water. A smaller size of IL molecule was found to have a significant influence on the densities of the mixture with increasing temperature. These behaviors strongly agree with the studies carried out by Rodríguez and Brennecke [21] and Domańska et al. [34, 35]. A similar trend was observed by Gonzalez et al. [17] and Gomez et al.

TABLE 8: Experimental density  $\rho$  and excess molar volume  $V_m^E$  for the binary system [emim][EtSO<sub>4</sub>](1) + Quinoline(2).

$x_{IL}$	$\rho$ $\text{g}\cdot\text{cm}^{-3}$	$V_m^E$ $\text{cm}^3\cdot\text{mol}^{-1}$	$x_{IL}$	$\rho$ $\text{g}\cdot\text{cm}^{-3}$	$V_m^E$ $\text{cm}^3\cdot\text{mol}^{-1}$
$T = 298.15 \text{ K}$			$T = 303.15 \text{ K}$		
0.2	1.1373	-0.8139	0.2	1.1334	-0.8054
0.3	1.1388	1.14189	0.3	1.1353	1.1327
0.4	1.1342	3.89602	0.4	1.1313	3.8265
0.5	1.1780	0.06978	0.5	1.1762	-0.1535
0.6	1.2034	-1.5676	0.6	1.1947	-0.8666
0.7	1.2234	-2.7068	0.7	1.2207	-2.8231
0.8	1.2305	-2.2468	0.8	1.2273	-2.2721
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.2	1.1296	-0.8204	0.2	1.1260	-0.8525
0.3	1.1316	1.1313	0.3	1.1278	1.1408
0.4	1.1274	3.8725	0.4	1.1269	3.4589
0.5	1.1731	-0.2196	0.5	1.1697	-0.2619
0.6	1.1939	-1.2486	0.6	1.1912	-1.3799
0.7	1.2177	-2.9089	0.7	1.2145	-2.9731
0.8	1.2239	-2.3007	0.8	1.2206	-2.3295
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.2	1.1223	-0.8657	0.2	1.1185	-0.8793
0.3	1.1241	1.1494	0.3	1.1203	1.1577
0.4	1.1232	3.4875	0.4	1.1195	3.5157
0.5	1.1664	-0.2947	0.5	1.1631	-0.3448
0.6	1.1882	-1.4611	0.6	1.1849	-1.5165
0.7	1.2113	-3.0258	0.7	1.2079	-3.0690
0.8	1.2173	-2.3602	0.8	1.2139	-2.3924

[17, 18], which reported the experimental data for densities of binary mixture [emim][EtSO<sub>4</sub>] with ethanol and water at several temperatures. This is also consistent with the measurements of García et al. [36] which reported the effect of [emim][EtSO<sub>4</sub>] and [emim][EtSO<sub>4</sub>] with aliphatic and aromatic hydrocarbons in the binary systems.

**3.2.3. Effect of Composition on Density.** The experimental values of densities for [emim][EtSO<sub>4</sub>] with aromatic nitrogen/sulphur and water are given from Tables 6 to 11. As expected density of mixture increases with increasing mole fraction of [emim][EtSO<sub>4</sub>]. The densities for [emim][EtSO<sub>4</sub>] with PY, TS and water increases with increasing mole fraction of [emim][EtSO<sub>4</sub>] at different temperature. Further the  $n$ - $\pi$  interaction ( $n = \text{H}(\text{CH}), \text{O}, \text{N}, \text{F}$ ) [34], weak hydrogen bond interaction [6, 36], van der waals interaction [6, 36], CH- $\pi$  bond interaction [37, 38] and  $\pi$ - $\pi$  interaction [39] plays a significant role when aromatic nitrogen/sulphur is mixed with [emim][EtSO<sub>4</sub>]. The nitrogen and sulphur atom of aromatic compounds forms hydrogen bond with hydrogen in imidazolium ring or with the hydrogen located on the alkyl group of the imidazolium cation. It should be noted that the electrostatic interaction is mostly weaker between [emim] and [EtSO<sub>4</sub>] due to the ethyl substitution on the

