Synthesis and characterization of physicochemical properties of hydrophilic imidazolium-based ionic liquids

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Abstract−A series of ionic liquids based on Octyl and Decyl methylimidazolium with different anions such as chloride, glycinate, dihydrogen phosphate and trihydrogen diphosphate, were synthesized and characterized by ^{1}HNMR and elemental analysis. IL containing trihydrogen diphosphate anion, was synthesized for the first time. Physicochemical properties, including density, viscosity, surface tension, refractive index, and pH, were measured in temperature range 283.15 to 363.15 K and atmospheric pressure. The effects of temperature, alkyl chain, and anion type on physicochemical properties were investigated. The results revealed that the physicochemical properties decreased as a function of temperature. Unlike viscosity, other properties, such as density, surface tension, refractive index and pH values, decreased, while alkyl chain length increased. Understanding ILs properties and determining their unique abilities helps researchers to use them in new applications. These long alkyl chain ILs, are being used as surfactants to reduce Oil/Water interfacial tension in EOR process.

Keywords: Hydrophilic Ionic Liquids, Physicochemical Properties, 1-Octyl3-methylimidazolium Based Ionic Liquids, Temperature Dependence

INTRODUCTION

Ionic liquids (ILs) are organic salts completely composed of ions which have been a favored ecofriendly choice for researchers in contrast to common solvents, during the last decade [1-3]. Due to their unique physiochemical properties e.g., having very low vapor pressure, low melting point, high ionic conductivity [4-7], high thermal and chemical stabilities and non-flammability [8], ILs have been increasingly investigated in many fields such as oil industry [9-11], biotechnology, material science [12,13], electrochemistry, novel solvents, separation technology [14-18], catalysis, fuel cells, nanotechnology [19,20]. Employing ionic liquids in the oil industry is widespread, from the deposition of asphaltene and paraffin to dehydration and desalting of crude oil [9] and enhanced oil recovery [21]. Long alkyl chain ILs, exhibit characteristics of cationic surfactants (long carbon chain substituents appended to a charged cationic head group) [22]. Nowadays, dialkylimidazolium based ILs are mostly studied, in contrast to the past. Attempts in preparation of pure and halogen free imidazolium based ILs have been made by numerous researchers [23,24]. This type of ILs can be produced by the quaternization of alkylimidazoles with a suitable alkylation agent [25]. The physicochemical properties, such as viscosity, density, thermal stability, melting point, and solubility behaviors, can be tuned by slight structural changes of the corresponding cation, anion and alkyl chain length [26,27]. Use of ILs in various fields, requires investigation in their physicochemical properties. It is hoped that the data on physicochemical properties of investigated ILs, can be used by scientists to apply them in various industries such as chemical, pharmaceutical and medical instead of toxic solvents.

The aim of the present work was to synthesize and study the physicochemical properties of four imidazolium based ionic liquids having the same cation (1-Octyl-3-methylimidazolium) but different anions (Cl^-, Gly, $H_2PO_4^-$ and $H_3P_2O_7^-$) and 1-Decyl-3-methylimidazolium with Cl^- anion. The five hydrophilic ILs namely 1-Octyl-3-methylimidazolium chloride [C_8mim][Cl], 1-Octyl-3-methylimidazolium Glycinate [C_8mim][Gly], 1-Octyl-3-methylimidazolium dihydrogen phosphate [C_8mim][DHP], 1-Octyl-3-methylimidazolium Trihydrogen diphosphate [C_8mim][THDP] and 1-Decyl-3-methylimidazolium Chloride [C_{10}mim][Cl] were synthesized and characterized using ^{1}HNMR and elemental analysis CHNO.

The physicochemical properties for these ILs were studied as a function of cation or anion type and temperature. There is a limited number of studies of experimental physicochemical data for synthesized ILs. Among these ionic liquids, [C_8mim][THDP] has not yet been synthesized. All of these ILs are expected to be used as surfactants in water injection process in EOR. Water injection process is faced with many problems, such as formation damage which is caused by the confluence of injected water and formation water in reservoir. In general, phosphate containing species and chemicals such as diphosphoric acid, polyphosphoric acid, and EDTA are used as inhibitors to solve this problem. In this research work, we tried to synthesize the task specific ILs that are used as surfactant and anti-scalene. Molecular structures of the synthesized ILs are shown in Fig. 1.

The ILs properties, accurately measured at atmospheric pres-

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Ionic Liquid	Cation part	Anion part	Abbreviation	Formula	M.W (g/mol)
1-Octyl-3-methylimidazolium chloride		Cl^-	[C$_8$mim][Cl]	$C_{12}H_{23}ClN_2$	230.78
1-Octyl-3-methylimidazolium glycinate			[C$_8$mim][Gly]	$C_{14}H_{27}N_3O_2$	269.4
1-Octyl-3-methylimidazolium dihydrogen phosphate			[C$_8$mim][DHP]	$C_{12}H_{25}N_2O_4P$	292.312
1-Octyl-3-methylimidazolium threehydrogen diphosphate			[C$_8$mim][THDP]	$C_{12}H_{26}N_2O_7P_2$	372.29
1-Decyl-3-methylimidazolium Chloride		Cl^-	[C$_{10}$mim][Cl]	$C_{14}H_{27}ClN_2$	258.2

Fig. 1. Chemical structures of the synthesized ionic liquids.

sure and temperature from 283.15 K to 363.15 K, include density, viscosity, surface tension, refractive index and pH.

