

Effect of Temperature and Anion on Densities, Viscosities, and Refractive Indices of 1-Octyl-3-propanenitrile Imidazolium-Based Ionic Liquids

Abobakr K. Ziyada*^{,†} and Cecilia D. Wilfred[‡]

[†]Chemical Engineering Department and [‡]Fundamental and Applied Sciences Department, Universiti Teknologi PETRONAS, Tronoh 31750, Perak, Malaysia

Supporting Information

ABSTRACT: A series of 1-octyl-3-propanenitrile imidazolium based room temperature ionic liquids incorporated with different sulfonate-based anions were synthesized and characterized using ¹H NMR, Fourier transform infrared spectroscopy (FTIR), and elemental analysis. The density and viscosity were measured at T = (293.15 to 353.15) K, the refractive index was measured at T = (298.15 to 383.15) K, and the thermal expansion coefficient was estimated from the density values. The effects of the anions on these physical properties and on the lattice energy were discussed.



INTRODUCTION

Room temperature ionic liquids (RTILs) are liquid organic salts at room temperature, which are generally composed of bulky asymmetric organic cations (e.g., pyridinium, imidazolium, phosphonium, ammonium) and inorganic or organic anions (e.g., Cl⁻, BF₄⁻, PF₆⁻, CF₃SO₃⁻, NTf₂⁻) with different molecular sizes.¹ These compounds received increasing interest and intensive investigation due to the distinctive combination of properties that resulted from their ionic nature. Moreover, the structures of these compounds can be designed to achieve the desired properties tailored for a specific application by the careful selection of the ions or by incorporating new functionalities such as hydroxyl, carboxylic, amine, and fluorous groups.^{2,3} The physiochemical properties of ILs depend on the structures of the cation and anion; hence the alkyl chain length and functionality have a remarkable influence on these properties. RTILs exhibit many distinctive properties such as negligible vapor pressure, high thermal stability, nonflammability, a wide electrochemical window, high electrical conductivity, and high solvation capacity.² The distinctive properties of RTILs resulted in a superfluity of an increasing number of applications.³ The bulk of research involves using RTILs as solvents and/or catalysts in many reactions; they enhance the synthetic processes, decrease the environmental load, increase reaction efficiency, and provide higher yields, selectivity, and rate enhancements. Moreover, there has also been an increasing interest in using the RTILs for gas separations.⁴ Further development of RTILs to other important processes often require synthesis of new ionic liquids with favorable properties. Further, the structure-property correlations are still not well understood. Hence, controlling and adjusting the cationic, anionic, or both components is important for extending the knowledge and applications of relevant types of RTILs.

Recent advances in functionalized ILs further enhanced their applications. Imidazolium-based functionalized ILs has proven to be more adaptable and attractive compared to other functionalized ILs due to the capability to tune and control their properties to a greater extent which results in an increased number of applications.⁵

Many researchers studied the thermophysical properties of the nitrile functionalized ILs and reported the effect of the alkyl chain linking the nitrile group and the imidazolium ring.⁶ Imidazolium-based nitrile functionalized ILs with a long length of the alkyl chain attached to the N-3 of the imidazolium ring and incorporating sulfonate-based anions have been synthesized recently by our group.⁷ Moreover, accurate and reliable basic experimental data of thermophysical properties are essential for a better understanding of the new ILs. This is essential for choosing an appropriate liquid for each of their envisaged applications and required for the improvement of the property prediction methods.⁸

The present study involves the synthesis of new series of 1octyl-3-propanenitrile imidazolium based RTILs [CNC₂Oim] incorporating different sulfonate-based anions such as dodecylsulfate (DDS), dioctysulfosuccinate (DOSS), benzenesulfonate (BS), sulfobenzoic acid (SBA), and trifluoromethanesulfonate (TFMS).^{3,7,9} The synthesized RTILs in the present work

```
Received:September 10, 2013Accepted:March 13, 2014Published:April 21, 2014
```

were characterized using Fourier transformation infrared spectroscopy–attenuated total reflectance (FTIR-ATR), elemental analysis (CHNS), and ¹³C and ¹H NMR spectra. Moreover, an effort was made to measure the essential thermophysical properties at atmospheric pressure. The molar refraction, thermal expansion coefficient, lattice energy, and standard molar entropy were estimated from the experimental values.

EXPERIMENTAL SECTION

Materials. In the present study the ionic liquids were synthesized using chemicals of analytical grade. The CAS (Chemical Abstracts Service) number, source, and grades of the chemicals used are as follows: imidazole (288-32-4, Aldrich 99 %), acrylonitrile (107-13-1, Aldrich 99 %), methanol, anhydrous (67-56-1, Sigma-Aldrich 99.8 %), 1-bromooctane (111-81-1, Aldrich 99 %), ethylacetate, anhydrous (141-78-6, Sigma-Aldrich 99.8 %), sodium dodecylsulfate (205-788-1, Sigma-Aldrich 99.8 %), sodium dodecylsulfate (209-406-4, Aldrich 98 %), sodium benzenesulfonate (515-42-4, Aldrich 97 %), sodium 3-sulfobenzoic acid (17625-03-5, Aldrich 97 %), sodium triflouromethanesulfonate (2926-30-9, Aldrich 98 %), and diethyl ether (60-29-7, Sigma-Aldrich 99 %). All chemicals used in the present study were used without further purification.

