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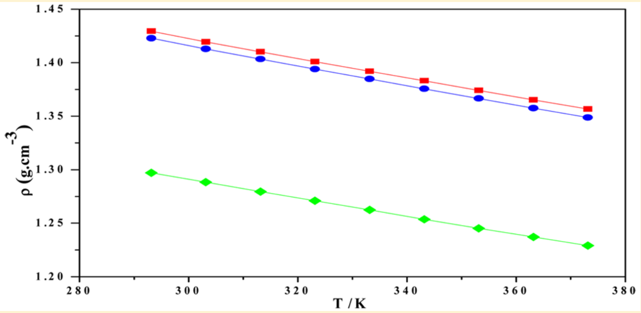
Physicochemical Properties of New Imidazolium-Based Ionic Liquids Containing Aromatic Group

Massoud Kermanioryani,*,[†] M. Ibrahim A. Mutalib,[†] Yue Dong,[‡] Kallidanthiyil Chellappan Lethesh,[§] Ouahid Ben Omar Ben Ghanem,[†] Kiki Adi Kurnia,[†] Noor Fathanah Aminuddin,[†] and Jean-Marc Leveque*,[∥]

[†]Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Perak, Malaysia
[‡]University of Oulu, Research Unit of Sustainable Chemistry, P.O.Box 3000, FIN-90014 Oulu, Finland
[§]Center for Biofuel and Biochemical Research, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Perak, Malaysia
[∥]Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Perak, Malaysia

Supporting Information

ABSTRACT: In this work, three novel imidazolium-based ionic liquids containing aromatic group in the cation combined with bis(trifluoromethylsulfonyl)imide anion were synthesized and characterized. Their thermophysical properties namely, density, viscosity, thermal decomposition, glass transition, and heat capacity were measured at various temperatures and atmospheric pressure. In addition, physicochemical properties such as molar volume (V_m) and crystal energy (U_{POT}) were also determined from the obtained density data. Novel group contribution parameters were obtained using Gardas and Coutinho model aiming at providing simple method to predict density and viscosity of ionic liquids.



1. INTRODUCTION

Room temperature ionic liquids (RTIL) are a new class of organic salts based on bulky organic cations and organic or inorganic anions with melting point below 100 °C.[1] Interestingly, their properties, such as density and viscosity, are tunable by selecting proper cations and anions combinations.[2] Nitrogen atom containing heterocyclic compounds such as imidazole, pyridine, pyrrolidine, and their derivatives remain as the most common cations affording different types of ILs when linked to various anions such as basic halides or more evolved organic/inorganic moieties like $[BF_4]^-$, $[PF_6]^-$, $[NTf_2]^-$, $[CH_3COO]^-$, prolinate [Pro], alaninate [Ala], and glycinate [Gly].[3−5] These families of compounds do display some unique and striking properties making them of high interest in both academia and industry such as high thermal stability, negligible vapor pressure enabling possible recycling, relatively high ionic conductivity, and good electrochemical stability. These properties make them very promising in various applications such as catalysis, capacitors, organic synthetic chemistry, batteries, solar cells, separation, adsorption process, and so forth.[6−12] Additionally, over the past decade, there is a growing interest in a new class of RTIL, which are called task-specific ILs (TSIL) specially designed for specific applications. These latters do contain a functional group that is incorporated either into the organic cation or into the anion to achieve a special task in a given chemical system.[13−17] In this present work, several important physicochemical properties of three newly synthesized TSILs—namely, 1-butyl-3*H*-benzoimidazolium bis(trifluoromethylsulfonyl)imide, $[BzBIm][NTf_2]$; 1-butyl-2-phenyl-imidazolium bis(trifluoromethylsulfonyl)imide, $[BPhIm][NTf_2]$; and 1-benzyl-3-butyl-imidazolum bis(trifluoromethylsulfonyl)imide $[BnBIm][NTf_2]$—were studied to investigate the impact of the location of aromatic groups at different positions on the imidazolium ring. The structure of the newly synthesized TSIL is given in Figure 1.

Notably, the density, viscosity, thermal decomposition, glass transition, and heat capacity of the TSILs were measured at different temperature and atmospheric pressure. Certain significant physicochemical and thermal properties also were determined from the experimental data. The thermal behavior of the TSILs was studied using thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses. Furthermore, on the basis of the experimental data, novel group contribution parameters for Gardas and Coutinho models[18,19] are proposed here for these newly synthesized cation aiming at predicting densities and viscosities of ILs not previously investigated experimentally.

