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# Investigation on physical and electrochemical properties of three imidazolium based ionic liquids (1-hexyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide and 1-butyl-3-methylimidazolium methylsulfate)

Ali Akbar Miran Beigi<sup>a,\*</sup>, Majid Abdouss<sup>b,\*</sup>, Maryam Yousefi<sup>a,b</sup>, Seied Mahdi Pourmortazavi<sup>c</sup>, Amir Vahid<sup>a</sup>

<sup>a</sup> Research Institute of Petroleum Industry, West Blvd. of Azadi Sport Complex, Tehran, Iran

<sup>b</sup> Department of Chemistry, Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran

<sup>c</sup> Faculty of Material and Manufacturing Technologies, Malek Ashtar University of Technology, Tehran, Iran

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#### ABSTRACT

Three types of imidazolium based ionic liquids, 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIM] [BF<sub>4</sub>]), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([EMIM][NTf<sub>2</sub>]) and 1-butyl-3-methylimidazolium methylsulfate ([BMIM][MeSO<sub>4</sub>]) were prepared and a variety of their fundamental properties such as kinematic ( $\nu$ ) and dynamic ( $\eta$ ) viscosities, thermal stability, surface tension ( $\sigma$ ), refractive index ( $n_D$ ), pH and density ( $\rho$ ) were investigated as a function of temperature. The coefficients of thermal expansion ( $\alpha_p$ ) of the pure liquids were also calculated from the experimental values of the density at different temperatures. Electrochemical studies of these pure fluids as media were also studied at screen printed glassy carbon electrode (SP-GCE). The measurements were performed on a single drop of ionic liquids at surface of a screen-printed three electrode cell. The results showed an ideal wide range of potential windows for studies of electrochemical behavior of some species such as hydrogen sulfide and thiols in the lipophilic and hydrophilic ionic liquids. These properties were studied for special purposes such as development of electroanalytical methods for trace determination of organosulfur compounds in petroleum and its products.

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# 1. Introduction

Ionic liquids (ILs) are molten salts [1] composed entirely of ions, and many of them are liquids at room temperature [2–8]. Room temperature ionic liquids (RTILs), often referred to as 'designer solvents', have been the great focus of scientists in various fields since they can be tuned for specific applications [9–13]. Nowadays, the most commonly studied ILs normally contain, imidazolium, ammonium, phosphonium, pyridinium, and pyrrolidinium cations, and tetrafluoroborate, hexafluorophosphate, bistrifluorosulfonylimide and triflate anions [3,14]. The physicochemical properties of ILs can be finely tuned by slight structural changes of the corresponding cations and anions [15–17]. To better understand the nature of ionic liquids and rationally expand their applications especially as pollutant scavenger and electrolyte, knowledge of their thermophysical and electrochemical properties is required. The design of industrial processes and new products based on ILs can only be achieved when their thermophysical properties, such as viscosity, density, surface tension, refractive index, and thermal decomposition, are adequately characterized [18,19]. The lack of some properties reported for the studied ionic

\* Corresponding authors.

*E-mail addresses:* miranbeigiaa@ripi.ir (A.A. Miran Beigi), majidabdouss@yahoo.com (M. Abdouss).

liquids and also disagreement in reports were of major reasons for present work. The aim of the present work is to study the physical and electrochemical properties of three imidazolium based ionic liquids. Eco-friendly imidazolium-based ionic liquids studied in this research have been used as a catalyst and as a reaction medium in irreversible reaction of H<sub>2</sub>S to form a thermally stable, oil-soluble alkyl sulfide. They can be applied at a wide range of temperatures, from ambient up to 350 F (177 °C) [15,20]. The investigated ionic liquids included water and oil-soluble scavengers which were characterized by <sup>1</sup>H NMR and IR spectra. Oil-soluble IL scavengers were used when water tolerance of the crude petroleum is an issue. The results show that the oil-soluble ILs were ideally used for viscous heavy oils and residuals. Thus, in this paper we wish to report the results of our studies on the physical, electrochemical, thermodynamic and transport properties of 1-hexyl-3-methylimidazolium tetrafluoroborate, [HMIM][BF<sub>4</sub>], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, [EMIM][NTf<sub>2</sub>], and 1-butyl-3-methylimidazolium methylsulfate, [BMIM][MeSO<sub>4</sub>] which are historically among the most important and commonly used ILs [21–23]. Molecular structures of the three ILs are shown in Fig. 1.

The properties of these three ILs, accurately measured at atmospheric pressure and temperature from 10 to 90 °C, include density, viscosity, thermal stability, surface tension, refractive index and pH. The electrochemical stability of the ionic liquids, as electrolytes for

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Fig. 1. Chemical structures of the ionic liquids.

voltammetric purposes, was also studied at screen printed glassy carbon electrode (SP-GCE).