EXPERIMENTAL SECTION

1. Materials

All starting materials and solvents were used as received without any further treatment, except for 1-methyl imidazole, 1-chlorooctane and 1-chlorodecane which was distilled before use. These materials included 1-methylimidazole (Merck, ≥99%), 1-chlorooctane (Merck, ≥98%), 1-chlorodecane (Merck, ≥98%), pyrophosphoric acid (Aldrich, technical grade), phosphoric acid (Merck, 85%), glycine (Aldrich, ≥98.5%), diethyl ether (Merck, ≥99%), silver nitrate (Merck, ≥99%), ethanol (Merck, ≥96%), potassium hydroxide (Merck, ≥99%), methanol (Merck, ≥99%), acetonitrile (Merck, ≥99%) and strongly basic anion exchanger, OH^- form (Merck). Nitrogen gas with high purity was prepared from Roham Gas Co. (Tehran, Iran). Water used was freshly deionized and distilled before use.

2. Apparatus and Procedure

The structures of synthesized ILs were identified by NMR (Bruker Avance 500 MHz spectrometer) and elemental analysis CHNO (Vario max, Elementar, Germany).

The density and viscosity was measured at atmospheric pressure and temperature range 283.15 K to 363.15 K, using an automated Anton Paar SVM-3000 digital double-tube visco-densimeter. The calibration was checked periodically with pure liquids (supplied by Cannon Co.) with known density and viscosity at several temperatures. The measurement uncertainty was estimated to be ±0.02% and ±0.01% for the density and viscosity, respectively.

Surface tension was measured using a KRUSS-K9 tensiometer (Germany) by the ring method. The measurement cell was ther-

mostated in a temperature controller with a temperature stability of ±0.02 K, regulated in a RC6 LAUDA thermostat. The precision of measurements was 0.1 mN·m^{-1}. The equipment was calibrated and certified by the supplier.

Refractive indices of synthesized samples were measured by using a refractometer Model J357 supplied by Rudolph Company. The apparatus was calibrated with isopropyl alcohol and water at different temperatures from 283.15 K to 363.15 K.

Water content measurement was by 851 Titrando, coulometric Karl Fischer apparatus supplied by Metrohm (Switzerland).

1% (W/V) solution of ionic liquids were prepared to measure the pH values. The pH and chloride content were measured by 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. Preparation of Ionic Liquids

3-1. 1-Octyl-3-methilimidazolium Chloride [C$_8$mim][Cl], 1-Decyl-3-methylimidazolium Chloride [C$_{10}$mim][Cl]

1-Methylimidazole (0.1 mol) and excess amount of 1-doroalkane (1-chlorooctane or 1-chlorodecane) (0.11 mol) were mixed without any additional solvent. The reaction mixture was heated and continually stirred at 343.15 K for 72-96 h in a round bottomed flask, fitted with a reflux condenser, under N$_2$ atmosphere. It was then cooled to room temperature and washed thrice with 50 ml diethyl ether to remove excess starting material. The resulting products were dried under vacuum at 333.15 K for 48 h to find slightly yellow [C$_8$mim][Cl] and colorless [C$_{10}$mim][Cl] viscous liquids [28]. Water content was 640 ppm and 480 ppm for [C$_8$mim][Cl] and [C$_{10}$mim][Cl], respectively. White AgCl precipitation was seen when AgNO$_3$ was tested, so, no further purification was required.

The synthesized ILs were characterized by ^{1}HNMR and CHNO elemental analysis, to prove the absence of impurities.

[C$_8$mim][Cl]: ^{1}HNMR (500 MHz, D$_2$O): δH=8.606 (1H, s), 7.36 (1H, s), 7.322 (1H, s), 4.048 (2H, t), 3.775 (3H, s), 1.724 (2H, m), 1.24-1.1 (10H, m), 0.745 (3H, t), elemental analysis for C$_{12}$H$_{23}$ClN$_2$ (230.78 g/mol), Calcd. (100×mass fraction): C: 62.45; H: 10.04; N: 12.14. Found (100×mass fraction): C: 62.33; H: 10.11; N: 11.98.

[C$_{10}$mim][Cl]: ^{1}HNMR (500 MHz, D$_2$O): δH=9.29 (1H, s), 7.76 (1H, s), 7.72 (1H, s), 4.15 (2H, t), 3.8 (3H, s), 1.72 (2H, m), 1.23 (14H, m), 0.82 (3H, t), elemental analysis for C$_{14}$H$_{27}$ClN$_2$ (258.83 g/mol), Calcd. (100×mass fraction): C: 64.96; H: 10.51; N: 10.82. Found (100×mass fraction): C: 64.8; H: 10.7; N: 10.72.

3-2. 1-Octyl-3-methylimidazolium Glycinate [C$_8$mim][Gly]

1-Octyl-3-methilimidazolium chloride was dissolved in deionized water and passed through an anion-exchange column filled with strongly basic anion exchanger resin, OH$^-$ form. A dilute solution of 1-octyl-3-methylimidazolium hydroxide was collected from the column. Then [C$_8$mim][OH] was added dropwise to excess amount of glycine and stirred for 12 h; the mixture was dried in a rotary evaporator at 333.15 K. The resulting IL was dissolved in acetonitrile:methanol (9 : 1) to precipitate unreacted glycine. The solution was filtered and dried in a rotary evaporator for remove all solvents. Finally, [C$_8$mim][Gly] was dried in a vacuum for 48 h [29]. The water content was about 500 ppm.

^{1}HNMR (500 MHz, CDCl$_3$): δH=8.79 (1H, s), 7.71 (1H, s), 7.65 (1H, s), 4.17 (2H, t), 3.81 (3H, s), 3.21 (2H, s), 2.98 (2H, s), 1.78 (2H, m), 1.2 (10H, m), 0.84 (3H, s), elemental analysis for C$_{14}$H$_{27}$N$_3$O$_2$ (269.4 g/mol), Calcd. (100×mass fraction): C: 62.42; H: 10.10; N: 15.6; O: 11.88. Found (100×mass fraction): C: 62.58; H: 10.07; N: 14.99; O: 11.82.