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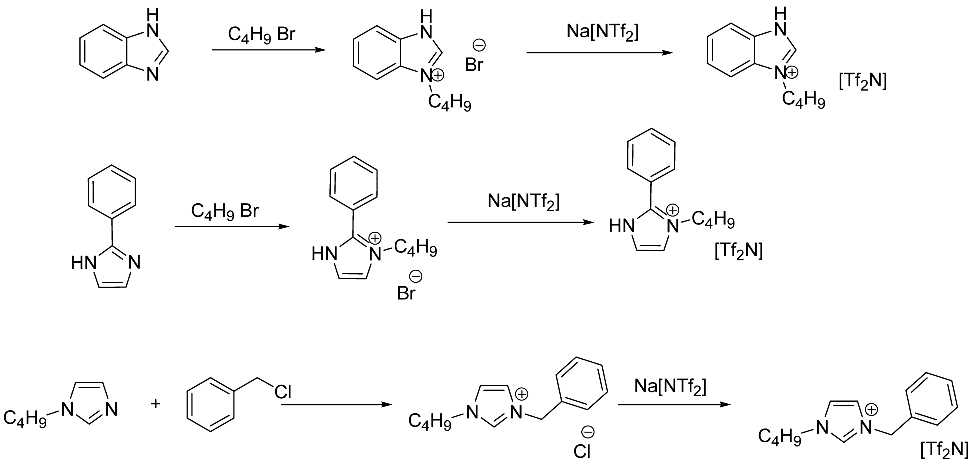

Figure 1. General route for the synthesis of studied ionic liquids. [BzBIm][NTf_2], [BPhIm][NTf_2], and [BnBIm][NTf_2].

2. EXPERIMENTAL SECTION

2.1. Materials. The following chemicals, namely, 1-bromo butane (≥98%), 2-phenylimidazole (≥95%), benzimidazole (≥99%), 1-butylimidazole (≥98%), and benzyl chloride (≥99%) were purchased from Merck. Sodium bis(trifluoromethanesulfonyl)imide (≥97%) was supplied by sigma Aldrich. Dichloromethane, acetonitrile (≥99.8%), and diethyl acetate (≥99.99%) were purchased from Fisher Scientific U.K. All reagents were used as received without any further purification. The chemical information table is given in Supporting Information (Table S1).

2.2. Synthesis of Ionic Liquids. *2.2.1. Synthesis of 1-Butyl-3H-BenzoImidazolium Bis(trifluoromethylsulfonyl)imide [BzBIm][NTf_2].* To a solution of benzimidazole (2.36 g, 0.02 mol) in acetonitrile (20 mL) in a three-neck round-bottom flask, 1-bromobutane (2.74 g, 0.02 mol) was added at room temperature. The mixture was then heated under reflux in a nitrogen atmosphere for 48 h. After the completion of the reaction, acetonitrile was evaporated using a rotary evaporator and the resulting slightly yellowish product was washed three times with ethyl acetate (ca. 25 mL) to remove the unreacted reagents. The solvent was then removed using a rotary evaporator and the product obtained was further dried in a vacuum oven (50 mbar) at 60 °C for 48 h. The IL was obtained as a highly viscous and pale yellow liquid with 96% yield (4.89 g). In the second step, to a solution of [BzBIm]Br (5.1 g, 0.02 mol) in water, a solution of sodium bis(trifluoromethylsulfonyl)imide (6.06 g, 0.02 mol) was added and the resulting solution was stirred for 24 h at room temperature. The hydrophobic IL formed was separated from water phase and washed several times with deionized water until the washing water gave no precipitate with $AgNO_3$ solution. Traces of water were then removed by drying under vacuum line (50 mbar) at 70 °C for 48 h. The IL was obtained as a pale yellow liquid with a 97% yield (8.57 g). ^1H NMR (500 MHz, MeOD) δ = 1.03 (t, 3H), 1.46 (m, 2H), 2.01 (m, 2H), 4.52 (t, 2H), 7.91 (m, 4H), 9.33 (s, 1H).

2.2.2. Synthesis of 1-Butyl-2-phenyl-imidazolium Bis(trifluoromethylsulfonyl)imide [BPhIm][NTf_2]. The 1-butyl-2-phenyl-imidazolium bis(trifluoromethylsulfonyl)imide was synthesized using a similar two-step general procedure described as for [BzBIm][NTf_2] from 2-phenyl-imidazole (2.88 g, 0.02 mol), 1-bromobutane (2.74 g, 0.02 mol), and sodium bis(trifluooromethylsulfonyl)imide (6.06 g, 0.02 mol), respectively, and was obtained with a 96% yield (9.23 g). ^1H NMR (500 MHz, MeOD) δ = 0.84 (t, 3H), 1.51 (m, 2H), 1.75 (m, 2H), 4.04 (t, 2H), 7.2 (m, 5H), 7.96 (m, 2H).