anion structure. Due to this very fact, the density of mixture increases with increasing mole fraction of [emim][EtSO<sub>4</sub>] at different temperatures. On the other hand, it is observed that the influence of composition have an important role on the interaction between [emim][EtSO<sub>4</sub>] and neutral aromatic species like pyrrole and water. Therefore, the probable explanation lies in the fact that [emim][EtSO<sub>4</sub>] have stronger interaction with similar molecules like pyrrole than dissimilar molecules such as pyridine, indoline, quinoline, and water. Similar and dissimilar compounds imply a similarity in their structure. For example, pyrrole or thiophene has a similar five member ring structure as compared to the imidazolium ring. Thus, IL and pyrrole/thiophene possessing different electronegative atom within their structure is known to play a significant role in enhancing the solubility.

But at the same time [emim][EtSO<sub>4</sub>] posses excellent structural orientation with dissimilar structure molecules like indoline, pyridine, quinoline, and water, since there is an enormous possibility to interact with each other via  $n$ - $\pi$  interaction ( $n = \text{H}(\text{CH}), \text{O}, \text{N}, \text{F}$ ) [34], weak hydrogen bond interaction [36], CH- $\pi$  bond interaction [37, 38], and  $\pi$ - $\pi$  interaction [39]. These similar trends are observed for systems such as: [emim][EtSO<sub>4</sub>](1) + PYRR(2),



TABLE 9: Experimental Density  $\rho$  and Excess molar volume  $V_m^E$  for the binary system [emim][EtSO<sub>4</sub>](1) + Indoline(2).

$x_{IL}$	$\rho$ $\text{g} \cdot \text{cm}^{-3}$	$V_m^E$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$x_{IL}$	$\rho$ $\text{g} \cdot \text{cm}^{-3}$	$V_m^E$ $\text{cm}^3 \cdot \text{mol}^{-1}$
$T = 298.15 \text{ K}$			$T = 303.15 \text{ K}$		
0.2	1.1329	-0.0172	0.2	1.1292	-0.0269
0.3	1.1339	2.0031	0.3	1.1303	2.0157
0.4	1.1619	0.6270	0.4	1.1584	0.6174
0.5	1.1723	1.1524	0.5	1.1685	1.1981
0.6	1.1874	0.8990	0.6	1.1839	0.9101
0.7	1.1976	1.1281	0.7	1.1942	1.1446
0.8	1.2088	1.0822	0.8	1.2053	1.1021
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.2	1.1255	-0.0410	0.2	1.1212	0.0209
0.3	1.1266	2.0214	0.3	1.1229	2.0263
0.4	1.1548	0.6119	0.4	1.1512	0.5993
0.5	1.1590	1.9779	0.5	1.1542	2.1489
0.6	1.1804	0.9066	0.6	1.1769	0.8998
0.7	1.1907	1.1439	0.7	1.1873	1.1428
0.8	1.2019	1.1067	0.8	1.1985	1.1096
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.2	1.1182	-0.0716	0.2	1.1145	-0.0865
0.3	1.1193	2.0312	0.3	1.1156	2.0355
0.4	1.1477	0.5877	0.4	1.1442	0.5727
0.5	1.1486	2.4399	0.5	1.1439	2.6034
0.6	1.1735	0.8942	0.6	1.1701	0.8848
0.7	1.1839	1.1417	0.7	1.1804	1.1379
0.8	1.1951	1.1095	0.8	1.1917	1.1126

[emim][EtSO<sub>4</sub>](1) + QU(2), and [emim][EtSO<sub>4</sub>](1) + INDO(2).