3-3. 1-Octyl-3-methylimidazolium Dihydrogen Phosphate [C$_8$mim][DHP]

0.1 mol of [C$_8$mim][Cl] and 0.15 mol of KOH were dissolved in 30 and 45 ml ethanol, respectively. Then KOH solution was added dropwise to the [C$_8$mim][Cl] solution in a round bottomed flask equipped with magnet stirrer, and KCl white precipitate was immediately observed. When all the KOH solution was added, the resulting mixture was stirred for another 5 min to ensure that the reaction was complete. [C$_8$mim][OH] solution in ethanol was obtained by filtering the reaction mixture to remove all KCl participation [30]. 0.33 mol of phosphoric acid per mol KOH was dissolved in water

and added to the [C$_8$mim][OH] solution. All the active protons of H$_3$PO$_4$ were neutralized to generate [C$_8$mim]$_3$PO$_4$ and K$_3$PO$_4$. Then, another 0.66 mol H$_3$PO$_4$ per mol of [C$_8$mim][OH] was added in two steps to obtain [C$_8$mim][DHP]. Finally, the IL was dried in a rotary evaporator and vacuum oven, respectively, to remove all solvents and water. The measured water content was 315 ppm for the Pale yellow viscous IL.

^{1}HNMR (500 MHz, CDCl$_3$): δH=9.04 (1H, s), 7.78 (1H, s), 7.82 (1H, s), 4.12 (2H, t), 3.88 (3H, s), 1.70 (2H, m), 1.16 (10H, m), 0.79 (3H, s), elemental analysis for C$_{12}$H$_{26}$N$_2$O$_7$P$_2$ (292.312 g/mol) Calcd. (100×mass fraction): C: 49.31; H: 8.62; N: 9.58; O: 21.89. Found (100×mass fraction): C: 49.5; H: 8.38; N: 9.44; O: 21.97

3-4. 1-Octyl-3-methylimidazolium Trihydrogen Diphosphate [C$_8$mim][THDP]

Because there have been no reports about synthesis of ionic liquids with pyrophosphate anion, [C$_8$mim][THDP] was synthesized by the method mentioned for [C$_8$mim][DHP] until [C$_8$mim][OH] was obtained. 0.25 mol pyrophosphoric acid per mol KOH was dissolved in water and added to [C$_8$mim][OH] solution. All the active protons of H$_4$P$_2$O$_7$ were neutralized to generate [C$_8$mim]$_4$P$_2$O$_7$ and K$_4$P$_2$O$_7$. Then, another 0.75 mol H$_4$P$_2$O$_7$ per mol of [C$_8$mim][OH] was added in three steps to obtain [C$_8$mim][THDP]. The mixture was placed in a rotary evaporator to remove all solvents and then was dried in a vacuum oven. The water content was 420 ppm for [C$_8$mim][THDP].

^{1}HNMR (500 MHz, CDCl$_3$): δH=8.66 (1H, s), 7.38 (1H, s), 7.34 (1H, s), 4.08 (2H, t), 3.81 (3H, s), 1.71 (2H, m), 1.2 (10H, m), 0.86 (3H, s), elemental analysis for C$_{12}$H$_{26}$N$_2$O$_7$P$_2$ (372.29 g/mol) Calcd. (100×mass fraction): C: 38.71; H: 7.04; N: 7.52; O: 30.08. Found (100×mass fraction): C: 39; H: 6.96; N: 7.44; O: 30.14.

Note that the results of the AgNO$_3$ test for halide impurities was negative for [C$_8$mim][Gly], [C$_8$mim][DHP] and [C$_8$mim][THDP], so no further purification was required.

RESULTS AND DISCUSSION

1. Physicochemical Properties of ILs

The experimental data on physicochemical properties of studied ILs are listed over a wide temperature range of 283.15 K to

Table 1. Density (ρ), dynamic viscosity (η), refractive index (n$_D$), surface tension (σ), thermal expansion (α_p), and pH of the ionic liquids at different temperatures

T/K	ρ/(g mL^{-1})	η/(mPa s)	n$_D$	σ/(mN m^{-1})	10^4 α_p/K	pH of 1% solution
			[C$_8$mim][Cl]			
283.15	1.0189				4.98	9.6197
293.15	1.0137	34100	1.51011		5.05	9.4989
298.15	1.0119	20900	1.50867	32.3	5.08	9.44
303.15	1.0081	11040	1.50721	32	5.11	9.388
313.15	1.0022	4130	1.5043	31.4	5.18	9.251
323.15	0.9970	1980	1.50152	30.9	5.24	9.13
333.15	0.9903	940	1.49871	30.2	5.31	9.028
343.15	0.9852	338	1.49587	29.8	5.38	8.8997
353.15	0.9791	137	1.49343	29.2	5.45	8.7748
363.15	0.9736	56	1.49079	28.8	5.52	8.6513