Synthesis of RTILs. The synthesis of the presently studied ionic liquids (Figure S1) involves three steps: incorporation of the nitrile group to imidazole followed by the formation of the desired cation (by the reaction of imidazole bearing nitrile group with 1-bromooctane) and finally anion exchange to form the final desired product. A nitrile functionalized IL was synthesized by direct quaternization reaction of the imidazole bearing nitrile group with 1-bromobutane as reported recently by our group.³

The reaction involved in the synthesis of 1-octyl-3-propanenitrile imidazolium bromide $[CNC_2Oim]$ Br and 1-octyl-3propanenitrile imidazolium incorporating sulfonate-based anions $[CNC_2Oim]$ X is shown in Figure S1. A sample of 0.5 mol of imidazole, methanol, and acrylonitrile were mixed and heated at 55 °C for 10 h in a nitrogen atmosphere. The product was distilled and reacted with an excess of 1bromooctane. The product was purified according to the standard procedure.³

For the synthesis of $[CNC_2Oim]$ DOSS, $[CNC_2Oim]$ Br (0.03 mol) and sodium dioctylsulfosuccinate (0.03 mol) were dissolved and mixed in acetone. The mixture was stirred at room temperature for 48 h; then, the solid precipitate and the solvent was removed. The product was cooled to room temperature and washed with diethyl ether and ethyl acetate. The solvent was removed at 80 °C under vacuum, and then the product was dried in a vacuum oven for 48 h.

1-Octyl-3-propanenitrile imidazolium dodecylsulfate $[CNC_2Oim]$ DDS was synthesized by mixing $[CNC_2Oim]$ Br (0.04 mol) and sodium dodecyl sulfate (0.04 mol) in 40 mL of hot dionized water (60 °C). The mixture was stirred for 48 h, and the product was dried under vacuum at 80 °C; then 50 mL of dichloromethane was added to the product, and the mixture was filtrated. The product was then washed with deionized water, and the remaining solvent was removed at 80 °C under vacuum and then dried in a vacuum oven for 48 h.

Sodium benzenesulfonate (0.04 mol), sodium sulfobenzoic acid (0.04 mol), and sodium trifluoromethanesulfonate (0.04 mol) were used to synthesize 1-octyl-3-propanenitrile imida-

zolium benzenesulfonate $[CNC_2Oim]$ BS, 1-octyl-3-propanenitrile imidazolium sulfobenzoic acid $[CNC_2Oim]$ SBA, and 1octyl-3-propanenitrile imidazolium trifluoromethylsulfonate $[CNC_2Oim]$ TFMS, respectively, and a similar procedure for the synthesis of $[CNC_2Oim]$ DDS was adopted.

Characterization. Fourier transform infrared (FTIR) spectra, ¹H and ¹³C NMR spectra, and elemental analysis were used to confirm the structures of the synthesized RTILs. FTIR spectra were recorded in a Shimadzu FTIR-8400S in the mid region (4000 cm⁻¹ to 400 cm⁻¹) using the attenuated total reflectance ((MIRacle ATR) measurement mode. ¹H and ¹³C NMR spectra were determined using A Burcher Avance 300 spectrometer, and deuterated water (D₂O) was used as a solvent. Elemental analysis was carried out using elemental analyzer (CHNS-932, LECO instruments).³

A coulometric Karl Fischer titrator DL 39 (Mettler Toledo) was used for the water content measurements of the present RTILs using CombiCoulomat fritless Karl Fischer reagent (Merck).^{3,10} The average value for a triplicate measurement was reported. The bromide content measurements were conducted using ion chromatography (Metrohm model 761 Compact IC) with (5.0 × 4.0) mm guard column (Metrosep A Supp 4/5) and (150 × 4.0) mm analytical column (Metrosep A Supp 5-150).¹⁰ The samples were diluted in acetonitrile, and the results were analyzed using Metrodata IC Net 2.3 software.