**3.2.4. Effect of Composition on Surface Tension.** Table 12 presents the variation of surface tension with mole fraction for all the studied binary systems. The values of surface tension exhibit a linear increase with increasing mole fraction of [emim][EtSO<sub>4</sub>] except for water. The fusion of benzene ring or addition of benzene ring with nitrogen species has significant influence on the surface tension. Thus, quinoline and indoline (Table 12) poss higher surface tension as compared to those compounds without additional benzene ring such as pyrrole, thiophene, pyridine, and water. For [emim][EtSO<sub>4</sub>]-water mixture, the surface tension linearly decreases with an increasing mole fraction due to the decreasing strength of hydrogen bond coupled with the high difference in their surface tensions (72.1 mN·m<sup>-1</sup> for water and 48.4 mN·m<sup>-1</sup> for [emim][EtSO<sub>4</sub>]). Although the nature of alkyl substitution at [emim][EtSO<sub>4</sub>] dominates the surface tension and can define the trend of surface tension, still the ratio of van der Waals interaction [33] and columbic interaction [6, 36, 40] plays an important part upon mixing. The observed trend and values are consistent with those reported by Gomez et al. [18] and Wandschneider et al. [23]. The surface tension of aromatic nitrogen and sulphur are

lower than [EMIM][EtSO<sub>4</sub>] however; a comparison could not be done because of the scarcity of literature data. [emim][EtSO<sub>4</sub>] with aromatic nitrogen/sulphur are highly governed by the nature of their structure as well as the electronegative atom located on the studied compound and [EMIM][EtSO<sub>4</sub>] structures. The observed values decreases in the order: [emim][EtSO<sub>4</sub>] < quinoline < pyrrole < pyridine < indoline < thiophene, that is, 48.4 < 46.5 < 41.7 < 37.5 < 32.6 < 31.7. Thus, trace of water and other impurities play an important role on surface tension of [emim][EtSO<sub>4</sub>] upon mixing. Thus, by adjusting the ratio of van der Waals interaction to columbic interaction [41] one can promote higher solvation capability of [emim][EtSO<sub>4</sub>] [42].

**3.2.5. Effect of Composition on Refractive Index.** Table 12 shows the experimental refractive index over the whole composition range of [emim][EtSO<sub>4</sub>]. The refractive index decreases over the mole fraction of [emim][EtSO<sub>4</sub>] except for water mixture, where the refractive index increases with increasing mole fraction of [emim][EtSO<sub>4</sub>]. This behaviour can be explained by an efficient packing in the [emim][EtSO<sub>4</sub>]-nitrogen/sulphur mixture as compared to [emim][EtSO<sub>4</sub>]-water mixture system. Among the six binary systems, the higher refractive index was observed for [emim][EtSO<sub>4</sub>] with quinoline which indicates an increased interaction with [emim][EtSO<sub>4</sub>]. The influence

TABLE 10: Experimental Density  $\rho$  and Excess molar volume  $V_m^E$  for the binary system [emim][EtSO<sub>4</sub>](1) + Thiophene(2).

$x_{IL}$	$\rho$ g.cm <sup>-3</sup>	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$x_{IL}$	$\rho$ g.cm <sup>-3</sup>	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>
$T = 298.15\text{ K}$			$T = 303.15\text{ K}$		
0.2	1.1598	52.8065	0.2	1.1577	54.1409
0.3	1.1679	65.7820	0.3	1.1654	64.9267
0.4	1.1889	42.5225	0.4	1.1851	36.4262
0.5	1.1943	19.7579	0.5	1.1905	20.8277
0.6	1.2079	-1.3906	0.6	1.2042	-13.4828
0.7	1.2127	-5.0043	0.7	1.2092	-15.6031
0.8	1.2199	-4.6987	0.8	1.2164	-8.3316
$T = 308.15\text{ K}$			$T = 313.15\text{ K}$		
0.2	1.1531	68.7926	0.2	1.1488	53.3051
0.3	1.1615	51.8879	0.3	1.1573	61.0223
0.4	1.1811	34.8293	0.4	1.1771	36.1422
0.5	1.1866	13.4028	0.5	1.1828	16.3931
0.6	1.2005	-16.7099	0.6	1.1968	-19.9785
0.7	1.2056	-16.4008	0.7	1.2024	-20.7949
0.8	1.2129	-20.7794	0.8	1.2094	-27.23
$T = 318.15\text{ K}$			$T = 323.15\text{ K}$		
0.2	1.1442	59.7818	0.2	1.1396	60.8412
0.3	1.1527	52.3702	0.3	1.1471	60.8360
0.4	1.1732	37.8967	0.4	1.1692	33.6579
0.5	1.1789	15.5642	0.5	1.1751	17.4040
0.6	1.1931	-24.2541	0.6	1.1895	-22.6699
0.7	1.1985	-25.3382	0.7	1.1949	-36.2777
0.8	1.2059	-27.0188	0.8	1.2024	-23.0099