# 2. Experimental section

#### 2.1. Preparation of ionic liquids

All reagents and solvents were A.R. grade products of Merck (Germany), unless otherwise indicated. High purity helium and nitrogen gases were obtained from Roham Gas Co. (Tehran, Iran). Water used was freshly deionized and distilled before use. The chemicals were used without further purification. The ILs were prepared from the corresponding chlorides according to the procedures reported in literature [24-27]. Generally, 1-alkyl-3-methylimidazolium tetrafluoroborates are synthesized by ion-exchange reaction of 1-alkyl-3-methylimidazolium halide and sodium tetrafluoroborate. Another route to their synthesis is the reaction of fluoroboric acid directly with 1-alkyl-3methylimidazolium halide. This reaction also forms a gaseous HX by-product, instead of AgX, which is removed easily and high purity ILs will be obtained at high yields. This reaction also reduces the cost because fluoroboric acid is cheaper than tetrafluoroborate salts. Similarly, the synthesis of 1-butyl-3-methylimidazolium methylsulfate occurred in two steps. First, the imidazole was deprotonized using sodium ethoxide and then alkylated with the hydrocarbon chain from chlorobutane to make 1-butylimidazole. Second, dimethlysulfate was added to the 1-butylimidazole, which reacted exothermically to create 1-butyl-3-methylimidazolium methylsulfate.

A general procedure for preparation of the ionic liquid [EMIM][NTf<sub>2</sub>] was also a reaction between 1-methylimidazole and 1-bromoethane in toluene at 110 °C to form 1-ethyl-3-methylidinium bromide ([EMIM][Br]). The reaction followed by ion exchange with lithium bis(trifluoromethylsulfonyl) imide in water. The corresponding two step preparation is shown in Scheme 1. All procedures were prescribed in detail in a previous work [28]. Before use, the prepared ILs were treated by heating in a vacuum oven at  $\approx -0.1$  MPa, via a three-step process, as follows. Firstly, the samples were dried at 50 °C for 1 h, then the temperature was raised to 70 °C, and the samples were kept for

another hour. Finally the samples were kept at 105 °C for further 2 h. After cooling, the samples were kept in glass vials, closed with screw caps to ensure a secure seal and prevent humidity. The samples were taken from the vial with a syringe through a silicone septum and immediately were put into the apparatus, for further measurements. The samples were also used for characterization of the three tested ILs as shown in Fig. S1 (supporting information section).

#### 2.2. Apparatus and procedure

The density ( $\rho$ ) and dynamic viscosity ( $\eta$ ) of the ILs were measured with an automated Anton Paar SVM-3000 digital double-tube visco-densimeter. The precision in experimental measurements has been found to be better than  $\pm 2 \times 10^{-4}$  g cm<sup>-3</sup> for the density and  $\pm 1 \times 10^{-4}$  mPa s for the dynamic viscosity. The instrument was calibrated and certified by the supplier company. The calibration was checked periodically with pure liquids (supplied by Cannon Co.) with known density, dynamic and kinematic viscosity at several temperatures.

The surface tension of the ILs was measured with a KRUSS-K9 tensiometer (Germany) by the ring method. The measurement cell was thermostated in a temperature controller with a temperature stability of  $\pm 0.02$  °C, regulated in a RC6 LAUDA thermostat. The equipment has a digital control unit for precise measurements with an uncertainty better than  $\pm 0.1$  mN m<sup>-1</sup>. The equipment was calibrated and certified by the supplier. However, the calibration was checked periodically with pure liquids of known surface tension.

Electrochemical measurements were carried out by screen printed voltammetry 910 P stat mini, supplied by Metrohm Co. (Switzerland) using three electrode cell consisted of a glassy carbon working electrode and Ag plate as the reference electrode. A graphic plate was also used as counter electrode.

A simultaneous TG/DTA thermal analyzer (Perkin Elmer PYRIS Diamond) was used to study thermal stability of the ionic liquids. Approximately 20 mg of the sample and reference (Pt foil) was placed in alumina pans and heated by a rate of 10 K min<sup>-1</sup> from 25 to 600 °C. In this study, the flow rate of nitrogen as purge gas was



50 mL min<sup>-1</sup> at 1 bar. TG mass and temperature calibrations were performed prior to the experiments [29].

Refractive indices were determined by using a refractometer Model J357 supplied by Rudolph Company. The apparatus was calibrated with iso-propyl alcohol and water at different temperatures from 10 to 90 °C. A 851 Titrando, coulometric Karl Fischer apparatus supplied by Metrohm (Switzerland) was used for the determination of trace amounts of water in ILs. The coulometric cell was consisted of a two-compartment cell separated by a ceramic diaphragm. Pyridine-free catholyte and anolyte reagents were synthesized as prescribed in our previous work [28] and were used in all measurements.

Aqueous solutions with mass concentration of 0.01 g cm<sup>-3</sup> of the ILs were prepared and used for pH measurements. The pH and chloride content measurements were obtained using a CH 9101 Herisau, Ion Analysis supplied by Metrohm (Switzerland). The instrument was calibrated with different pH buffers and sodium chloride as a primary standard.

# 3. Results and discussion

# 3.1. Physicochemical properties of ILs

Due to needs for experimental data for temperature dependence of physicochemical properties of [HMIM][BF<sub>4</sub>], [EMIM][NTf<sub>2</sub>] and [BMIM][MeSO<sub>4</sub>], their density, refractive index, dynamic and kinematic viscosities, pH, and surface tension were measured over a wide temperature range of 10 to 90 °C. The experimental values are listed in Table 1. The density ( $\rho$ ), refractive index ( $n_D$ ), dynamic

#### Table 1

Density ( $\rho$ ), dynamic viscosity ( $\eta$ ), refractive index ( $n_D$ ), surface tension ( $\sigma$ ), thermal expansion ( $\alpha_p$ ), and pH of the ionic liquids at different temperatures.