Table 1. Continued

T/K	ρ/(g mL^{-1})	η/(mPa s)	n_D	σ/(mN m^{-1})	$10^4 \, \alpha_p$/K	pH of 1% solution
			[C$_8$mim][Gly]			
283.15	1.0484			36.8	5.41	11.125
293.15	1.0421	479.9	1.4807	35.33	5.49	11.03
298.15	1.0388	342.1	1.47922	34.7	5.54	10.98
303.15	1.0362	238.9	1.4771	33.9	5.58	10.907
313.15	1.0298	135.4	1.47468	32.4	5.67	10.779
323.15	1.0233	78.8	1.47169	31	5.76	10.652
333.15	1.0171	49.4	1.46886	29.7	5.85	10.54
343.15	1.0111	33.1	1.46637	28.2	5.95	10.435
353.15	1.0043	24.19	1.46474	26.9	6.04	10.289
363.15	0.9978	16.68	1.46313	25.6	6.14	10.173
			[C$_8$mim][H$_2$PO$_4$]			
283.15						3.0267
293.15			1.4761			2.9364
298.15			1.47456		4.73	2.8915
303.15			1.47332		4.9	2.847
313.15	1.2773	12529	1.47116		5.24	2.756
323.15	1.2725	7156.67	1.4699	63.2	5.6	2.667
333.15	1.2679	4087.96	1.46897	59.45	5.95	2.58
343.15	1.262	2347	1.468	55.29	6.32	2.49
353.15	1.2564	1305.6	1.46691	50.8	6.69	2.395
363.15	1.2505	765	1.46592	46.02	7.06	2.307
			[C$_8$mim][H$_3$P$_2$O$_7$]			
283.15						2.82
293.15			1.47047			2.73
298.15	1.4255	6531.75	1.46949		4.79	2.685
303.15	1.4219	4743.03	1.46851		4.86	2.64
313.15	1.4163	2555.58	1.46654		5	2.555
323.15	1.4090	1347.68	1.46466	56.5	5.14	2.461
333.15	1.4030	710.62	1.46264	52.1	5.28	2.37
343.15	1.3946	383.2	1.46073	48.01	5.42	2.28
353.15	1.3895	198	1.4580	44.18	5.57	2.19
363.15	1.3812	107	1.45692	40.7	5.72	2.1
			[C$_{10}$mim][Cl]			
283.15						6.491
293.15			1.50018			6.376
298.15	0.9834		1.4988		5.88	6.31
303.15	0.9788		1.4971	31.1	5.93	6.228
313.15	0.9739	3818.23	1.49362	30	6.02	6.085
323.15	0.968	1669.21	1.48962	28.8	6.12	5.962
333.15	0.9619	811	1.48646	27.7	6.22	5.85
343.15	0.9558	430.87	1.48334	26.9	6.32	5.768
353.15	0.9501	248.15	1.48059	26.1	6.43	5.661
363.15	0.9433	152.46	1.47869	25.3	6.53	5.582

363.15 K in Table 1. The density (ρ), refractive index (n_D), surface tension (σ) and pH were fitted by least squares using the polynomial of second order expression given by Eq. (1).

$$Z = A_o + A_1 \times T + A_2 \times T^2 \qquad (1)$$

where z is ρ (g·cm^{-3}), n_D or s (mN·m^{-1}), T is the temperature (K)

and A_o, A_1 and A_2 are the adjustable parameters.

The viscosities values were fitted by using the following Vogel-Flucher-Tamman (VFT), Eq. (2):

$$\eta/(\text{mPa·s}) = A. \exp [B/(T/- T_0)] \qquad (2)$$

where A, B and T_0 are adjustable parameter and T is temperature

Table 2. Fitted parameters of Eq. (1) used for correlation of density, refractive index and surface tension of studied ILs

Physical property	A_0	A_1	A_2	R^2
[C₈mim][Cl]				
$\rho/(\text{g mL}^{-1})$	1.1594	−0.0004	-2×10^{-7}	0.9992
n_D	1.6249	−0.0005	3×10^{-7}	0.9999
$\sigma/(\text{mN m}^{-1})$	61.638	−0.1345	0.0001	0.9985
[C₈mim][Gly]				
$\rho/(\text{g mL}^{-1})$	1.1912	−0.0004	-3×10^{-7}	0.9999
n_D	1.703	−0.0012	10^{-6}	0.9987
$\sigma/(\text{mN m}^{-1})$	88.066	−0.2123	0.0001	0.9998
[C₈mim][H₂PO₄]				
$\rho/(\text{g mL}^{-1})$	1.2528	0.0006	-2×10^{-6}	0.9997
n_D	1.6575	−0.001	10^{-6}	0.9916
$\sigma/(\text{mN m}^{-1})$	1.8629	0.7415	−0.0017	1
[C₈mim][H₃P₂O₇]				
$\rho/(\text{g mL}^{-1})$	1.5436	−0.0002	-8×10^{-7}	0.9985
n_D	1.5278	−0.0002	-8×10^{-9}	0.9975
$\sigma/(\text{mN m}^{-1})$	360.24	−1.426	0.0015	1
[C₁₀mim][Cl]				
$\rho/(\text{g mL}^{-1})$	1.1309	−0.0004	-3×10^{-7}	0.9988
n_D	1.7138	−0.0011	1×10^{-6}	0.9984
$\sigma/(\text{mN m}^{-1})$	114.21	−0.422	0.0005	0.9993

Table 3. Fitted parameters of VFT Equation used for correlation of viscosity of studied ILs

|	A	B	T_0	R^2
[C₈mim][Cl]	1.82×10^{-9}	8352.937	20.29	0.9985
[C₈mim][Gly]	1.53×10^{-7}	8350.919	−90.79	0.9936
[C₈mim][H₂PO₄]	1.24×10^{-6}	8352.001	−48.71	0.9983
[C₈mim][H₃P₂O₇]	9.25×10^{-8}	8351.93	−35.0026	0.9972
[C₁₀mim][Cl]	5.59×10^{8}	8352.12	−22.7395	0.9969

[31].

The best fit parameters for density, refractive index, surface tension and viscosity are listed in Tables 2 and 3.

2. Density and Thermal Expansion

The effects of temperature, cation and anion type on the density of synthesized ILs are shown in Table 1 and Fig. 2. As expected, the measured densities decreased as a function of temperature. According to Fig. 2, the density of [C₈mim][Cl] and [C₁₀mim][Cl] decreased with increasing the alkyl chain length at each temperature. The accuracy of the density values was further evaluated by correlation with temperature either by linear, exponential, power or polynomial equations. The best correlation was obtained by polynomial equation (order 2) ($R^2>0.99$). The data clearly indicated that he density increased in the order [C₈mim][THDP]>[C₈mim][DHP] >[C₈mim][Gly]>[C₈mim][Cl]>[C₁₀mim][Cl].