2.2.3. Synthesis of 1-Benzyl-3-butyl-imidazolum Bis(trifluoromethylsulfonyl)imide [BnBIm][NTf_2]. The 1-benzyl-3-butyl-imidazolum bis(trifluoromethylsulfonyl)imide was synthesized using the general procedure as described for [BzBIm][NTf_2] from 1-butylimidazole (2.48 g, 0.02 mol), benzyl chloride (2.52g, 0.02 mol), and sodium bis(trifluoromethylsulfonyl)imide (6.06 g, 0.02 mol), respectively, and was obtained with a 98% yield (9.7 g). ^1H NMR (500 MHz, MeOD) δ= 0.98 (t, 3H), 1.38 (m, 2H), 1.90 (m, 2H), 4.25 (m, 2H), 5.46 (s, 2H), 7.44 (m, 5H), 7.66 (m, 2H).

2.3. Density and Viscosity Measurements. The measurement of density and viscosity of TSILs was carried out using Anton Paardensitometer (SVM 3000). The calibration of instrument was carried with Millipore-grade water according to the manual, for which the data was proven. Furthermore, the equipment was also used to measure the density and viscosity of other ILs published in literature[20,21] and support the viability of the equipment to determine the accurate properties of IL samples.

2.4. Thermal Analysis and Heat Capacity. *2.4.1. Thermal Decomposition.* Thermal decomposition temperature of TSIL was measured using PerkinElmer, Pyris V-3.81 thermal gravimetric analyzer. The samples were placed in sealed aluminum pans under nitrogen flow at a heating rate of 10 K/min with temperature precision of 1 K.

2.4.2. Glass Transition. A differential scanning calorimeter (Mettler Toledo, MODEL (DSC1/500) was used to measure glass transition temperature. Small amounts of TSILs samples were placed in sealed aluminum pans and cooled to 193.15 K and then heated to 393.15 K with a heating rate of 10 K/Min. The glass transition temperatures were determined with a temperature accuracy of 1 K.

2.4.3. Heat Capacity Measurements. To ensure the high accuracy of defining heat capacity of the TSILs, the sapphire method[22] was selected. Samples were set in sealed aluminum pans and the temperature was increased from 303.15 K until 353.15 K with a heating rate of 5 K/min. Each rise of temperature of 5 K was sustained for 15 min.

3. RESULTS AND DISCUSSION

3.1. Characterization. The ^1H NMR spectra were taken in deuterated methanol (MeOD) and recorded on a Bruker

Table 1. Chemical Name, Purification Method, Mole Fraction Purity, Analysis Method, and Water Content of ILs

chemical name	purification method	mole fraction purity	analysis method	water content (ppm)
1-butyl-3*H*-benzoimidazolium bis(trifluoromethanesulfonyl)imide	activated carbon + methanol	0.99	^{1}H NMR	418
1-butyl-2-phenyl-imidazolium bis(trifluoromethylsulfonyl)imide	activated carbon + methanol	0.99	^{1}H NMR	443
1-benzyl-3-butyl-imidazolum bis(trifluoromethylsulfonyl)imide	activated carbon + methanol	0.998	^{1}H NMR	411

Advance 500 spectrometer. It is very important that the examined TSILs are anhydrous as possible because the presence of water can significantly influence the physicochemical properties. Hence, all studied ILs were extensively dried in vacuum oven at 343.15 K for 48 h followed by the determination of water content by using a colulometric Karl Fischer titrator (DL 39, Mettler Toledo) using Hydranal coulomat AG reagent. The average of three measurements of water content of each IL, mole fraction purity, and analysis method are presented in Table 1.

3.2. Density. The densities of the studied ILs were determined in the temperature range of 293.15−373.15 K and the results are plotted in Figure 2. The ILs studied in this work allow us to investigate the cation structural impact, particularly the presence of aromatic ring on the cation, toward their density. The obtained data revealed that the density values follow the order: [BzBIm][NTf$_2$] ≥ [BPhIm][NTf$_2$] > [BnBIm][NTf$_2$]. Aiming at understanding the impact of aromatic ring on the cation, the obtained density data in this work is compared with nonaromatic IL from literature[23] and is plotted as a function of their molecular volume (Figure 3). According to the obtained data, the density of studied ILs are lower than some commercial [NTf$_2$] ILs with short alkyl chain length (<4) and have higher density than commercial [NTf$_2$] ILs with longer alkyl spacer length.[24] For example, the density of [MMIm][NTf$_2$] is 1.56 g/cm^3, which is higher than the studied ILs. On the other hand, the density of [NTf$_2$] ILs with six carbon atoms [HMIm][NTf$_2$] is 1.37 g/cm^3, which is lower than the ILs reported here.[25,26] It is clear that the density decreased with increasing molecular volume of the ILs. However, it is interesting to note that even though the density of aromatic group containing ILs studied in this work also decrease with increasing the molecular volume, [BzBIm][NTf$_2$] and [BPhIm][NTf$_2$] do not fall exactly on this relationship (see the dot lines in the Figure 2). The higher density of these two aromatic containing ILs might be due to the position of aromatic group and its subsequent influence on the π−π stacking interaction.