T/°C	$\rho/({\rm g}~{\rm mL}^{-1})$	$\eta/(\mathrm{mPa~s})$	n <sub>D</sub>	$\sigma/(mN m^{-1})$	$10^4  \alpha_p/{ m K}$	pH of 1% solution		
[HMIM][BF <sub>4</sub> ]								
10	1.1562	608.1	1.4265	41.4	5.343			
20	1.1492	311.7	1.4241	40.6	5.525	6.41		
25	1.1461	220.0	1.4223	40.4	5.623	6.25		
30	1.1425	167.3	1.4211	40.0	5.718			
40	1.1355	103.3	1.4183	39.8	5.909	5.77		
50	1.1280	63.77	1.4158	39.0	6.104			
60	1.1214	52.22	1.4137	38.2	6.302	5.12		
70	1.1122	28.48	1.4106	37.2	6.504			
80	1.1004	21.39	1.4080	36.6	6.709	4.49		
90	1.0874	15.87	1.4051	36.3	6.918	4.17		
95	1.0838	13.92	1.4038	35.9	7.025			
[EMIN	1][NTf <sub>2</sub> ]							
10	1.5311	55.92	1.4254	40.2	4.706			
20	1.5220	37.27	1.4232	39.8	5.518	6.48		
25	1.5168	31.13	1.4220	39.4	5.929	6.5		
30	1.5117	26.28	1.4206	39.0	6.344			
40	1.5020	19.67	1.4179	38.8	7.186	6.54		
50	1.4907	14.96	1.4153	38.6	8.045			
60	1.4780	11.84	1.4127	38.0	8.925	6.60		
70	1.4651	9.506	1.4101	37.2	9.828			
80	1.4494	7.820	1.4072	36.6	10.76	6.66		
90	1.4292	6.539	1.4045	36.0	11.72	6.69		
95	1.4230	6.054	1.4033	35.5	12.21			
[BMIN	1][MeSO₄]							
10	1.2117	220.6	1.4831	46.0	4.457			
20	1.2053	122.3	1.4777	44.4	4.810	7.60		
25	1.2019	93.78	1.4771	43.7	4.988	7.55		
30	1.1983	73.35	1.4765	43.4	5.167			
40	1.1923	46.85	1.4745	42.6	5.530	7.39		
50	1.1853	32.21	1.4719	42.0	5.899			
60	1.1774	23.02	1.4694	41.2	6.274	7.18		
70	1.1668	17.05	1.4673	39.8	6.656			
80	1.1538	13.14	1.4650	39.0	7.0453	6.96		
90	1.1400	10.34	1.4626	38.1	7.443	6.85		
95	1.1356	9.257	1.4615	37.6	7.645			

viscosity ( $\eta$ ), and surface tension ( $\sigma$ ) values were fitted by the method of least squares using the following equations [30]:

$$z = A_0 + A_1 t /^{\circ} C + A_2 (t /^{\circ} C)^2$$
(1)

and

$$\ln \eta(\text{mPa s}) = A_0 / (t/^{\circ}C) - A_1$$
(2)

where z is  $\rho/(\text{g cm}^{-3})$ ,  $n_D$  or  $\sigma/(\text{mN m}^{-1})$ ,  $T/^{\circ}\text{C}$  is the temperature and  $A_0$ ,  $A_1$  and  $A_2$  are the adjustable parameters. The corresponding correlation parameters are listed in Table 2, together with their standard deviations (S.D.). The S.D. values were calculated by applying the following expression:

S.D. = 
$$\left[\sum \left(z_{exp} - z_{calc}\right)^2 / n\right]^{1/2}$$
(3)

where, *z* and *n* are the property values and the number of experimental points, respectively.

A comparison between the experimental and literature data for the physical and electrochemical properties of the studied ILs, at two temperatures (i.e., 20 and 25 °C), is also made in Table 3. Experimental data for [HMIM][BF<sub>4</sub>], [EMIM][NTf<sub>2</sub>] and [BMIM][MeSO<sub>4</sub>] are in good agreement with available literature values.

#### 3.2. Density and thermal expansion

Data on density for the ILs at temperatures ranging from 10 to 90 °C are shown in Fig. 2. As seen, the densities of [HMIM][BF<sub>4</sub>] and [EMIM][NTf<sub>2</sub>], in entire temperature range studied, and those of [BMIM][MeSO<sub>4</sub>], at temperatures lower than 55 °C are larger than corresponding water densities. It is interesting to note that the density of ILs studied decrease nearly linear with increasing temperature, but at a rate less than that for molecular organic solvents. Density data for some of studied ILs are already available in the open literature, and the relative deviations between the experimental data obtained in this work are also presented in Fig. 2 (A, B and C) and Table S1 (supporting information section).

The density data for [HMIM][BF<sub>4</sub>] are in good agreement with available literature values, the relative deviation values are ranging from 0.06 to -0.33% [31,32], and for [EMIM][NTf<sub>2</sub>], the deviations from our data and the literature are ranging from 0.13 to 0.17%

 Table 2

 Fitting parameters of Eqs. (1) and (2) and standard deviations in Eq. (3) used for correlation of the physical properties of ILs studied.