Density and Viscosity Measurements. Values of density and viscosity of the present RTILs were measured using a Stabinger viscometer (Anton–Paar model SVM3000) at atmospheric pressure and over the temperature range (293.15 to 353.15) K.³ The temperature was controlled precisely to within \pm 0.01 °C. The reproducibility of the density and viscosity measurements are \pm 5·10⁻⁴ g·cm⁻³ and 0.35 %, respectively. The instrument was calibrated using standard calibration fluid followed by ionic liquids with a known density and viscosity.^{3,10}

Refractive Index Measurements. The refractive index values of the present RTILs were determined using an ATAGO programmable digital refractometer (RX-5000 alpha) with a measuring accuracy of $\pm 4 \cdot 10^{-5}$ in a temperature range (298.15 to 333.15) K at atmospheric pressure.¹⁰ The temperature of the apparatus was controlled to within ± 0.05 °C. Pure organic solvents with known refractive indices were used to calibrate and check the instrument before each series of measurements.^{3,10} The samples were dried and kept in desiccators prior to the measurement; then the samples were directly placed into the measuring cell. Three experiments were performed for each IL in the whole temperature range studied in the present work to confirm the reproducibility of the results.

RESULTS AND DISCUSSION

The ¹H and ¹³C NMR spectral data, elemental analysis, water content, and bromide contents (as mass fraction) are shown in the Supporting Information. The main feature in the FTIR spectra of the present RTILs was the characteristic absorption of a CN group in the ranges (2245 to 2255) cm⁻¹ and (1562 to 1664) cm⁻¹. Moreover the characteristic absorption of a SO₃ group ranging from (1190 to 1218) cm⁻¹ and (1122 to 1163) cm⁻¹ was observed. The FTIR exhibits C–H bond and weaker C–H bonds stretches at (2920 to 3150) cm⁻¹ and (2855 to 2880) cm⁻¹, respectively, which are possibly resulting from the hydrogen bonds with the anions.¹¹ Furthermore, [CNC₂Oim] DOSS exhibits C=O and C–O–C stretches at (1730 and 1159) cm⁻¹, respectively, [CNC₂Oim] SBA exhibits C=O and

Table 1. Density Values (ρ) for the Ionic Liquids Investigated as a Function of Temperature at Pressure $p = 0.1 \text{ MPa}^a$

			$ ho/(extrm{g}\cdot extrm{cm}^{-3})$		
T/K	[CNC ₂ Oim] DOSS	[CNC ₂ Oim] DDS	[CNC ₂ Oim] SBA	[CNC ₂ Oim] BS	[CNC ₂ Oim] TFMS
293.15	1.0579	1.0849	1.1859	1.2087	1.2331
298.15	1.0543	1.0817	1.1828	1.2052	1.2294
303.15	1.0508	1.0785	1.1794	1.2019	1.2256
308.15	1.0473	1.0751	1.1757	1.1987	1.2220
313.15	1.0439	1.0724	1.1721	1.1956	1.2184
318.15	1.0404	1.0686	1.1690	1.1923	1.2147
323.15	1.0370	1.0655	1.1656	1.1888	1.2112
328.15	1.0336	1.0623	1.1619	1.1854	1.2076
333.15	1.0302	1.0592	1.1583	1.1828	1.2040
338.15	1.0267	1.0561	1.1549	1.1795	1.2005
343.15	1.0233	1.0532	1.1512	1.1764	1.1960
348.15	1.0199	1.0500	1.1481	1.1721	1.1932
353.15	1.0165	1.0469	1.1444	1.1691	1.1897
^a Standard uncer	tainties u are $u(T) = 0.01$]	K. $u(v) = 0.01$ MPa. and u	$\mu(\rho) = 5 \cdot 10^{-4} \text{ g} \cdot \text{cm}^{-3}.$		

Table 2. Viscosity Values (η) for the Ionic Liquids Investigated as a Function of Temperature at Pressure $p = 0.1 \text{ MPa}^a$

	$\eta/(\mathrm{mPa}\cdot\mathrm{s})$				
T/K	[CNC ₂ Oim] DOSS	[CNC ₂ Oim] DDS	[CNC ₂ Oim] SBA	[CNC ₂ Oim] BS	[CNC ₂ Oim] TFMS
293.15			23617.2	12692.5	6784.2
298.15		21645.1	14420.2	8291.9	4135.2
303.15	16785.3	12998.5	9263.4	4880.1	2798.9
308.15	10623.7	8322.7	5820.8	3110.7	1816.5
313.15	6374.8	5094.2	3685.0	2097.8	1181.9
318.15	4059.2	3195.1	2404.8	1311.2	753.4
323.15	2672.6	2071.3	1524.7	883.5	503.4
328.15	1783.3	1390.8	1065.6	565.9	341.9
333.15	1226.1	974.8	701.7	378.0	235.7
338.15	866.3	694.8	455.3	253.8	165.0
343.15	604.1	461.4	298.6	172.5	107.9
348.15	417.8	329.6	188.2	120.1	74.5
353.15	284.6	230.0	121.4	88.9	52.8
Standard uncert	value and $u(T) = 0.01$ I	$X_{i} u(p) = 0.01 \text{ MPa}_{i}$ and t	the relative standard unce	rtainty for viscosity $u_r(\eta)$	$) = 3.5 \cdot 10^{-3}.$

C-O-H stretch at (1562 and 1161) cm⁻¹, respectively, and [CNC₂Oim] TFMS exhibits CF₃ stretches at (1226 and 1159) cm⁻¹.