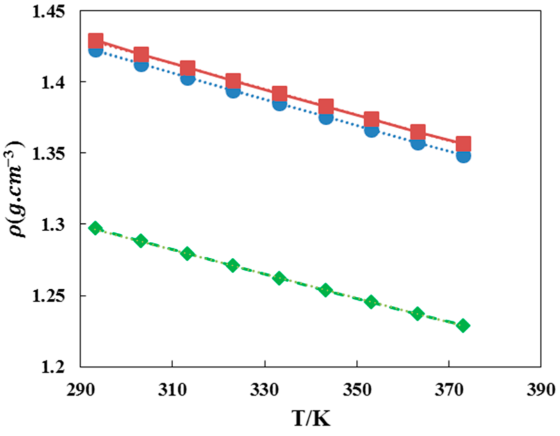

Figure 2. Density as a function of temperature: ■—■, [BzBIm][NTf$_2$]; ●······●, [BPhIm][NTf$_2$]; and ◆—·—◆, [BnBIm][NTf$_2$].

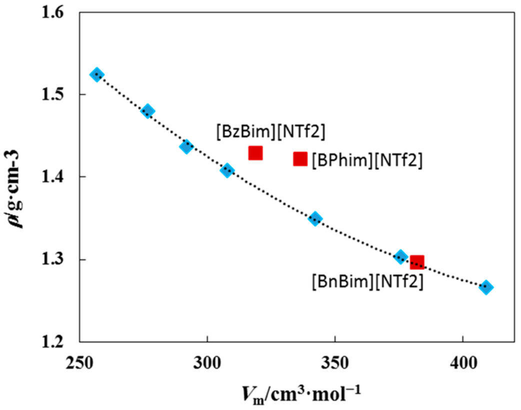

Figure 3. Plot of V_m versus density of [NTf$_2$]-based ionic liquids: ◆, nonaromatic IL; ■, aromatic-containing IL. The line does not have any specific physical meaning.

When looking at the three structures shown in Figure 1, it can be assumed that when the degrees rotation freedom between the imidazolium and aromatic rings increases, the rotation ability of the aromatic ring increases and resulted in lower intermolecular π−π interaction. Typically, the presence of the methylene group of the benzyl group in [BnBIm][NTf$_2$] leads to a 3D structure where the free rotation of the phenyl group is authorized leading to decreased intermolecular π−π interactions. On the other hand, the flat 2D structure of the [BzBIm][NTf$_2$] offers enhanced intermolecular π−π forces and thus higher density value.

The density decreased with increasing temperature; a common trend observed for the density−temperature dependence of ILs. The experimental densities (ρ) were fitted using the least-squares method based on the equation

$$\rho/(\mathrm{g\cdot cm})^{-3}=A_0 + A_1T \tag{1}$$

where ρ denotes the density of the ILs, A_0 and A_1 are the correlation coefficients, and T is the temperature in Kelvin. Plot of ρ (g·cm^{-3}) against T (K) is shown in Figure 2. The correlation coefficients were calculated from the slope and intercept of the plot, respectively, and their estimated values with the standard deviations (SD) are presented in Table 2. According to the R^2 values, which are close to 1 (0.99) for all three studied ILs, it was concluded that the experimental densities were a good fit.

By using the experimental densities, the other thermophysical properties, such as molar volume (V_m) and crystal energy (U_{POT}), were determined.

3.2.1. Molar Volume. The molar volumes (V_m) of the ILs were calculated according to eq 2 at standard temperature and pressure

$$V_m/(\mathrm{cm^3\cdot mol^{-1}}) = \frac{M}{\rho} \tag{2}$$

where M is the molar mass (g·mol^{-1}) and ρ is the density (g·cm^{-3}). The values of V_m are tabulated in Table 2. According to the V_m values, it is deduced that the molar volume (V_m) of

Table 2. Fitting Parameter Values A_0, A_1, and R^2 for Densities, Standard Deviation SD, Molar Volume V_m, and Crystal Energy U_{POT} of ILs at 298.15 K and 0.1 MPa[a]

parameter	[BzBIm][NTf$_2$]	[BPhIm][NTf$_2$]	[BnBIm][NTf$_2$]
A_0	1.6942	1.6927	1.5463
$A_1 \times 10^4$	−9	−9	−9
R^2	0.9997	0.9997	0.9998
SD	2.13×10^{-03}	7.78×10^{-03}	1.62×10^{-02}
V_m (cm^3·mol^{-1})	309.242	338.136	381.698
U_{POT} (kJ·mol^{-1})	397.02	389.09	377.21