Physical property	A <sub>0</sub>	<i>A</i> <sub>1</sub>	A <sub>2</sub>	$R^2$	S.D.
[HMIM][BF <sub>4</sub> ]					
$ ho/(g mL^{-1})$	1.1627	-0.0006	$-9.0 \times 10^{-7}$	0.9997	0.0010
n <sub>D</sub>	1.4290	-0.0003	$-6.0 \times 10^{-8}$	0.9993	0.0008
$\eta/(mPa s)$	-4.2624	1976.3		0.9948	0.0238
$\nu/(mm^2 s^{-1})$	-4.2067	1942.1		0.9943	0.0240
$\sigma/(mN m^{-1})$	41.981	-0.0611	$-4.0 \times 10^{-5}$	0.9906	0.0285
$[EMIM][NTf_2]$					
$ ho$ /(g mL $^{-1}$ )	1.5366	-0.0006	$-6.0 \times 10^{-6}$	0.9991	0.0010
n <sub>D</sub>	1.4284	-0.0003	$-6.0 \times 10^{-8}$	0.9999	0.0011
$\eta/(mPa s)$	-2.4101	1165.7		0.9962	0.0064
$\nu/(mm^2 s^{-1})$	-2.4606	1126.2		0.9951	0.0065
$\sigma/(mN m^{-1})$	40.406	-0.0268	-0.0003	0.9903	0.1485
[BMIM][MeSO <sub>4</sub> ]					
$ ho/(g mL^{-1})$	1.2167	-0.0005	$2.0 \times 10^{-6}$	0.9992	0.0036
n <sub>D</sub>	1.4813	-0.0002	$-5.0 \times 10^{-7}$	0.9979	0.0011
$\eta/(mPa s)$	-3.5880	1660.3		0.9938	0.0086
$\nu/(mm^2 s^{-1})$	-3.5536	1625.9		0.9928	0.0075
$\sigma/(mN m^{-1})$	45.579	-0.063	-0.0002	0.9946	0.179

# Table 3

Experimental and literature values of densities ( $\rho$ ), refractive indices ( $n_D$ ), dynamic viscosities ( $\eta$ ), surface tensions ( $\sigma$ ), electrochemical windows ( $\Delta E$ ), thermal decomposition ( $t_d$ ) and pH of the ionic liquids at 20.0 and 25.0 °C.

Property	[HMIM][I	BF <sub>4</sub> ]			[EMIM][N	lTf <sub>2</sub> ]			[BMIM][M	/IM][MeSO <sub>4</sub> ]		
	Present work		Literature		Present work		Literature		Present work		Literature	
	20.0 °C	25.0 °C	20.0 °C	25.0 °C	20.0 °C	25.0 °C	20.0 °C	25.0 °C	20.0 °C	25.0 °C	20.0 °C	25.0 °C
$ ho/(g mL^{-1})$	1.1492	1.1461	1.1531 <sup>a</sup> 1.1485 <sup>b</sup>	1.1453 <sup>c</sup> 1.1493 <sup>d</sup> 1.1481 <sup>e</sup>	1.5220	1.5168	1.5240 <sup>f</sup> 1.5233 <sup>g</sup>	1.5190 <sup>f</sup> 1.5132 <sup>g</sup>	1.2053	1.2019	1.21295 <sup>h</sup> 1.2018 <sup>i</sup>	1.20956 <sup>h</sup>
<i>n</i> <sub>D</sub>	1.4241	1.4223	1.4292 <sup>j</sup>	1.4237 <sup>k</sup>	1.4232	1.4220	1.4235 <sup>1</sup>	1.4225 <sup>1</sup>	1.4777	1.4771	1.48076 <sup>m</sup> 1.4793 <sup>n</sup>	1.47942 <sup>m</sup> 1.4792 <sup>o</sup> 1.4782 <sup>n</sup>
$Log \eta/(mPa s)$	2.494	2.342	2.497 <sup>p</sup>	2.447 <sup>q</sup>	1.571	1.493	1.591 <sup>r</sup>	1.5051 <sup>s</sup>	2.14240	2.03574	2.461 <sup>t</sup>	2.329 <sup>t</sup>
$\sigma/(mN m^{-1})$	40.6	40.4	38.64 <sup>u</sup>	36.8 <sup>v</sup> 39.2 <sup>w</sup>	39.8	39.4	36.94 <sup>x</sup>	41.62 <sup>y</sup> 35.71 <sup>z</sup>	44.4	43.7	44.1 <sup>z(1)</sup>	43.3 <sup>z(1)</sup>
$\Delta E/V$	4.56		-		5.38		4.5 <sup>Z(2)</sup> 4 78 <sup>z(3)</sup>		5.66		-	
$t_d/^{\circ}C$	310		283 <sup>z(4)</sup> 239 <sup>z(5)</sup>		390		455 <sup>z(6)</sup> 440 <sup>z(7)</sup>		317		-	
pH 1% aqueous soln.	6.41	6.25	6.61 <sup>z(8)</sup>		6.48	6.5	-		7.60	7.55	-	