The density values for the studied RTILs are presented in Table 1. [CNC₂Oim] TFMS has the utmost value, and [CNC₂Oim] DOSS has the lowest value of density among the studied RTILs. The density values for the five [CNC2Oim]based RTILs studied decreased in the following order: [CNC₂Oim]TFMS, [CNC₂Oim]SBA, [CNC₂Oim]BS, [CNC₂Oim]DDS, and [CNC₂Oim]DOSS, which is similar to the size of the anions order. Compared with the density of the [CNC₂Oim]Br IL, the present RTILs incorporating DOSS and DDS anions show lower density values, while SBA, BS, and TFMS anions show higher values of density. Moreover, the density values of the investigated RTILs are lower compared with the other nitrile-functionalized ILs reported by Zhao et al.;¹¹ the densities of [CNC₂Mim]BF₄, [CNC₃Mim]BF₄, and [CNC₄Mim]Cl were (2.15, 1.87, and 1.61) g·cm⁻³, respectively. The effect of each anion on the density values was studied taking into account that the present RTILs are incorporating the same cations and all of the anions are incorporating the SO₃ group. The differences in density are resulted from the contributions of the anions. The density values decrease as the anion size increase, and this trend is consistent with the literature. 12 Figure S2 shows that density decreases linearly with increasing temperature as expected. As is general for the ILs, linear performance is common as a result of the great difference between their critical temperatures and their working temperature range.¹³

The viscosity values of [CNC2Oim]DOSS, [CNC2Oim]-DDS, [CNC₂Oim]SBA, [CNC₂Oim]BS, and [CNC₂Oim]-TFMS ILs at atmospheric pressure and at temperature T=(293.15 to 353.15) K are shown in Table 2 and Figure S3. The RTILs investigated show higher viscosities compared with other nitrile functionalized ILs; for [CNC₃Mim]BF₄ and [CNC₄Mim]Cl the viscosities are (352 and 5222) mPa·s, respectively.^{11,14} Furthermore, these RTILs show lower viscosity compared to the same RTILs incorporating the bromide anion; for [CNC2Oim] Br the viscosity at 308.15 is 19620.3 mPa s.³ The high viscosity of the RTILs incorporating the DOSS and DDS anions may be owing to the large volume of the anions which results in low ion mobility.¹⁵ The viscosity values of the investigated RTILs decrease following the anion order: DOSS, DDS, SBA, BS, and TFMS. These results show that a higher anion size results in higher viscosity which is in consistence with the literature.¹² As shown in Figure S3, the viscosity values decrease as temperature increases, and a linear correlation was obtained by plotting the viscosity values logarithm versus the reciprocal of the absolute temperature (1/T).

Table 3. Refractive Index Values (n_D) for the Ionic Liquids Investigated as a Function of Temperature at Pressure $p = 0.1 \text{ MPa}^a$

			n _D			
T/K	[CNC ₂ Oim] DOSS	[CNC ₂ Oim] DDS	[CNC ₂ Oim] SBA	[CNC ₂ Oim] BS	[CNC ₂ Oim] TFMS	
298.15	1.47692	1.47928	1.51801	1.52174	1.52679	
303.15	1.47518	1.47758	1.51692	1.52084	1.52584	
308.15	1.47393	1.47597	1.51572	1.51973	1.52470	
313.15	1.47253	1.47454	1.51450	1.51856	1.52356	
318.15	1.47099	1.47274	1.51321	1.51740	1.52248	
323.15	1.46946	1.47098	1.51191	1.51619	1.52119	
328.15	1.46798	1.46963	1.51058	1.51499	1.51991	
333.15	1.46636	1.46785	1.50912	1.51373	1.51873	
^a Standard uncertainties u are $u(T) = 0.05$ K, $u(p) = 0.01$ MPa, and $u(n_D) = 5 \cdot 10^{-4}$.						

The refractive index values for the investigated RTILs are presented in Table 3. Among the studied anions, TFMS shows the highest value for the refractive index, while DOSS shows the lowest value. The refractive index value of the SBA anion is in good agreement with that reported for $[CNC_2Oim]$ Br, 1.51473_i^3 while DOSS and DDS anions show lower values. Generally the refractive indices for the investigated RTILs are in the range from (1.45965 to 1.52174). These values are in comparison to other nitrile functionalized ILs (1.4188 to 1.5454).^{3,11} The values of the refractive index decrease linearly with increasing temperature as is shown in Figure S4.

The dependence of density (ρ), refractive index ($n_{\rm D}$), and viscosity (η) for the present RTILs on temperature can be represented by the following empirical equations:^{3,10}

$$\rho = A_0 + A_1 T \tag{1}$$

$$n_{\rm D} = A_2 + A_3 T \tag{2}$$

$$\log \eta = A_4 + (A_5/T)$$
(3)

where *T* is the absolute temperature; A_0 , A_1 , A_2 , A_3 , A_4 , and A_5 are fitting parameters. The method of least-squares was used to estimate the fitting parameters, and the results are presented in Tables 4, 5, and 6 together with the standard deviations (SD).