The results demonstrated that the nature of the anion, significantly affected the density. The higher density value for [C₈mim] [THDP] was due to presence of more heteroatoms in comparison with other anions. In general, the density of ILs was increased when anion molecular weight was increased. To best of our knowledge,
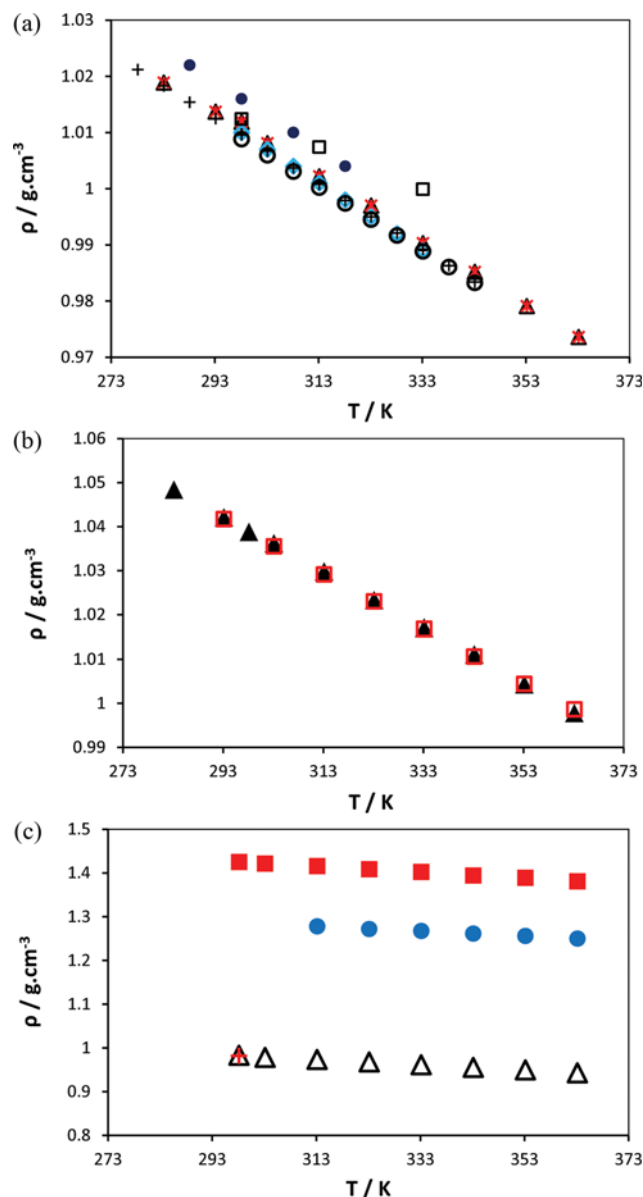
Fig. 2. **Experimental values of density, ρ (g/cm³) against temperature (K) for (a) ([C₈mim][Cl]), (△) our work, (□) Seddon et al. [32], (+) Singh et al. [33], (✕) Mac Dowell et al. [34], (◇) AlTuwaim et al. [35], Yan et al. [36], and (●) Gomez et al. [37]. (b) [C₈mim][Gly], (▲) our work, (□) Ghanem et al. [38], (c) (■) [C₈mim][THDP], (●) [C₈mim][DHP], (△) [C₁₀mim][Cl], (+) M. G. Freire et al. [39].**

a limited number of experimental density data have been reported in literature for the studied ionic liquids. Several density measurements were reported for [C₈mim][Cl], by Seddon et al. [32], Singh et al. [33], Mac Dowell et al. [34], AlTuwaim et al. [35], Yan et al. [36] and Gomez et al. [37]. Our results were compared with their data and were good agreement with them (0.25%-0.47% at 298.15 K). There is just one report in the case of [C₈mim][Gly] and [C₁₀mim] [Cl]. Ghanem et al. [38] reported density of [C₈mim][Gly] in the temperature range 293.15 K to 373.15 K (within 0.04% at 293.15 K). Freire et al. [39] measured the density of [C₁₀mim][Cl] at 298.15 K
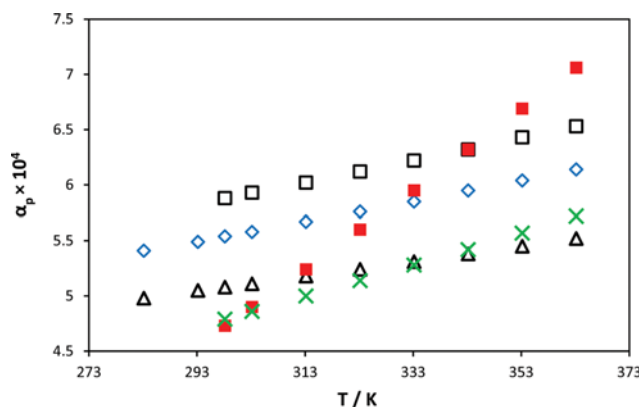
Fig. 3. Experimental values of thermal expansion α_p against temperature (K) for ($\triangle$) [C$_8$mim][Cl], ($\diamondsuit$) [C$_8$mim][Gly], ($\square$) [C$_{10}$mim][Cl], ($\blacksquare$) [C$_8$mim][DHP] and ($\times$) [C$_8$mim][THDP].

(0.9821 g·cm^{-3}), which is in a very good agreement with our measured value (0.9834 g·cm^{-3}). There is no report for densities of [C$_8$mim][DHP] and [C$_8$mim][THDP] in the literature.