<sup>a</sup>Ref. [31], <sup>b</sup>Ref. [32], <sup>c</sup>Ref. [1], <sup>d</sup>Ref. [31], <sup>e</sup>Ref. [52], <sup>f</sup>Ref. [33], <sup>g</sup>Ref. [35], <sup>h</sup> Ref. [36], <sup>i</sup>Ref. [37], <sup>j</sup>Ref. [53], <sup>k</sup>Ref. [54], <sup>l</sup>Ref. [42], <sup>m</sup>Ref. [17], <sup>n</sup>Ref. [44], <sup>o</sup>Ref. [43], <sup>p</sup>Ref. [31], <sup>q</sup>Ref. [55], <sup>r</sup>Ref. [38], <sup>s</sup>Ref. [56], <sup>k</sup>Ref. [56], <sup>k</sup>Ref. [57], <sup>k</sup>Ref. [58], <sup>y</sup>Ref. [59], <sup>z</sup>Ref. [59], <sup>z</sup>Ref. [60], <sup>z(1)</sup>Ref. [17], <sup>z(2)</sup>Ref. [61], <sup>z(3)</sup>Ref. [62], <sup>z(4)</sup>Ref. [56], <sup>z(5)</sup>Ref. [1], <sup>z(6)</sup>Ref. [63], <sup>z(7)</sup>Ref. [64], <sup>z(8)</sup>Ref. [65], <sup>z(6)</sup>Ref. [57], <sup>k</sup>Ref. [58], <sup>y</sup>Ref. [59], <sup>z</sup>Ref. [60], <sup>z(1)</sup>Ref. [17], <sup>z(2)</sup>Ref. [61], <sup>z(3)</sup>Ref. [62], <sup>z(4)</sup>Ref. [56], <sup>z(5)</sup>Ref. [1], <sup>z(6)</sup>Ref. [63], <sup>z(7)</sup>Ref. [64], <sup>z(8)</sup>Ref. [65], <sup>z(6)</sup>Ref. [57], <sup>k</sup>Ref. [58], <sup>y</sup>Ref. [58], <sup>y</sup>Ref. [59], <sup>z</sup>Ref. [59], <sup>z</sup>Ref. [50], <sup>z(1)</sup>Ref. [61], <sup>z(3)</sup>Ref. [62], <sup>z(4)</sup>Ref. [56], <sup>z(5)</sup>Ref. [1], <sup>z(6)</sup>Ref. [63], <sup>z(7)</sup>Ref. [64], <sup>z(8)</sup>Ref. [65], <sup>z(6)</sup>Ref. [57], <sup>k</sup>Ref. [58], <sup>y</sup>Ref. [58], <sup>y</sup>Ref. [58], <sup>y</sup>Ref. [58], <sup>z(6)</sup>Ref. [58], <sup>z(6)</sup>Ref. [58], <sup>z(7)</sup>Ref. [58], <sup>z(7)</sup>Ref. [58], <sup>z(7)</sup>Ref. [58], <sup>z(8)</sup>Ref. [59], <sup>z(8)</sup>Ref. [59], <sup>z(8)</sup>Ref. [50], <sup>z(4)</sup>Ref. [50], <sup>z(4)</sup>Ref. [56], <sup>z(4)</sup>Ref. [56], <sup>z(5)</sup>Ref. [1], <sup>z(6)</sup>Ref. [63], <sup>z(7)</sup>Ref. [64], <sup>z(8)</sup>Ref. [56], <sup>z(6)</sup>Ref. [56], <sup>z(6)</sup>Ref. [56], <sup>z(6)</sup>Ref. [56], <sup>z(6)</sup>Ref. [56], <sup>z(6)</sup>Ref. [57], <sup>z(8)</sup>Ref. [58], <sup>z</sup>



**Fig. 2.** Comparison of density data for [HMIM][BF<sub>4</sub>] (A): ( $\blacklozenge$ ) this work; ( $\blacklozenge$ ) Seddon et al. [31]; ( $\blacktriangle$ ) Taguchi et al. [32], for [EMIM][NTf<sub>2</sub>] (B): ( $\blacklozenge$ ) this work; ( $\blacklozenge$ ) Tokuda et al. [33]; ( $\bigstar$ ) Yao et al. [35], for [BMIM][MeSO<sub>4</sub>] (C): ( $\blacklozenge$ ) this work; ( $\blacklozenge$ ) Fernandez et al. [36]; ( $\bigstar$ ) Sanchez et al. [37].

[33–35], and for [BMIM][MeSO<sub>4</sub>], the deviations are ranging from 0.2 to -0.6% [36,37].

The coefficients of thermal expansion for [HMIM][BF<sub>4</sub>], [EMIM] [NTf<sub>2</sub>] and [BMIM][MeSO<sub>4</sub>] are defined by the following equation:

$$\begin{aligned} \alpha_p &= -1/\rho \Big( \mathrm{g.cm^{-3}} \Big) \Big( \partial \rho \Big( \mathrm{g.cm^{-3}} \Big) / \partial \big( t/^\circ \mathrm{C} \big) \Big) p \end{aligned} \tag{5}$$
$$= - \Big( A_1 + 2A_2(t/^\circ \mathrm{C}) \big) / A_0 + A_1 \Big( t/^\circ \mathrm{C} \big) + A_2 \big( t/^\circ \mathrm{C} \big)^2 \Big), \end{aligned}$$

where,  $\alpha_p$  is the coefficient of thermal expansion,  $\rho$  is the IL density, and  $A_0$ ,  $A_1$  and  $A_2$  are the adjustable parameters calculated in Eq. (1). The thermal expansion coefficients for each of ILs at several temperatures are summarized in Table 1, and temperature dependence of the  $\alpha_p$  values is illustrated in Fig. S2 (supporting information section). The  $\alpha_p$  values at 25 °C are 5.623, 5.929, and  $4.988 \times 10^{-4}$  °C<sup>-1</sup> for [HMIM] [BF<sub>4</sub>], [EMIM][NTf<sub>2</sub>] and [BMIM][MeSO<sub>4</sub>], respectively. The results show that the variation of the volume expansivity quantified by the thermal expansion coefficient could be considered as independent of the temperature for these ILs.