[a] Standard deviation values were calculated using $\mathrm{SD} = \sqrt{\frac{\sum (Z_{exp} - Z_{cal})}{n}}$ where SD, n, Z_{exp}, and Z_{cal} are the standard deviations, number of experimental points, and experimental and calculated data values, respectively.

studied ILs decreased in the order of [BnBIm][NTf$_2$] > [BPhIm][NTf$_2$] > [BzBIm][NTf$_2$]. By increasing the molar mass of ILs (M), the molar volume (V_m) of ILs increase accordingly.

3.2.2. Crystal Energy. The crystal energy (U_{POT}) is defined as the energy needed to form salts from separated ions, molecules or atoms which is calculated according to Glasser's theory[27] by using the following equation:

$$U_{POT}/(\mathrm{KJ\cdot mol^{-1}}) = 1981.2\left(\frac{\rho}{\mathrm{M}}\right)^{1/3} + 103.8 \tag{3}$$

where ρ and M are density and molar mass of ILs, respectively, and the U_{POT} values are listed in Table 2. Because of their lower crystal energies compared to inorganic fused salts, ILs are liquids at room temperature. For example, the U_{POT} values of [BzBIm][NTf$_2$], [BPhIm][NTf$_2$], and [BnBIm][NTf$_2$] are 397.02 kJ·mol^{-1}, 389.09 kJ·mol^{-1}, and 377.21 kJ·mol^{-1}, respectively, which are much lower than inorganic salts such as NaI, NaCl, and $CaCO_3$ with U_{POT} values 682 kJ·mol^{-1}, 786 kJ·mol^{-1}, and 2804 kJ·mol^{-1}, respectively.[28] The calculated U_{POT} values are in accordance with literature[5] and follow the trend [BzBIm][NTf$_2$] > [BPhIm][NTf$_2$] > [BnBIm][NTf$_2$], clearly showing that the lower the molecular weight is, the more compact the ILs are, leading thus to a higher lattice energy.

3.2.3. Isobaric Thermal Expansion Coefficient. The experimental density values were used to calculate the isobaric thermal expansion coefficients (α) using the following equation:

$$\alpha(\mathrm{K^{-1}}) = \frac{1}{V_m}\left(\frac{\delta V_m}{\delta T}\right)_p = -\left(\frac{\delta \rho}{\delta T}\right)_p \tag{4}$$

The values of the isobaric thermal expansion coefficient are shown in Table 3. The α values of the studied ILs are in the order [BnBIm][NTf$_2$] > [BPhIm][NTf$_2$] ≥ [BzBIm][NTf$_2$]. It is found that the temperature has no significant effect on the coefficients of thermal expansion of the present ILs. The thermal expansion coefficients of these ILs are higher than [BMIm][NTf$_2$], which has same alkyl chain length as that of the studied ILs.[29]

3.3. Viscosity. The dynamic viscosity measurements of the studied TSILs were carried out at different temperatures and the results are plotted in Figure 4. The viscosities of the TSILs decrease in the order of [BzBIm][NTf$_2$] > [BPhIm][NTf$_2$] > [BnBIm][NTf$_2$], which was expected according to the structures of ILs. Indeed, the observed trend is similar to the one obtained for density measurements and as mentioned before, the degrees rotation freedom between the imidazolium and the different types of aromatic rings greatly influence the nature of the intermolecular $\pi-\pi$ interactions thus impacting viscosity, that is, the lesser the degrees of rotational freedom, the stronger the intermolecular $\pi-\pi$ interactions. This explains why the viscosity of [BzBIm][NTf$_2$] and [BPhIm][NTf$_2$] are particularly much higher than of commercial ILs ones bearing side alkyl chain. For example the viscosity values of [BzBIm][NTf$_2$], [BPhIm][NTf$_2$] and [BnBIm][NTf$_2$] at 20 °C are 1150.40 mPa·s, 753.71 mPa·s and 86.75 mPa·s, respectively, which are higher than the viscosity values of [EMIm][NTf$_2$] and [BMIm][NTf$_2$] with 34 mPa·s and 52 mPa·s, respectively.[25,30,31]

Table 3. Isobaric Thermal Expansion Coefficient α, of ILs as a Function of Temperature

	$\alpha \cdot 10^4/(\mathrm{K^{-1}})$		
T/K	[BzBIm][NTf$_2$]	[BPhIm][NTf$_2$]	[BnBIm][NTf$_2$]
293.15	6.29	6.30	7.02
303.15	6.33	6.34	7.07
313.15	6.37	6.38	7.12
323.15	6.41	6.42	7.17
333.15	6.45	6.46	7.22
343.15	6.50	6.50	7.27
353.15	6.54	6.55	7.33
363.15	6.58	6.59	7.38
373.15	6.63	6.63	7.44