of an increasing mole fraction of [emim][EtSO<sub>4</sub>] on the mixture refractive index has shown that except for [emim][EtSO<sub>4</sub>] + water system, refractive index increases in the order: [emim][EtSO<sub>4</sub>] + quinoline > [emim][EtSO<sub>4</sub>] + indoline > [emim][EtSO<sub>4</sub>] + pyrrole > [emim][EtSO<sub>4</sub>] + pyridine > [emim][EtSO<sub>4</sub>] + thiophene. The ratio of van der Waals and coulombic force [41] again causes the refractive index of the mixture to decrease with increasing mole fraction of [emim][EtSO<sub>4</sub>]. Therefore, these results suggest that [emim][EtSO<sub>4</sub>] have more influence on the separation of aromatic nitrogen/sulphur rather than water. Besides, the ability of [emim][EtSO<sub>4</sub>] to create a favorable hydrogen bond with aromatic nitrogen/sulphur, significantly increases the solubility of [emim][EtSO<sub>4</sub>] in aromatic nitrogen/sulphur.

**3.2.6. Effect of Composition on Excess Molar Volume.** The excess molar volume  $V_m^E$  gives information over the net destruction of interactions and packing phenomena that appears in the mixing process [43, 44]. The excess molar volume  $V_m^E$  was calculated from experimental density data for all studied systems according to (2). These calculated values are given in Tables 6 to 11. The excess molar volume  $V_m^E$  of [emim][EtSO<sub>4</sub>] + pyrrole systems (Figure 3) system exhibits a linear trend with increasing mole fraction of [emim][EtSO<sub>4</sub>] due to insufficient amount of pyrrole in

the liquid phase. Therefore, it does not cause a volume contraction upon mixing with [emim][EtSO<sub>4</sub>] at different temperatures. It can be observed from Tables 6–11 that the excess molar volume strongly depends on composition than temperature. A similar phenomena has been observed for [BMIM][BF<sub>4</sub>] + water system by Seddon et al. [43] and [BMIM][PF<sub>6</sub>] + [BMIM][BF<sub>4</sub>] with benzene, acetonitrile, and 1-propanol at by Huo et al. [44]. It should be noted that [emim][EtSO<sub>4</sub>] produces another IL, that is, [emim][HSO<sub>4</sub>] when in contact with water molecules due to the high dissociation of ions [45, 46].

Thus, the Ionic Liquid in a mixture can be explained by two different types of interactions: (1) if the sign and magnitude of the excess molar volume is positive implies physical interaction mainly via dispersion forces or weak dipole-dipole interaction; (2) negative values refers to the chemical or specific interaction which includes charges transfer, CH- $\pi$  bond interaction  $n$ - $\pi$  interactions, formation of hydrogen bond, and so forth. The sign and magnitude of the excess molar volume is negative upon mixing with two similar aromatic structure of molecules indicates a strong  $\pi$ - $\pi$  stacking [47, 48].

**3.3. Combined Effect of Temperature and Composition on Transport Properties.** The trend in the performance of experimental data for density (Tables 6 to 11) of the

TABLE 11: Experimental density  $\rho$  and excess molar volume  $V_m^E$  for the binary system [emim][EtSO<sub>4</sub>](1) + water(2).