#### 3.3. Viscosity

Data on viscosity for the ILs at temperatures ranging from 10 to 90 °C are also shown in Fig. 3. Unfortunately, the high viscosity of ILs will negatively affect most of their operational processes [34]. Since the viscosities of ILs are governed essentially by van der Waals interactions and H-bonding and, thus, an increased alkyl chain length and presence of bulkier side chains, which can reduce the rotational freedom of molecules, or use of organofluoroanions makes the salt more viscous, as can be seen from Table 1. On the other hand, it is obvious that the ionic liquids with larger cations ([HMIM]<sup>+</sup>>[BMIM]<sup>+</sup>>[EMIM]<sup>+</sup>) show higher dynamic and kinematic viscosities.

As is obvious from Fig. 3, the viscosity of ILs will decrease more or less exponentially with increasing temperature. The empirical Eq. (2) is thus applicable to describe the temperature dependence of the viscosity of ionic liquid systems. On the other hand, the presence of a more planar structure is known to result in less viscosity because the planarity allows relatively facile slip between molecules.

Muhammad et al. [1] reported temperature dependence of viscosity and density for dried [HMIM][BF<sub>4</sub>] with its chloride and water impurities. Some large deviations were due essentially to the salt



**Fig. 3.** Temperature dependence of kinematic viscosity  $(\nu, \blacktriangle)$  and dynamic viscosity  $(\eta, \blacklozenge)$  for [HMIM][BF<sub>4</sub>] (A), [EMIM][NTf<sub>2</sub>] (B) and [BMIM][MeSO<sub>4</sub>] (C). Comparison of viscosities as a function of temperature (K) for [HMIM][BF<sub>4</sub>] (A) ( $\blacklozenge$ ) this work; ( $\Box$ ) Seddon et al. [31], for [EMIM][NTf<sub>2</sub>] (B): ( $\blacklozenge$ ) this work; ( $\Box$ ) Tokuda et al. [38]; (+) Camper et al. [39], for [EMIM][MeSO<sub>4</sub>] (C): ( $\blacklozenge$ ) this work; ( $\Box$ ) Pereiro et al. [43]; (+) Fernandez, A. et al. [36].

impurities especially halides. We have reported some of impurities available in our studied RTILs in Table 4, and their characterization in the supporting information section. However, excellent agreements were observed for [HMIM][BF<sub>4</sub>] [32] and [EMIM][NTf<sub>2</sub>] [38,39] when comparing experimental viscosities with available literature values. Fig. 3 (A, B and C) shows comparison of viscosity as function of temperature. [HMIM][BF<sub>4</sub>] viscosity values were lower (within 0.1%) than those of Seddon et al. [31]. Positive deviations (ranging from 0.12 to 1.2%) for dynamic viscosity were also observed for [EMIM][NTf<sub>2</sub>] when compared with Seddon et al. [31] and Tokuda

#### Table 4

Impurity contents of the studied ILs.

Species	Test method	Results		
		[HMIM] [BF <sub>4</sub> ]	[EMIM] [NTf <sub>2</sub> ]	[BMIM] [MeSO <sub>4</sub> ]
Water content <sup>a</sup> , mass%	Karl Fischer	0.017	0.026	0.194
Total chlorine, mass%	Flask combustion	< 0.25	< 0.25	< 0.25
Chloride, ppm	Potentiometry	<10	<10	<10
Bromide, ppm	Potentiometry	<10	<10	<10
Sulfate, ppm	Turbidimetry	<5.0	<5.0	<5.0
Heavy metals (as Pb), ppm	Turbidimetry	< 0.2	<0.2	<0.2
Ash content, mass%	Electric furnace	< 0.001	< 0.001	< 0.001
	and gravimetry			

<sup>a</sup> The water content results are obtained after drying treatment described in the Experimental section.

et al. [33]. The deviations can be due essentially to the salt's impurities including water and halide content and also to the experimental technique adopted.

## 3.4. Surface tension

Available data on the surface tension of the studied ILs are very limited. In general, the liquid/air surface tension values for ILs are somewhat higher than conventional solvents such as hexane (18 mN m<sup>-1</sup>), but not as high as water (73 mN m<sup>-1</sup>). The temperature dependence of surface tension ( $\sigma$ ) for the ionic liquids studied is shown in Fig. 4. As seen, for imidazolium derivatives [HMIM][BF4], [EMIM][NTf2] and [BMIM][MeSO4], the surface tension decreases with increasing lipophilic property of the ILs. It is necessary to say that only two reports were found in the survey on the literature for pure [HMIM][BF4].

# 3.5. Refractive index and pH

The refractive index of a substance describes its ability to refract light as it moves from one medium to another and, therefore, the higher the refractive index of a compound, the more the light refracted. For most practical purposes, a high refractive index is considered to be a value greater than 1.4 (i.e., above the range of most common organic materials).

As an application, in order to non-destructively locate inclusions in unpolished diamonds and other minerals by optical means, it is desirable to immerse these minerals in a fluid with the same refractive index [40]. Unfortunately, however, many available high refractive index immersion compounds, such as  $Asl_3$  (RI = 2.2) or  $SnI_4$  (RI = 2.1), are solid at room temperature, poisonous, unstable, and extremely unpleasant. Diiodomethane saturated with sulfur is another commercially available high refractive index (RI = 1.78) room temperature liquid, but this is also a harmful material [41]. Since the physical properties of ionic liquids (as green alternative compounds) can be tuned by varying their cationic and/or anionic parts, it is possible to develop immersion fluids for mineralogical studies which are relatively benign.