The thermal expansion coefficient was calculated according to the following equation for synthesized ILs:

$$\alpha_p = -(A_1 + 2A_2 \times T)/(A_0 + A_1 \times T + A_2 \times T) \tag{4}$$

where, α_p is thermal expansion coefficient, A$_0$, A$_1$ and A$_2$ are the adjustable parameters calculated by Eq. (1). The calculated thermal expansion coefficients are listed in Table 1, and temperature dependence of the α_p values is illustrated in Fig. 3. The calculated α_p for [C$_{10}$mim][Cl], [C$_8$mim][Cl], [C$_8$mim][Gly], [C$_8$mim][THDP] and [C$_8$mim][DHP] was (5.88, 5.54, 5.08, 4.79 and 4.73)×10^{-4} K^{-1}, respectively, at 298.15 K. Due to small variations of α_p values as a function of temperature, it can be concluded that α_p is independent of the temperature for all ILs.

3. Viscosity

The experimental data of ILs viscosity as a function of temperature is shown in Table 1 and Fig. 4. As expected, in Fig. 4, the viscosity of ILs significantly decreased with increasing temperature. At high temperature, the movement of ILs molecules is much faster and free; thus the viscosity is reduced. According to Fig. 4, the order of viscosity was as follows: [C$_8$mim][DHP]>[C$_8$mim][THDP]>[C$_{10}$mim][Cl]>[C$_8$mim][Cl]>[C$_8$mim][Gly]. The viscosity of studied ILs was increased with increasing alkyl chain length from C$_8$ to C$_{10}$, which was caused by increasing the van der Waals interaction between the aliphatic alkyl chains [40,41]. The main reason for high viscosity of [C$_8$mim][DHP] and [C$_8$mim][THDP] is the presence of hydrogen bonding in anion structure and also high molecular weight of these anions compared with others. Seddon et al. [32], AlTuwaim et al. [35], Gomez et al. [37], and Gonzalez et al. [42] reported viscosity of [C$_8$mim][Cl] at several temperatures which their measured values were in a good agreement (0.08%-0.47% at 298.15 K) with our work. In the case of [C$_8$mim][Gly] there was only one report. The deviations between our results and the measured values by Ghanem et al. [38] is 1.3% at 293 K. To the best of our knowledge, there is not any viscosity report for [C$_{10}$mim][Cl], [C$_8$mim][DHP] and [C$_8$mim][THDP] in literature.
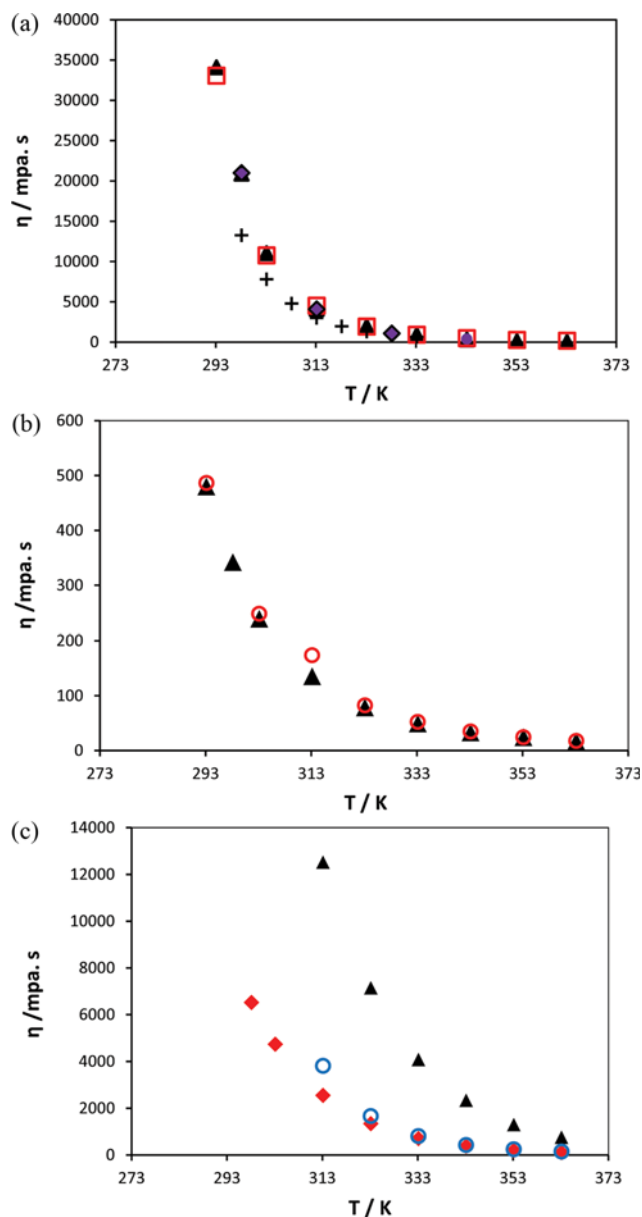

Fig. 4. Experimental values of viscosity η (mpa·s) against temperature (K), (a) [C$_8$mim][Cl], ($\triangle$) our work, ($\square$) Seddon et al. [32], ($+$) AlTuwaim et al. [35], ($\bullet$) Gomez et al. [37], ($\diamondsuit$) Gonzalez et al. [42], (b) [C$_8$mim][Gly], ($\blacktriangle$) our work, ($\bigcirc$) Ghanem et al. [38], (c) ($\blacklozenge$) [C$_8$mim][THDP], ($\blacktriangle$) [C$_8$mim][DHP] and ($\bigcirc$) [C$_{10}$mim][Cl].