Table 4. Coefficients of Equation 1 for the Density of the RTILs Listed in Table 1 and Standard Deviations (SD) Calculated Using Equation 4

ionic liquid	A_0	A_1	SD
[CNC ₂ Oim] DOSS	1.25950	-0.00069	$0.54 \cdot 10^{-3}$
[CNC ₂ Oim] DDS	1.27076	-0.00063	$1.47 \cdot 10^{-3}$
[CNC ₂ Oim] SBA	1.38990	-0.00065	$1.34 \cdot 10^{-3}$
[CNC ₂ Oim] BS	1.40032	-0.00065	$1.34 \cdot 10^{-3}$
[CNC ₂ Oim] TFMS	1.44563	-0.00073	$1.47 \cdot 10^{-3}$

Table 5. Coefficients of Equation 2 for the Refractive Index of the RTILs Listed in Table 3 and Standard Deviations (SD) Calculated Using Equation 4

A_2	A_3	SD
1.56551	-0.00030	$0.675 \cdot 10^{-3}$
1.57618	-0.00033	$1.560 \cdot 10^{-3}$
1.59390	-0.00025	$1.247 \cdot 10^{-3}$
1.59087	-0.00023	$0.387 \cdot 10^{-3}$
1.59631	-0.00023	$0.818 \cdot 10^{-3}$
	$\begin{array}{c} A_2 \\ 1.56551 \\ 1.57618 \\ 1.59390 \\ 1.59087 \\ 1.59631 \end{array}$	$\begin{array}{c c} A_2 & A_3 \\ \hline 1.56551 & -0.00030 \\ 1.57618 & -0.00033 \\ 1.59390 & -0.00025 \\ \hline 1.59087 & -0.00023 \\ 1.59631 & -0.00023 \end{array}$

The standard deviations were calculated by applying the following expression:³

Table 6. Coefficients of Equation 3 for the Viscosity of the RTILs Listed in Table 2 and Standard Deviations (SD) Calculated Using Equation 4

ionic liquid	A_4	A_5	SD
[CNC ₂ Oim] DOSS	3750.75	-8.16300	$1.26 \cdot 10^{-2}$
[CNC ₂ Oim] DDS	3759.78	-8.29300	$1.45 \cdot 10^{-2}$
[CNC ₂ Oim] SBA	3897.85	-8.89036	$2.86 \cdot 10^{-2}$
[CNC ₂ Oim] BS	3768.40	-8.73200	$1.23 \cdot 10^{-2}$
[CNC ₂ Oim] TFMS	3635.15	-8.55184	$1.45 \cdot 10^{-2}$

$$SD = \sqrt{\frac{\sum_{i}^{n_{dat}} (Z_{exp} + Z_{cal})^2}{n_{dat}}}$$
(4)

where, n_{dat} is the number of experimental points and Z_{exp} and Z_{cal} are the experimental and calculated values, respectively.

The values of density as a function of temperature were used to estimate the thermal expansion coefficients using the following equation.¹⁰

$$\alpha_p / (K^{-1}) = -(1/\rho) \cdot (\partial \rho / \partial T)_p = -(A_1) / (A_0 + A_1 T)$$
(5)

where α is the coefficient of thermal expansion in K⁻¹, ρ is the density, and A_0 and A_1 are the fitting parameters of eq 1. The thermal expansion coefficients of this series of ILs (Table 7) do not noticeably change with temperature for the range T = (293.15 to 353.15) K studied in the present work. The present ILs show weak temperature dependency for the coefficients of thermal expansion, $\alpha_P = (5.93 \cdot 10^{-4} \text{ to } 6.79 \cdot 10^{-4})$ K⁻¹, which are markedly smaller than those for molecular organic liquids and adequately agree with those reported for ammonium, imidazolium-, phosphonium-, and pyridinium-based ILs ($\alpha_P = (5.0 \cdot 10^{-4} \text{ to } 6.5 \cdot 10^{-4})$ K⁻¹).¹⁶

The refractive index values are informative about the behavior of the molecules in solution and the forces between these molecules using its relation with the electronic polarizability of the molecule. This informative relation was takes the equation form known as the Lorenz–Lorentz equation.¹³ This equation takes the form:

$$R_M = \frac{N_A \alpha_e}{3\varepsilon_0} = V_m \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right)$$
(6)

where R_M is the molar refraction in cm³·mol⁻¹, N_A is the Avogadro's number in mol⁻¹, α_e is mean molecular polarizability (electronic polarizability), ε_0 is the permittivity of free space, V_m is the molar volume in cm³·mol⁻¹, and n_D is the refractive index. The molar refraction and molar volume for the studied RTILs are presented in Table S1.