Fig. 5 shows temperature dependence of refractive index for the studied ILs as a set of fluids which have been designed to have refractive indices > 1.4, and also possess low environmental impact and good shelf life. As can be seen from Fig. 5, for all three ILs, the refracted index linearly decreases with increasing temperature. It is noteworthy that, in all ranges of temperatures, the ILs used possess refractive indices > 1.4. In survey on the literature, only one literature was found for comparing refractive index data for [EMIM][NTf<sub>2</sub>] [42] in a wide range of temperature. Fig. 5 also shows comparison of experimental refractive indices with the literature for [EMIM][NTf<sub>2</sub>] and [BMIM][MeSO<sub>4</sub>]. The refractive index data obtained were slightly lower (within 0.02-0.03%) than Tariq et al. [42] for [EMIM][NTf<sub>2</sub>] and lower (within 0.07-0.2%) than Pereiro et al. [43] and Singh et al. [44].



**Fig. 4.** Temperature dependence of surface tension ( $\sigma$ ) for [HMIM][BF<sub>4</sub>]: ( $\blacklozenge$ ) this work; ( $\blacklozenge$ ) Ghatee, M.H. et al. [55], for [EMIM][NTf<sub>2</sub>]: ( $\blacktriangle$ ) this work, for [BMIM][MeSO<sub>4</sub>]: ( $\blacklozenge$ ) this work; ( $\varkappa$ ) Pereiro et al. [43].



**Fig. 5.** Plots of temperature dependence of experimental values of refractive indices  $(n_D)$  of [HMIM][BF<sub>4</sub>] ( $\blacklozenge$ ) this work (synthesized sample); ( $\bigcirc$ ) this work (Aldrich sample); [EMIM][NTf<sub>2</sub>] ( $\blacklozenge$ ) this work; ( $\aleph$ ) Tariq et al. [42], [BMIM][MeSO<sub>4</sub>] ( $\blacktriangle$ ) this work; ( $\blacklozenge$ ) Pereiro et al. [43]; (+) Singh et al. [44].

Owing to the fact that the presence of impurities can significantly affect some properties of the ILs such as refractive index, pH and electrochemical window, we measured several common impurities in the prepared ILs and the results are summarized in Table 4. In the case of pH, It is well documented that many chemical reactions are sensitive to pH values, that is, the yield of products and even the nature of the products may be altered appreciably if the pH changes significantly during the course of reaction. This is especially true in biochemical reactions where the pH is important to the proper metabolism and functioning of animals and plants.

Since ILs, as a new class of buffers, can maintain the apparent pH for a non-aqueous system at an optimum value, it was useful to provide the pH values and temperature dependence of ILs used in this experiment. The temperature effect on pH appears to be almost negligible as shown in Fig. S3 (supporting information). Although the pH values provided by the literature (Table 3) are almost the same for all the ionic liquids investigated, these values are misleading, as most pH meters are only suitable for determining the proton concentrations of the aqueous liquids, not those of novel liquids like ionic liquids. We recommend to measure pH of defined solutions of ILs (i.e., 1% aqueous solution for hydrophilic and intermediate ILs), and saturated solutions of the lipophilic ILs, or measurement by using a universal non-aqueous glass electrode.

#### 3.6. Thermal analysis studies

Data on the thermal behavior of ionic liquids such as ([HMIM][BF<sub>4</sub>]), ([EMIM][NTf<sub>2</sub>]), and ([BMIM][MeSO<sub>4</sub>]) is required in order to obtain thermal stability information for their use in chemical process, development of contacting equipments and storage conditions [45,46]. Thermal analysis has an important role in the characterization and determination of thermal stability of novel materials such as ionic liquids [47]. Therefore, thermal properties of the investigated ionic liquids have been characterized by TG/DTG/DTA techniques. Thermograms of the studied ILs, ([HMIM][BF<sub>4</sub>]), ([EMIM][NTf<sub>2</sub>]), and ([BMIM][MeSO<sub>4</sub>]), are shown in Fig. S4 (supporting information section).

The TG/DTG and DTA curves of [HMIM][BF<sub>4</sub>] (Fig. S4a) showed no thermal event before 300 °C, which confirms that this ionic liquid is thermally stable in the temperature range of 25–300 °C. Above this temperature DTA curve shows that the sample undergoes an endothermal phenomenon during temperature range of about 310–500 °C; which corresponds to the thermal decomposition of [HMIM][BF<sub>4</sub>]. The maximum DTA peak temperature for thermal decomposition of this ionic liquid was observed at 452 °C. Meanwhile, the TG/DTG curves of [HMIM][BF<sub>4</sub>] show a significant mass loss over this broad temperature range (310 to 500 °C), with  $\Delta m = 98\%$ .

Table 5	
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Summary of TG/DTG/DTA results for investigated ionic liqu
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Ionic liquid	Maximum DTA peak T/°C	Decomposition T-Range/°C	Mass loss/∆m%
[HMIM][BF <sub>4</sub> ]	452	310-500	98
[EMIM][NTf <sub>2</sub> ]	418	390-510	94
[BMIM][MeSO <sub>4</sub> ]	383	317-438	92

Therefore, TG/DTG curves confirm DTA data that shows main thermal decomposition of the ionic liquid sample happened in this temperature range.