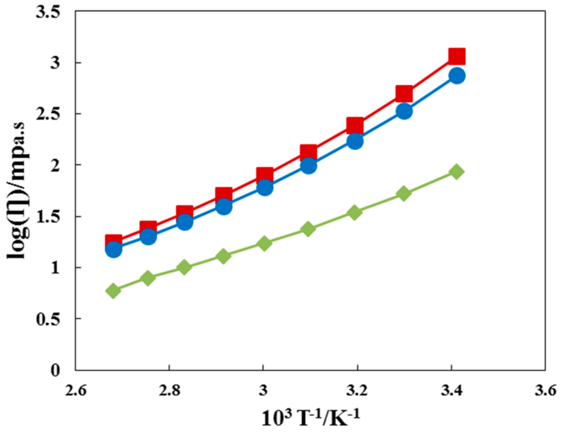

Figure 4. Viscosity as a function of temperature: ■, [BzBIm][NTf$_2$]; ●, [BPhIm][NTf$_2$]; ◆, [BnBIm][NTf$_2$].

The experimental viscosities (η) for ILs were fitted by the following equation:

$$\log \eta(\mathrm{Pa\cdot s}) = A_2 + \frac{A_3}{T} \tag{5}$$

where η denotes the viscosity of the ILs, and A_2 and A_3 are the correlation coefficients and T is temperature (K). By plotting the logarithm viscosities of ILs over $1/T$, the A_2 and A_3 are estimated from intercept and slope of plot, respectively, and the values are presented in Table 4.

3.4. Thermal Decomposition. Thermal gravimetric analysis (TGA) experiments were performed for the studied ILs to compare their thermal stability with the commercially available ones. Thermal decompositions (T_d) were determined in terms of onset temperature (T_s) and the results are present in Table 5 and plotted in Figure 5. The T_d values of the ILs were within the range of 677−694 K and the thermal stability increased in the order of [BzBIm][NTf$_2$] > [BPhIm][NTf$_2$] > [BnBIm][NTf$_2$]

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Table 4. Fitting Parameter Values for Viscosities with Correlation Coefficient R^2

IL	A	B	T_0	R^2
[BzBIm][NTf$_2$]	−1.20	455.58	186.26	1
[BPhIm][NTf$_2$]	−0.98	390.78	191.84	1
[BnBIm][NTf$_2$]	−1.01	377.86	165.17	0.99

Table 5. Decomposition Temperature in Terms of Onset Temperature T_s and Glass Transition Temperature T_g of ILs at 0.1 MPa[a]

	[BzBIm][NTf$_2$]	[BPhIm][NTf$_2$]	[BnBIm][NTf$_2$]
T_d/K	694.67	681.85	677.83
T_g/K	220.68	220.18	187.02

[a] The standard uncertainties are $u(T_d) = 1$ K, $u(T_g) = 1$ K, $u(p) = 0.01$ MPa.

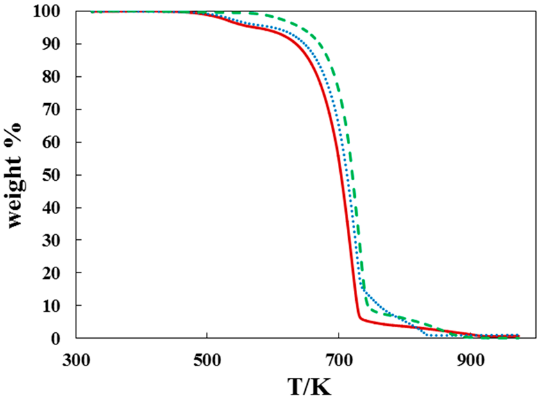

Figure 5. Thermogravimetric profiles of ILs: red —, [BzBIm][NTf$_2$]; blue ······, [BPhIm][NTf$_2$]; green – –, [BnBIm][NTf$_2$].

with 694.67 K, 681.85 K, and 677.83 K, respectively. Previous studies have reported[8,32] that as the molecular weight of the IL increases, the T_d value decreases accordingly, which is in accordance with our results. For example the T_d values for [EMIm][NTf$_2$], [PMIm][NTf$_2$], and [BMIm][NTf$_2$] are 728.15 K, 725.15 K, and 712.15 K, respectively.

3.5. Glass Transition Temperature. The glass transition temperature (T_g) is defined as the midpoint of a small heat capacity change on heating from the amorphous glass state to a hard and relatively frangible state and vice versa. The T_g values for the studied ILs follow the trend [BzBIm][NTf$_2$] > [BPhIm][NTf$_2$] > [BnBIm][NTf$_2$].