Table 7. Coefficients of T	Thermal Expansion (α_p) for	or the Ionic Liquids	Investigated as a Function	of Temperature

	$10^4 \alpha_p / \mathrm{K}^{-1}$				
T/K	[CNC ₂ Oim] DOSS	[CNC ₂ Oim] DDS	[CNC ₂ Oim] SBA	[CNC ₂ Oim] BS	[CNC ₂ Oim] TFMS
293.15	6.53	5.80	5.81	5.37	5.93
298.15	6.55	5.82	5.83	5.39	5.94
303.15	6.57	5.83	5.84	5.40	5.96
308.15	6.59	5.85	5.86	5.42	5.98
313.15	6.61	5.87	5.88	5.43	6.00
318.15	6.63	5.89	5.90	5.45	6.02
323.15	6.66	5.90	5.91	5.46	6.03
328.15	6.68	5.92	5.93	5.48	6.05
333.15	6.70	5.94	5.95	5.49	6.07
338.15	6.72	5.96	5.97	5.51	6.09
343.15	6.75	5.97	5.98	5.52	6.11
348.15	6.77	5.99	6.00	5.54	6.13
353.15	6.79	6.01	6.02	5.55	6.15

The molar refractions are often dealt as a quantity of the hard-core molecular volumes¹³ and consequently were used to calculate the molar free volume (unoccupied part of the molar volume of a substance)¹⁷ of the present RTILs. The molar free volumes for the present RTILs are decreasing following the order [CNC₂Oim] DOSS, [CNC₂Oim] DDS, [CNC₂Oim] SBA, [CNC₂Oim] BS, and [CNC₂Oim] TFMS. The refractive indices of the present RTILs decrease as the molar free volume increases; this behavior is in good agreement with that reported in the literature for other imidazolium-based RTILs.¹⁸ [CNC₂Oim] DOSS shows very high molar refraction, while the other ILs in this study show comparable values when compared with the values (47.93 to 121.73) cm³·mol⁻¹ reported for the ILs [C_nmim]X (where n = 2 to 14, X = NTf₂, PF₆, BF₄, OAc, MeSO₄).¹³

Thermodynamics is essential and principal to the science of matter. None of the experimental, simulation, or theoretical studies can afford dependable data for hypothesized materials or conserve pace with the rate of synthesis of new materials. Correlation methods can fill this gap. Glasser and Jenkins¹⁹ depict a range of advanced relationship methods that rely on volume to estimate thermodynamic quantities.

Based on the thermodynamic correlations for a linear entropy–volume relationship, Glasser and Jenkins²⁰ plotted some absolute entropies values against molecular volumes, for organic liquids, and find very satisfactory linear regressions. The relationships have small intercepts that agrees to the zero-volume entropy influences of the entities concerned. Glasser and Jenkins²⁰ used the following equation to estimate the standard molar entropy for ionic liquids:

$$S^0 = 1246.5(V_m) + 29.5 \tag{6}$$

$$V_m = 10^{21} \cdot M / (N_A \rho) \tag{7}$$

where S^0 is the standard entropy at 298.15 K in J·K⁻¹·mol⁻¹, V_m is the molecular volume in nm³, M is the molecular weight in g·mol⁻¹, N_A is the Avogadro's number in mol⁻¹, and ρ is the density in g·cm⁻³. The standard entropies for the nitrile-functionalized ILs were estimated using eq 6, and the results are showed in Table S2. The present RTILs show high values compared to other ILs; for [C_n Mim] alanine and [C_n Mim] glycine; where n = 2 to 6, the standard entropy ranges from (396.9 to 535.8) J·K⁻¹·mol⁻¹ and from (360.2 to 498.8) J·K⁻¹·mol⁻¹, respectively.²¹

The lattice energy of IL is dependent on the interaction energy between ions. Moreover, the underlying reason for forming the IL at room temperature is the low crystal energy.^{21a} Glasser theory²² was used to estimate the lattice energies of the synthesized RTILs using the following equation:

$$U_{\rm POT} = 1981.2(\rho/M)^{1/3} + 103.8 \tag{8}$$

where U_{POT} is the lattice energy in kJ·mol⁻¹. The results presented in Table S2 show that lattice energies of the inorganic fused salts are much elevated than that of the present synthesized RTILs; among the alkali chlorides the minimal lattice energy (U_{POT}) is 602.5 kJ·mol^{-.21a} The results indicate that the lattice energies for the nitrile-functionalized ILs are lower than that of the other ILs (for [C_n Mim] glycine and [C_n Mim] alanine (where n = 2 to 6), the lattice energies are ranging from (429 to 469) kJ·mol⁻¹ and (421 to 456) kJ·mol⁻¹, respectively.^{21a} Also, these values are lower than that reported by Guan; for [C_n Mim] Gly and [C_n Mim] Glu the lattice energies are in the range (410 to 450) kJ·mol⁻¹.²³ The results of the lattice energy for the present RTILs show that the lattice energy was found to decrease as the anion volume increased.