4. Surface Tension

The measured experimental surface tension (σ) values of the studied ILs are shown in Table 1 and Fig. 5, in the temperature range of 283.15 K to 363.15 K and atmospheric pressure. The measured surface tension for ILs was lower than water (71.9 mN·m^{-1}) and higher than most of the common organic solvents (ethanol: 21.9 mN·m^{-1}) [43]. According to Fig. 5, the surface tension values decreased with increasing temperature. The results indicated that the cation and anion of ILs had an effect on the surface tension, since the cation and anion were present at the interface, so both of them collaborated in surface energy [44]. The surface tension values fol-
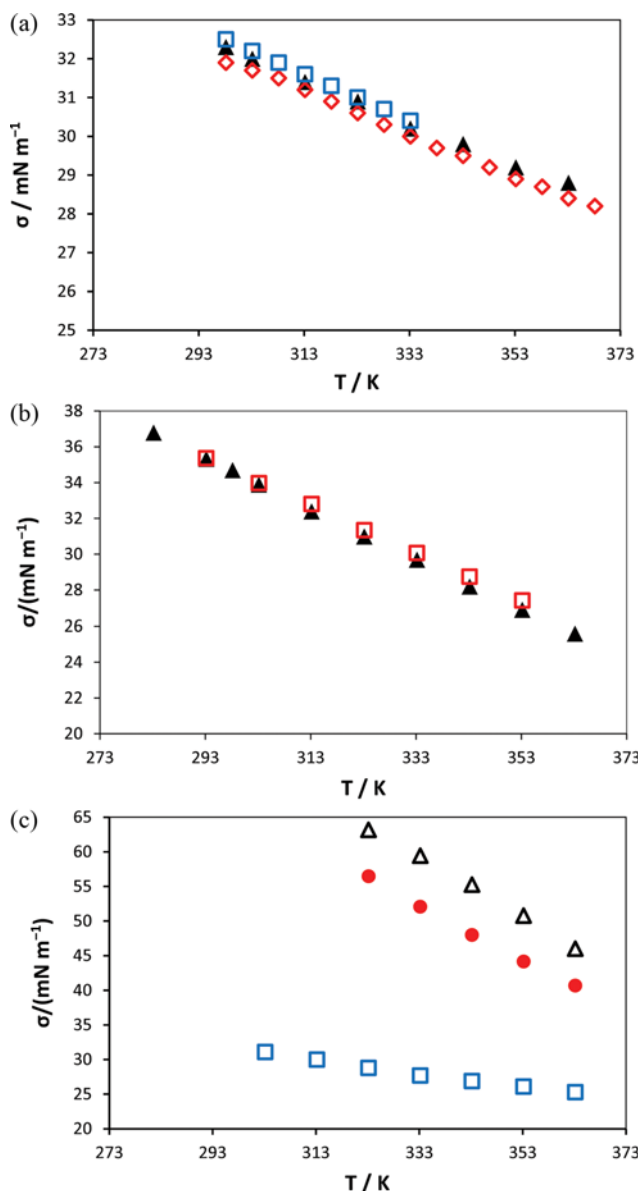
Fig. 5. Experimental values of surface tension σ (mN m^{-1}) against temperature (K), (a) [C$_8$mim][Cl], (▲) our work, (◇) Ghatee et al. [46], (□) AlTuwaim et al. [35], (b) [C$_8$mim][Gly], (▲) our work, (□) Ghanem et al. [38], (c) (△) [C$_8$mim][DHP], (●) [C$_8$mim][THDP] and (□) [C$_{10}$mim][Cl].

Fig. 6. Experimental values of refractive index n$_D$, against temperature (K), (a) [C$_8$mim][Cl], (▲) our work, (■) Singh et al. [33], (◇) Gomez et al. [37], (○) AlTuwaim et al. [35], (b) (+) [C$_8$mim][Gly], (△) [C$_8$mim][DHP], (□) [C$_8$mim][THDP] and (●) [C$_{10}$mim][Cl].

lowed the order: [C$_8$mim][DHP]>[C$_8$mim][THDP]>[C$_8$mim][Gly]>[C$_8$mim][Cl]>[C$_{10}$mim][Cl], whereas at higher temperatures, the surface tension was increased as follows: [C$_8$mim][DHP]>[C$_8$mim][THDP]>[C$_8$mim][Cl]>[C$_8$mim][Gly]>[C$_{10}$mim][Cl]. Furthermore, increasing the alkyl chain length led to an increase in the van der Waals forces, and as a result the surface tension was decreased [45]. The high surface tension for [C$_8$mim][DHP] and [C$_8$mim][THDP] was due to existence of hydrogen bond in these anions. Available data on the surface tension of the studied ILs are very limited. Ghatee et al. [46] reported the surface tension of [C$_8$mim][Cl] in temperature range 298.15 K to 373.15 K that our results (32.3 mN·m^{-1} at 298.15 K) were in a good agreement with the result obtained
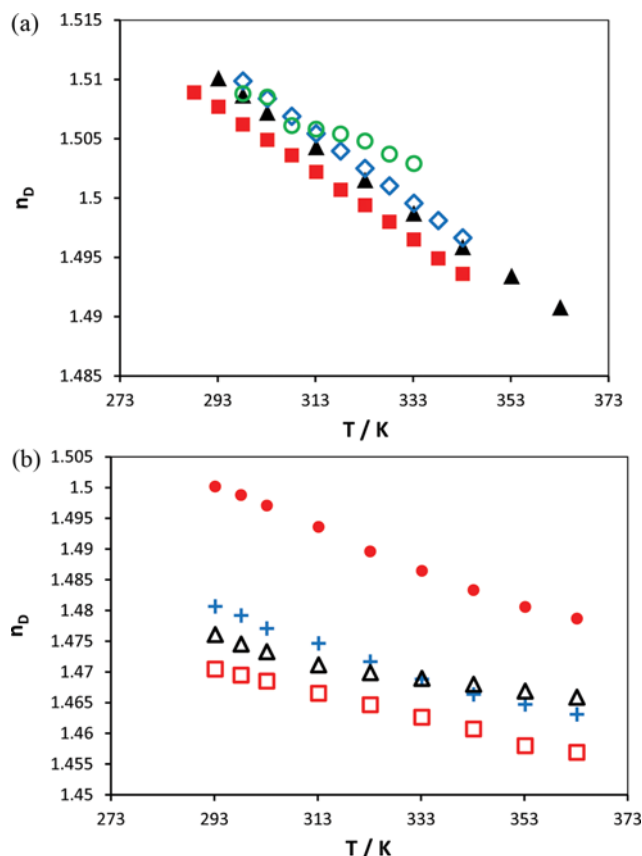
by Ghatee et al. (31.9 mN·m^{-1}). Another measurement of surface tension was conducted by AlTuwaim et al. [35] for [C$_8$mim][Cl] in the temperature range 298.15 K to 333.15 K. The deviation between our measurements (32.3 mN·m^{-1} at 298.15 K) and AlTuwaim's work (32.5 mN·m^{-1} at 298.15 K) was slight.