$x_{IL}$	$\rho$ $\text{g}\cdot\text{cm}^{-3}$	$V_m^E$ $\text{cm}^3\cdot\text{mol}^{-1}$	$x_{IL}$	$\rho$ $\text{g}\cdot\text{cm}^{-3}$	$V_m^E$ $\text{cm}^3\cdot\text{mol}^{-1}$
$T = 298.15 \text{ K}$			$T = 303.15 \text{ K}$		
0.2	1.1773	-0.3474	0.2	1.1739	-0.3179
0.3	1.1886	0.1805	0.3	1.1857	0.2208
0.4	1.2004	0.3416	0.4	1.1947	0.3714
0.5	1.1989	1.3230	0.5	1.1954	1.3729
0.6	1.2054	1.5315	0.6	1.2019	1.5756
0.7	1.2135	1.3619	0.7	1.2101	1.4004
0.8	1.2275	0.1941	0.8	1.2243	0.2051
$T = 308.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.2	1.1689	-0.2282	0.2	1.1685	-0.3429
0.3	1.1816	0.2527	0.3	1.1780	0.2814
0.4	1.1936	0.3995	0.4	1.1901	0.4261
0.5	1.1919	1.4068	0.5	1.1884	1.4413
0.6	1.1985	1.6067	0.6	1.1949	1.6365
0.7	1.2065	1.4351	0.7	1.2033	1.4387
0.8	1.2209	0.2052	0.8	1.2177	0.2079
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
0.2	1.1673	-0.4496	0.2	1.1669	-0.5882
0.3	1.1744	0.2884	0.3	1.1709	0.3079
0.4	1.1866	0.4341	0.4	1.1830	0.4529
0.5	1.1848	1.4599	0.5	1.1824	1.3913
0.6	1.1915	1.6559	0.6	1.1879	1.6839
0.7	1.1999	1.4474	0.7	1.1965	1.4652
0.8	1.2143	0.2076	0.8	1.2109	0.2097

TABLE 12: Experimental surface tension  $\sigma$ , refractive index  $nD$  for the binary systems: (a) [emim][EtSO<sub>4</sub>] + PY, (b) [emim][EtSO<sub>4</sub>] + PYRR, (c). [emim][EtSO<sub>4</sub>] + QU, (d) [emim][EtSO<sub>4</sub>] + INDO, (e) [emim][EtSO<sub>4</sub>] + TS, and (f) [emim][EtSO<sub>4</sub>] + Water at 298.15 K.

$x_{IL}$	[emim][EtSO <sub>4</sub> ] + PY		[emim][EtSO <sub>4</sub> ] + PYRR		[emim][EtSO <sub>4</sub> ] + QU	
	$\sigma/\text{mN}\cdot\text{m}^{-1}$	$nD$	$\sigma/\text{mN}\cdot\text{m}^{-1}$	$nD$	$\sigma/\text{mN}\cdot\text{m}^{-1}$	$nD$
0.2	37.2	1.4893	39.3	1.4972	41.2	1.5356
0.3	38.1	1.4867	39.9	1.4904	41.4	1.5318
0.4	39.1	1.4852	40.3	1.4867	42.5	1.5237
0.5	39.6	1.4826	40.6	1.4849	42.9	1.5003
0.6	42.4	1.4808	41.8	1.4845	43.1	1.5000
0.7	46.7	1.4799	41.9	1.4779	43.7	1.4989
0.8	47.1	1.4721	42.6	1.45779	44.5	1.4928
$x_{IL}$	[emim][EtSO <sub>4</sub> ] + INDO		[emim][EtSO <sub>4</sub> ] + TS		[emim][EtSO <sub>4</sub> ] + WATER	
	$\sigma/\text{mN}\cdot\text{m}^{-1}$	$nD$	$\sigma/\text{mN}\cdot\text{m}^{-1}$	$nD$	$\sigma/\text{mN}\cdot\text{m}^{-1}$	$nD$
0.2	41.4	1.5774	31.5	1.4736	52.6	1.4356
0.3	43.1	1.5761	36.4	1.4662	51.5	1.4516
0.4	43.6	1.5584	37.1	1.4624	50.4	1.4524
0.5	44.2	1.5581	45.6	1.4608	49.2	1.4537
0.6	44.5	1.5418	47.2	1.459	47.8	1.4562
0.7	45.2	1.5022	48.4	1.4524	47.8	1.4569
0.8	47.1	1.5006	49.0	1.443	46.2	1.4660