CONCLUSIONS

In the present work we have synthesized and characterized five RTILs containing [CNC₂Oim] cation incorporating five different anions (DOSS, DDS, SBA, BS, TFMS). The thermophysical properties of the present RTILs such as densities, viscosities, and refractive indices were measured in atmospheric pressure at different temperatures to explore the effect of anion nature and temperature on those properties. The density and refractive index increase with the decrease of the anion volume, while the viscosities show the opposite trend. The presently RTILs showed lower densities, higher viscosities, and comparable refractive indices compare with other nitrile functionalized ILs. The density values of the present RTILs were correlated linearly and used to calculate the thermal expansion coefficient. The temperature dependence of the thermal expansion coefficient was studied, and these ionic liquids show a weak temperature dependency. The experimental results showed that the type of possible interactions between cation and anion and the nature of the producing ions determine the ionic liquid properties.

ASSOCIATED CONTENT

Supporting Information

Table S1, molar volume (V_{molar}) and molar refraction (R_m) values of [CNC₂Oim] based ILs at temperatures (298.15 to 333.15) K; Table S2, estimated values of molecular volume (V_m), standard molar entropy (S^0), and crystal energy (U_{POT}) for the ionic liquids investigated; Figure S1, synthesis route for the present RTILs; Figure S2, plot of density against temperature; Figure S3, plot of viscosity against temperature; Figure S4, plot of refractive index against temperature. This material is available free of charge via the Internet at http:// pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E mail: abubakrkhz@yahoo.com; abubakrkhz@uofg.edu.sd.

Present Address

A.K.Z.: Applied Chemistry and Chemical Technology Department, University of Gezira, Wad Medani-Sudan.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The author would like to thank Universiti Teknologi PETRONAS and PETRONAS Ionic Liquids Centre for the facilities provided in this work and PETRONAS sponsorship for A.K.Z.

REFERENCES

(1) Lopes, J. N. C.; Cordeiro, T. C.; Esperancüa, J. M. S. S.; Guedes, H. J. R.; Huq, S.; Rebelo, L. P. N.; Seddon, K. R. Deviations from Ideality in Mixtures of Two Ionic Liquids Containing a Common Ion. *J. Phys. Chem. B* **2005**, *109*, 3519–3525.

(2) Newington, I.; Perez-Arlandis, J. M.; Welton, T. Ionic liquids as Designer Solvents for Nucleophilic Aromatic Substitutions. *Org. Lett.* **2007**, *25*, 5247–5250.

(3) Ziyada, A. K.; Wilfred, C. D.; Bustam, M. A.; Man, Z.; Murugesan, T. Thermophysical Properties of 1-Propyronitrile-3alkylimidazolium Bromide Ionic Liquids at Temperatures from (293.15 to 353.15) K. J. Chem. Eng. Data **2010**, *55*, 3886–3890.

(4) Karadas, F.; Atilhan, M.; Aparicio, S. Review on the Use of Ionic Liquids (ILs) as Alternative Fluids for CO₂ Capture and Natural Gas Sweetening. *Energy Fuels* **2010**, *24*, 5817–5828.

(5) Schrekker, H. S.; Stracke, M. P.; Schrekker, C. M. L.; Dupont, J. Ether-functionalized imidazolium hexafluorophosphate ionic liquids for improved water miscibilities. *Ind. Eng. Chem. Res.* **2007**, *46* (22), 7389–7392.

(6) (a) Carlisle, T. K.; Bara, J. E.; Gabriel, C. J.; Noble, R. D.; Gin, D. L. Interpretation of CO_2 solubility and selectivity in nitrile-functionalized room-temperature ionic liquids using a group contribution approach. *Ind. Eng. Chem. Res.* **2008**, 47 (18), 7005–7012. (b) Zhang, J.; Zhang, Q.; Qiao, B.; Deng, Y. Solubilities of the gaseous and liquid solutes and their thermodynamics of solubilization in the novel roomtemperature ionic liquids at infinite dilution by gas chromatography. J. *Chem. Eng. Data* **2007**, 52 (6), 2277–2283.

(7) Ziyada, A. K.; Bustama, M. A.; Wilfred, C. D.; Murugesan, T. Densities, viscosities and refractive Indices of 1-Hexyl-3-propanenitrile imidazolium Ionic Liquids Incorporated with Sulfonate –based Anions. J. Chem. Eng. Data **2011**, *56*, 2343–2348.

(8) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem.* **2001**, *3* (4), 156–164. (9) Ziyada, A. K.; Bustam, M. A.; Murugesan, T.; Wilfred, C. D. Effect of sulfonate-based anions on the physicochemical properties of 1-alkyl-3-propanenitrile imidazolium ionic liquids. *New J. Chem.* **2011**, 35, 1111–1116.