The DTA and TG/DTG curves of [EMIM][NTf<sub>2</sub>] (Fig. S4b) show that this ionic liquid is thermally stable up to about 380 °C. However, at higher temperatures, TG/DTG curves for [EMIM][NTf<sub>2</sub>] present a significant mass loss step between 390 and 510 °C, with  $\Delta m = 94\%$ . DTA curve exhibits an exothermal event in this temperature range and minimum DTA peak temperature for this ionic liquid was observed at 418 °C. Over 510 °C, the TG/DTG/DTA curves indicate no considerable thermal event for this sample.

The DTA and TG/DTG curves for [BMIM][MeSO<sub>4</sub>] are shown in Fig. S4c. As is obvious from the DTA curve, a main thermal decomposition occurred above 310 °C, where the ionic liquid sample undergoes an endothermic decomposition. This result agrees with the corresponding TG/DTG curves for this sample. The mass loss ( $\Delta m = 92\%$ ) occurs in the temperature range of 310–440 °C. Such thermal pattern suggests that [BMIM][MeSO<sub>4</sub>] is thermally stable until 300 °C. However, a small mass loss was observed in the temperature about 250 °C; which is due to the trace amounts of water remained in the ionic liquid sample. The thermoanalytical data given in Table 5 for the studied ionic liquids in this investigation shows the following thermal stability order: [EMIM][Mrf<sub>2</sub>]>[BMIM][MeSO<sub>4</sub>] ≥ [HMIM][BF<sub>4</sub>].

# 3.7. Electrochemical window

The electrochemical window is defined as the potential interval observed between the reduction potential of the organic cationic part and the oxidation potential of the anionic part of pure ILs. A wide electrochemical window makes ILs promising electrolytes for electrochemical power applications. Most ILs possess a wide potential window of > 4.0 V. It has been found that, for some ionic liquids, the potential of anode limit proportionally decreases with increasing highest occupied molecular orbit energy calculated for the anion [48]. It has also been shown that the quantum chemical calculations are an excellent tool to predict the electrochemical window of ionic



**Fig. 6.** Cyclic voltammograms of the purified tested ionic liquids. Conditions: quasireference electrode, Ag wire; working electrode, SP-GCE (O.D. 2.2 mm); temperature, 25 °C; scan rate, 100 mV s<sup>-1</sup>.



**Fig. 7.** Square wave voltammogram (SWV) of hydrogen sulfide and ethanethiol in pure [EMIM][NTf2] (A) and blank sample (B); working electrode, SP-GCE (O.D. 2.2 mm); temperature, 25  $^{\circ}$ C; scan rate, 100 mV s<sup>-1</sup>.

liquids, which can be correlated to the calculated difference in energy level of LUMO of the cation (reductive stability) and HOMO of the anion (oxidative stability) [49,50].

Furthermore, these calculations can be used to predict the possible electrochemical breakdown products of ionic liquids. On this basis in the electrochemical breakdown of [EMIM][NTf<sub>2</sub>], 1-ethyl-3-methylimidazolium radicals are formed, which can react with each other via a radical-radical coupling reaction as well as a disproportionation reaction.

In this work, the electrochemical windows of the investigated ILs were experimentally obtained using cyclic voltammetric studies at a SP-GCE and using a Ag wire as a quasi-reference electrode, as shown in Fig. 6. As can be seen, the electrochemical windows for the ILs studied are ranging from about 4 V to 6 V, and decrease in the order [BMIM][MeSO<sub>4</sub>]>[EMIM][NTf<sub>2</sub>]>[HMIM][BF<sub>4</sub>].

Moreover, we also carried out the quantitative experiments to develop new method for simultaneous determination of hydrogen sulfide and thiol group in the studied ILs. Unfortunately standard methods, such as UOP-163 [51], suffer from interfering constituents in the sample matrix and are time-consuming, using large sample size and toxic solvents, while the present technique describes a sensitive and selective method based on square wave voltammetry (SWV) on only one single drop of ionic liquid. Fig. 7 shows SWV voltammogram of hydrogen sulfide and ethanethiol in pure [EMIM] [NTf<sub>2</sub>] by using SP-GCE. Although the analytes were electroactive in all three ILs, well-defined individual reversible peaks were observed at -0.2530 V and 0.2634 V in [EMIM][NTf<sub>2</sub>], which were due to the oxidation of H<sub>2</sub>S and ethanethiol, respectively. Other inherent advantages of [EMIM][NTf<sub>2</sub>] are hydrophobic property and electrochemical stability as a solvent for organic and even inorganic compounds. Since this ionic liquid has a very low viscosity and is thermally stable, it can easily be dried under high vacuum at 100 °C. Water contents below 50 ppm can be reached very easily, which makes [EMIM][NTf<sub>2</sub>] an ideal ionic liquid for electrochemistry.

# 4. Conclusion

The data of physical properties on ionic liquids are essential for both theoretical research and industrial application. The establishment of a database will definitely promote research and development of ionic liquids. Thus, here, we carefully measured several important properties of ionic liquids 1-hexyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide and 1-butyl-3-methylimidazolium methylsulfate in a wide range of temperature. So, more attention should be paid on the measurement of physicochemical properties of ionic liquids. Also because of inherent advantages of the ionic liquids, such as a scavenger for some environmental pollutants (i.e. hydrogen sulfide), we considered to study some important properties like thermal decomposition, thermal expansion, electrochemical window, solubility, pH and water content more than the others. These properties will be used for objectives in our further researches.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.molliq.2012.10.025.

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