studied binary systems has been presented as a function of temperature and mole fraction of [emim][EtSO<sub>4</sub>]. In general for all the systems other than water, densities were found to decrease with increasing temperature. It can be seen that the variation of the thermodynamic property is much dependent on composition as compared to temperature. This can be explained by the composition of [emim][EtSO<sub>4</sub>], which plays a significant role upon mixing than temperature over the transport properties of mixtures. Water molecules are influenced by hydrogen bonding upon mixing, which is more temperature dependent; therefore, the columbic force [36] and other interaction parameters [6, 34, 35, 37–39] are negligible. The aromatic nitrogen/sulphur with [emim][EtSO<sub>4</sub>] is influenced by composition and by nature of species which are strongly recognized with several possible interaction parameters as discussed earlier and also due to the effective structural orientation of similar molecules. This behaviour is more consistent with information available in the literature [41]. Thus, it is observed that the mole fraction of [emim][EtSO<sub>4</sub>] has significant influence on the separation of aromatic nitrogen and sulphur.

**3.4. Combined Effect of Temperature and Composition on Thermodynamic Properties.** The combined effect of temperature and composition gives the information about the net destruction of interaction and packing effect for all the studied systems. The excess molar volume is negative for [emim][EtSO<sub>4</sub>](1) + PY(2) (Table 6) mixture over the entire mole fraction of [emim][EtSO<sub>4</sub>] as the temperature is raised; however, the maximum interaction occurs between  $0.4 < x_{IL} < 0.5$ . For the system [emim][EtSO<sub>4</sub>](1) + TS(2) (Table 10), a negative excess molar volume are seen when  $x_{IL} > 0.5$  irrespective of temperature. The excess molar volume and density is seen to vary linearly with respect to temperature and mole fraction for all the systems. It was thus observed that the size and shape of the components in mixture and the nature of electro negative atom located on the structure of the compounds greatly affect the thermodynamic properties.

## 4. Conclusion

The aromatic nitrogen/sulphur compounds and water were found to be completely miscible in [emim][EtSO<sub>4</sub>]. It was found that as compared to temperature, concentration [emim][EtSO<sub>4</sub>] has a greater influence on the interaction and packing effect of [emim][EtSO<sub>4</sub>] with aromatic nitrogen/sulphur and water. This is mainly due to the stronger interaction between similar structure molecules ([emim][EtSO<sub>4</sub>] + Thiophene/Pyrrole) than that between dissimilar structure molecules (i.e., [emim][EtSO<sub>4</sub>] + water mixture). The surface tension increases with increasing mole fraction of [emim][EtSO<sub>4</sub>] in the order of TS > PY > PYRR > INDO > QU. The refractive index decreases in the order: QU < INDO < PYRR < PY < TS with mole fraction. Furthermore, the excess molar properties for all the systems are negative especially at room temperature, which suggest effective packing between studied molecules. Thus, the study

reveals that [emim][EtSO<sub>4</sub>] might be a alternative solvent or the desulphurization and denitrification of diesel oil.

## Abbreviations

[emim]:	1-Ethyl-3-Methylimidazolium
[EtSO <sub>4</sub> ]:	Ethylsulphate
[emim][EtSO <sub>4</sub> ]:	1-Ethyl-3-Methylimidazolium ethylsulphate
PY:	Pyridine
PYRR:	Pyrrole
INDO:	Indoline
QU:	Quinoline
TS:	Thiophene.

## Acknowledgment

The authors are grateful to the Department of Science and Technology (DST), Government of India, for the financial support through Project SR/FTP/08-08 under the Fast Track Scheme.

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