(10) Yunus, N. M.; Mutalib, M. I. A.; Man, Z.; Bustam, M. A.; Murugesan, T. Thermophysical properties of 1-alkylpyridinum bis-(trifluoromethylsulfonyl)imide ionic liquids. *J. Chem. Thermodyn.* **2010**, *42*, 491–495.

(11) Zhao, D.; Fei, Z.; Scopelliti, R.; Dyson, P. J. Synthesis and Characterization of Ionic Liquids Incorporating the Nitrile Functionality. *Inorg. Chem.* **2004**, *43*, 2197–2205.

(12) Torrecilla, J. S.; Palomar, J.; Garcí, J. N.; Rodríguez, F. Effect of Cationic and Anionic Chain Lengths on Volumetric, Transport, and Surface Properties of 1-Alkyl-3-methylimidazolium Alkylsulfate Ionic Liquids at (298.15 and 313.15) K. *J. Chem. Eng. Data* **2009**, *54*, 1297–1301.

(13) Tariq, M.; Forte, P. A. S.; Costa, M. F.; Canongia, J. N.; Rebelo, L. P. N. Densities and refractive indices of imidazolium- and phosphonium-based ionic liquids: Effect of temperature, alkyl chain length, and anion. *J. Chem. Thermodyn.* **2009**, *41*, 790–798.

(14) Zhang, Q.; Li, Z.; Zhang, J.; Zhang, S.; Zhu, L.; Yang, J.; Zhang, X.; Deng, Y. Physicochemical Properties of Nitrile-Functionalized Ionic Liquids. J. Phys. Chem. B 2007, 111, 2864–2872.

(15) Yao, M.; Fan, M.; Liang, Y.; Zhou, F.; Xia, Y. Imidazolium hexafluorophosphate ionic liquids as high temperature lubricants for steel-steel contacts. *Wear* **2010**, *268*, 67–71.

(16) (a) Kilaru, P.; Baker, G. A.; Scovazzo, P. Density and surface tension measurements of imidazolium-, quaternary phosphonium-, and ammonium-based room-temperature ionic liquids: data and correlations. *J. Chem. Eng. Data* **2007**, *52* (6), 2306–2314. (b) Gu, Z.; Brennecke, J. F. Volume expansivities and isothermal compressibilities of Imidazolium and Pyridinium-based ionic liquids. *J. Chem. Eng. Data* **2002**, *47*, 339–345.

(17) Soriano, A. N.; Doma, B. T., Jr.; Li, M. H. Measurements of the density and refractive index for 1-n-butyl-3-methylimidazolium-based ionic liquids. *J. Chem. Thermodyn.* **2009**, *41* (3), 301–307.

(18) (a) Brocos, P.; Piñeiro, Á.; Bravo, R.; Amigo, A. Refractive indices, molar volumes and molar refractions of binary liquid mixtures: concepts and correlations. *Phys. Chem. Chem. Phys.* **2003**, *5* (3), 550–557. (b) Hasse, B.; Lehmann, J.; Assenbaum, D.; Wasserscheid, P.; Leipertz, A.; Fröba, A. P. Viscosity, Interfacial Tension, Density, and Refractive Index of Ionic Liquids [EMIM][MeSO₃], [EMIM]-[MeOHPO₂], [EMIM][OcSO₄] and [BBIM][NTf₂] in Dependence on Temperature at Atmospheric Pressure. *J. Chem. Eng. Data* **2009**, 54 (9), 2576–2583.

(19) Glasser, L.; Jenkins, H. D. B. Volume-based thermodynamics: a prescription for its application and usage in approximation and prediction of thermodynamic data. *J. Chem. Eng. Data* **2010**, *56* (4), 874–880.

(20) Glasser, L.; Jenkins, H. D. B. Standard absolute entropies, S°298, from volume or density Part II. Organic liquids and solids. *Thermochim. Acta* **2004**, *414*, 125–130.

(21) (a) Fang, D. W.; Guan, W.; Tong, J.; Wang, Z. W.; Yang, J. Z. Study on Physicochemical Properties of Ionic Liquids Based on Alanine $[C_nmim]Ala$ (n = 2,3,4,5,6). *J. Phys. Chem. B* **2008**, *112*, 7499–7505. (b) Yang, J.-Z.; Zhang, Q.-G.; Wang, B.; Tong, J. Study on the Properties of Amino Acid Ionic Liquid EMIGly. *J. Phys. Chem. B* **2006**, *110*, 22521–22524.

(22) Glasser, L. Lattice and phase transition thermodynamics of ionic liquids. *Thermochim. Acta* **2004**, 421, 87–93.

(23) Guan, W.; Tong, J.; Chen, S. P.; Liu, Q. S.; Gao, S. L. Density and Surface Tension of Amino Acid Ionic Liquid 1-Alkyl-3methylimidazolium Glutamate. *J. Chem. Eng. Data* **2010**, 639–646.