3.6. Heat Capacity. The heat capacity (C_p) analyses for studied ILs were performed in the temperature range of 303.15–353.15 K and the results are plotted in Figure 6. The C_p values of the studied ILs are relatively higher compared to analogs of imidazolium ILs with same anion but with side alkyl chain. For instance, the C_p of 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide [EMIm][NTf$_2$] and 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide [BMIm][NTf$_2$] at 323.15 K are 532.2 and 543.9 J·mol^{-1}·K, respectively,[33] whereas the C_p value of [BnBIm][NTf$_2$], [BPhIm][NTf$_2$], and [BzBIm][NTf$_2$] at 323.15 K are 706.15, 643.24, and 571.78 J·mol^{-1}·K, respectively. It is known that the larger the number of degrees of freedom available, the larger will be the specific heat capacity of a substance. This goes again in the direction of consolidating our hypothesis based on the high impact exerted by the nature of the aromatic ring grafted on the imidazolium ring on several physicochemical properties of ILs presented in this work.

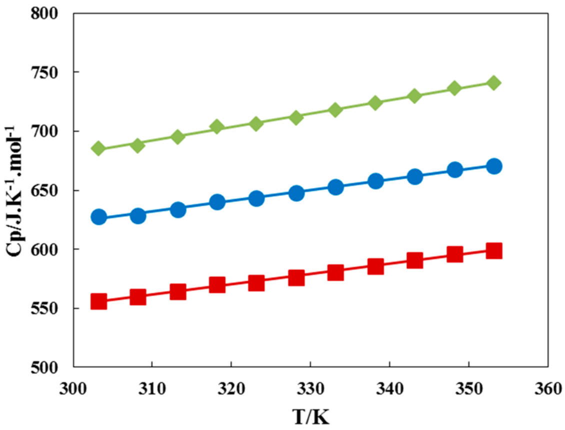

Figure 6. Experimental heat capacity C_p as a function of temperature of ILs: ■, [BzBIm][NTf$_2$]; ●, [BPhIm][NTf$_2$]; ◆, [BnBIm][NTf$_2$].

3.7. Group Contribution. With the high number of possible cation and anion to form ILs, a simple equation to predict the physical properties of novel (or not yet synthesized) ILs is very important.[34] The density data measured in this work were also used to broaden the group contribution parameter values in the extension of the Ye and Shreeve group contribution method[35] previously proposed by Gardas and Coutinho,[19] intended to enable the prediction of densities of ILs not experimentally addressed. The contributions of the three novel cations were estimated according to the following equation:

$$\rho = \frac{M_w}{NV(a + bT + cp)} \qquad (6)$$

where ρ is the density in kg·m^{-3}, M_w is the IL molecular weight in kg·mol^{-1}, N is Avogadro constant, V is the IL volume in m^3, T is the temperature in K, and p is the pressure in MPa. The coefficients a, b, and c were previously proposed using a large set of experimental data and using the following values of 0.8005 ± 0.002, $(6.652 \pm 0.007) \times 10^{-4}$ K^{-1}, and $(-5.919 \pm 0.024) \times 10^{-4}$ MPa^{-1}, respectively.[19,36]

The new proposed ionic volumes are given in Table 6 along with those previously reported for the —CH$_2$— and [NTf$_2$].

Table 6. Group Contribution Parameters, V, $a_{i\eta}$, and $b_{i\eta}$ of the Group Contribution Method for the Prediction of Density and Viscosity According to the Gardas and Coutinho Model

ionic species	V/A^3	$a_{i\eta}$	$b_{i\eta}$/K
	Cations		
benzoimidazolium	202	−2.526	1174
2-phenylimidazolium	269	−2.223	1080
1-benzylimidazolium	306	−1.041	661
	Anion[19,36]		
[NTf$_2$]	248	−1.119	94.2
	Additional Group[19,36]		
—CH$_2$—	28	−0.07528	40.92

Table 7 compares the experimental density data with the predicted density based on the group contribution method and their density–temperature dependence. In general, with the absolute average deviation of 0.06%, the predicted values are in good agreement with the experimental data. The predicted cation volume by the Gardas and Coutinho[19,36] showing a strict

Table 7. Comparison between Experimental and Predicted Density and Viscosity Using Gardas and Coutinho[19,36] Group Contribution Model