There was just one report by Ghanem et al. [38] for [C$_8$mim][Gly] at temperature range 293.15 K to 353.15 K, which their experimental values were higher than those measured in this study, with deviation 0.099% in 293.15 K. The comparison between our experimental data and those reported in literature, is shown graphically in Fig. 5.

Note that no surface tension data are available in the literature for [C$_8$mim][DHP], [C$_8$mim][THDP], and [C$_{10}$mim][Cl].

5. Refractive Index and pH

The refractive index is a key parameter for determining the purity and electronic polarizability of ionic liquids. The temperature dependence of refractive indices for studied ILs is presented in Table 1 and Fig. 6. The n$_D$ values for the synthesized ILs decreased in a linear manner with increasing temperature. Fig. 6 shows the effects of temperature, anion and cation type of ILs on the refractive indices values. The results show that the shorter alkyl chain length of [C$_8$mim][Cl] led to the higher refractive index. It can be explained that, ILs with longer alkyl chain cannot be close packed
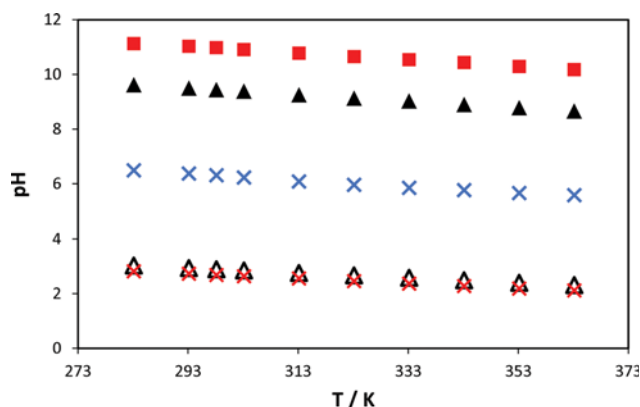
Fig. 7. Experimental values of pH, against temperature (K), (▲) [C$_8$mim][Cl], (■) [C$_8$mim][Gly], (△) [C$_8$mim][DHP], (×) [C$_8$mim][THDP] and (✕) [C$_{10}$mim][Cl].

in microscopic structure [36]. Increasing trend of refractive index for studied ILs was as follows: [C$_8$mim][Cl]>[C$_{10}$mim][Cl]>[C$_8$mim][Gly]>[C$_8$mim][DHP]>[C$_8$mim][THDP]. For synthesized ILs, the refractive indices values were higher than 1.45, which is higher than the range of most organic materials.

Only a few reports are available in the literature for the refractive index of the investigated ILs in this research work. Singh et al. [33], Gomez et al. [37] and AlTuwaim et al. [35] reported a refractive index of [C$_8$mim][Cl] in a wide temperature range, which is in a good agreement with our experimental values. The deviations between our results and the mentioned reports were 0.16, 0.08 and 0.0086 at 293.15 K, respectively. There are no reported refractive indices values of [C$_{10}$mim][Cl], [C$_8$mim][Gly], [C$_8$mim][DHP] and [C$_8$mim][THDP] in the literature.

The measured pH values of 1% aqueous ionic liquids solution are presented as a function of temperature in Table 1 and Fig. 7. As can be seen, the pH change was low when temperature was increased. The studied ILs included alkali and acidic ionic liquids in the pH range of 2 to 11. It was necessary to measure the pH values of ionic liquids for their special application as surfactant in the EOR process.

CONCLUSION

Five hydrophilic imidazolium based ionic liquids were synthesized and characterized by ^{1}HNMR and CHNO elemental analysis, which [C$_8$mim][THDP] has not been synthesized yet. The experimental data of physicochemical properties for [C$_8$mim][Cl], [C$_8$mim][Gly], [C$_8$mim][DHP], [C$_8$mim][THDP] and [C$_{10}$mim][Cl] were reported in temperature range 283.15 K to 263.15 K and atmospheric pressure. These properties included density, thermal expansion, viscosity, surface tension, refractive index and pH.

Due to the unique properties of ionic liquids, understanding their physicochemical properties, helps researchers to apply them in various fields. To the best of our knowledge, there are scarce reports for our synthesized ionic liquids in literature, so this work can be as a database for these ILs.

All measured properties decreased as the temperature increased.

The results showed that both anion and cation affected physicochemical properties of ionic liquids. The density, surface tension, refractive index and pH values decreased when alkyl chain length was increased, while the viscosity had an inverse trend. The density values for [C$_8$mim][THDP] (1.4255 g·cm^{-3} at 298.15 K) were higher than other studied ILs, because the molecular weight of THDP onion was larger than others. The higher viscosity and surface tension values for [C$_8$mim][THDP] and [C$_8$mim][DHP] were due to presence of hydrogen bonding in the mentioned anions. The measured surface tension values were lower than water (71.9 mN·m^{-1}) and larger than most common organic solvents (ethanol: 21.9 mN·m^{-1}). [C$_8$mim][DHP] (63.2 mN·m^{-1} at 333.15 K) had the highest surface tension among studied ILs. For synthesized ILs, the refractive indices were higher than 1.45, which was higher than the range of most organic materials. Finally, determining the pH of investigated ILs required using them as surfactants in enhanced oil recovery process.

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