	ρ/g·cm^{-3}			η/mPa·s		
T/K	experiment	predicted	AAD	experiment	predicted	AAD
			[BzBIm][NTf$_2$]			
293.15	1.4228	1.4226	0.01	1150.4	1084.44	5.73
303.15	1.4128	1.4132	0.03	497.14	493.95	0.64
313.15	1.4033	1.4039	0.04	244.69	250.20	2.25
323.15	1.3940	1.3947	0.05	133.61	138.12	3.37
333.15	1.3848	1.3856	0.06	79.3	81.83	3.19
343.15	1.3756	1.3766	0.08	50.425	51.42	1.97
353.15	1.3665	1.3678	0.09	33.921	33.95	0.07
363.15	1.3575	1.3591	0.12	23.966	23.37	2.49
373.15	1.3488	1.3504	0.12	17.589	16.68	5.19
			[BPhIm][NTf$_2$]			
293.15	1.4293	1.4281	0.08	753.71	704.60	6.52
303.15	1.4195	1.4187	0.06	339.74	338.45	0.38
313.15	1.4101	1.4093	0.06	173.94	179.50	3.20
323.15	1.4009	1.4001	0.06	98.778	103.15	4.43
333.15	1.3919	1.3910	0.07	60.902	63.31	3.96
343.15	1.3830	1.3820	0.07	40.104	41.05	2.37
353.15	1.3740	1.3731	0.07	27.866	27.87	0.03
363.15	1.3652	1.3643	0.06	20.237	19.68	2.76
373.15	1.3566	1.3557	0.07	15.215	14.37	5.57
			[BnBIm][NTf$_2$]			
293.15	1.2971	1.2955	0.12	86.75	87.31	0.64
303.15	1.2883	1.2869	0.11	52.838	53.15	0.59
313.15	1.2796	1.2784	0.09	34.648	34.60	0.15
323.15	1.2710	1.2700	0.08	23.822	23.78	0.19
333.15	1.2624	1.2618	0.05	17.243	17.09	0.90
343.15	1.2537	1.2536	0.01	12.965	12.74	1.70
353.15	1.2453	1.2456	0.02	10.021	9.81	2.15
363.15	1.2372	1.2376	0.03	7.9322	7.75	2.33
373.15	1.2292	1.2298	0.04	5.9353	6.26	5.49
			0.06			2.53

dependence of density with the ILs cation containing aromatic ring—an increase in the ionic volume of the cation results in less denser fluid, as observed experimentally.

The contribution of each aromatic-containing cation to the viscosity of the related ILs was also estimated using group contribution method proposed by Gardas and Coutinho[19,36] according to the following equation:

$$A_{\eta} = \sum_{i=1}^{k} n_i a_{i,\eta} \tag{7}$$

$$B_{\eta} = \sum_{i=1}^{k} n_i b_{i,\eta} \tag{8}$$

where n_i is the number of groups of type i and k is the total number of different groups in the molecule. The obtained parameters $a_{i\eta}$ and $b_{i\eta}$ are also provided in Table 7 and allow us to predict the viscosity values of novel ILs with similar cations. The predictive viscosity for the studied ILs is presented also in Table 7. The average relative deviation predicted by the Gardas and Coutinho model was found to be 2.53%. The cation nature and temperature—dependence viscosity is well predicted.

4. CONCLUSION

In this investigation, the physicochemical and thermal properties of some new task specific ionic liquids, namely, [BzBIm][NTf$_2$], [BPhIm][NTf$_2$], and [BnBIm][NTf$_2$] were studied. The densities and viscosities of the ILs were found to follow the trend of [BzBIm][NTf$_2$] > [BPhIm][NTf$_2$] > [BnBIm][NTf$_2$]. As expected, the densities and viscosities values decrease with increasing temperature. The measured thermal stability (T_d) and glass transition temperature (T_g) decrease in the order of [BzBIm][NTf$_2$] > [BPhIm][NTf$_2$] > [BnBIm][NTf$_2$] The heat capacities of studied ILs decrease in order of [BnBIm][NTf$_2$] > [BPhIm][NTf$_2$] > [BzBIm][NTf$_2$] and the obtained values are higher than imidazolium based ILs with short alkyl chain length. The results indicate that the presence of the different types of aromatic groups in ILs structures as functional groups exerts a major influence in the physicochemical properties of ILs notably through number of available degrees of freedom by strengthening/weakening intermolecular $\pi-\pi$ interactions. The novel group contribution parameter for the novel cation is presented, aiming at providing simple method to predict the density and viscosity of ILs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.5b00983.

^{1}H NMR spectra for all synthesized ILs and experimental density (ρ), viscosity (η), and heat capacity (C_p) as a function of temperature, and 95% confidence intervals for density coefficients A_0 and A_1 and DSC thermograms of ILs at various temperatures. (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: masoud.kermani1984@gmail.com. Phone: +60-195577289.
*E-mail: jm.leveque@petronas.com.my. Phone: +60-53687425.

Notes

The authors declare no competing financial interest.

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