

Thermo Physical Properties of Brönsted Acidic Ionic Liquids Based on Quaternary Ammonium Cation Binary Mixtures with Water at various temperatures from (293.15 to 363.15) K

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Abstract

The Brönsted Acidic Ionic Liquids (BAILs) $[\text{Bu}_3\text{NH}][\text{H}_2\text{PO}_4]$, $[\text{Bu}_3\text{NH}]\text{HSO}_4$, $[\text{Bu}_3\text{NH}]\text{NO}_3$, $[\text{Bu}_3\text{NH}]\text{Cl}$ were synthesized and characterized using TLC, FT-IR, ¹H-NMR and elemental analysis. Experimental densities (ρ), dynamic viscosities (η), surface tension (σ), electrical conductivity (κ), refractive indices (nD) and thermal conductivity (λ), that were investigated as a function of temperature under (293.15 to 363.15) K conditions, for binary systems with water ionic liquids at atmospheric pressure. A common and effective way to evaluate the acidity of Brönsted acids was the Hammett method (H_o) which can use them for BAILs, pH and pK_a . Also densities, dynamic viscosity, surface tension, ionic conductivity, refractive indices and thermal conductivity deviations, and dynamic viscosity deviations in for the binary systems with water were fitted to a Vogel-Fulcher-Tammann (VFT) equation. The present synthesized ionic liquids show a weak temperature dependency on physical properties. To conclude, there were some explanations on the structure effect of the ILs on the physical properties, the quality of this study would be substantially promoted as follow: $[\text{Bu}_3\text{NH}][\text{H}_2\text{PO}_4] > [\text{Bu}_3\text{NH}][\text{HSO}_4] > [\text{Bu}_3\text{NH}][\text{NO}_3] > [\text{Bu}_3\text{NH}][\text{Cl}]$

Key Words: Brönsted Acidic Ionic Liquids (BAILs); Room Temperature Ionic Liquids (RTILs); Thin Liquid Chromatography (TLC); Vogel-Fulcher-Tammann (VFT).

basic physical-chemical properties of this ionic liquid are either in short supply or absent [5].

To devise any process involving ionic liquids on an industrial level, it is essential to know a series of physical properties including viscosity, density, surface tension, refractive Index, ionic conductivity, thermal conductivity, etc. Furthermore, the presence of water in the ionic liquid phase can considerably affect their physical properties [6]. In spite of the interesting feature and practical importance of ILs, there are limited literature reports for the accurate measurements of many of their fundamental physical and chemical properties at various temperatures [7]. Thus, in this paper we wish to report the results of our studies on the physical, thermodynamic and transport properties of BAILs. Properties such as dynamic viscosity, density, surface tension, refractive Index, thermal stability, ionic conductivity, thermal conductivity Hammett value (H_o) and pH , for various ionic liquids including, $[\text{Bu}_3\text{NH}][\text{H}_2\text{PO}_4]$ +water, $[\text{Bu}_3\text{NH}][\text{HSO}_4]$ +water, $[\text{Bu}_3\text{NH}][\text{NO}_3]$ +water, and $[\text{Bu}_3\text{NH}]\text{Cl}$ +water were determined as a function of the temperature in the range of (293.15, 363.15) K and atmospheric pressure.

Experimental section

Preparation of ionic liquids and Pyritization of ILs

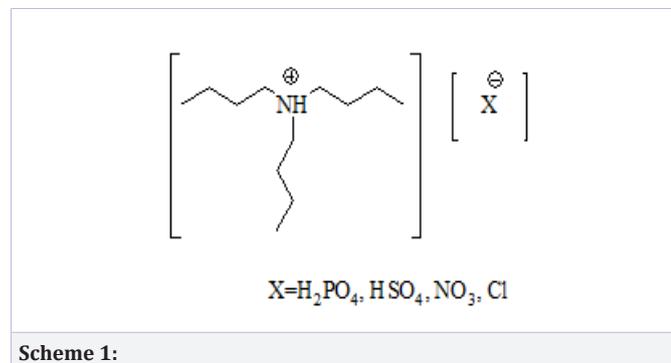
Materials: Water used was freshly deionized and distilled before use. Tributylamine was purchased from the Sigma-Aldrich. (>99 % of purity), Sulfuric acid (98%) and nitric acid (78%) and phosphoric acid (99%) and Choleric acid (37%) were purchased from Merck. The purity of the ILs were confirmed by FT-IR and ¹H-NMR spectroscopy and elemental analysis. The BAILs were prepared from the corresponding chlorides according to the procedures reported in literature [8].

Synthesis of ILs: $[\text{Bu}_3\text{NH}][\text{H}_2\text{PO}_4]$, $[\text{Bu}_3\text{NH}][\text{HSO}_4]$, $[\text{Bu}_3\text{NH}][\text{NO}_3]$, $[\text{Bu}_3\text{NH}]\text{Cl}$. Initially, tri-butylamine Chloride was added in to a round-bottom flask, dichloromethane was added and stirred thoroughly, and then concentrated Brönsted acids in to 1:1

Introduction

One of the main principles of green chemistry is the avoiding using dangerous solvents in chemical synthesis [1], and also decrease employing expensive toxic solvents and the generation of hazardous wastes [2]. In recent years, ionic liquids (ILs) have attracted increasing interest and been successfully used in a variety of reactions as environmentally benign solvents and catalysts due to their comparatively low viscosities, low vapor pressure, and high thermal and chemical stability [3]. Room temperature ionic liquids (RTILs) are novel and new class of substances with high potential to substitute many traditional organic solvents in reaction and separation processes [4]. In spite of their importance and attention, accurate values for many of the

ratio was also added slowly at room temperature for 3 h under atmosphere. The resulting ionic liquids were dried using rotary evaporated under vacuum conditions. Produce the ionic liquids in 86%. Scheme 1



[Bu₃NH]H₂PO₄, FT-IR (NaCl): 3000, 2962, 2875, 2388, 2340, 1472, 1105, 962, 741, 522, cm⁻¹. ¹H-NMR (400MHz, DMSO-*d*₆): δ 9.36 (s, 1H, NH), 2.84 (t, 6H, J=7.2, CH₂), 1.56 (m, 6H, CH₂), 1.27 (m, 6H, CH₂), 0.89 (m, 9H, CH₃) ppm.

[Bu₃NH]HSO₄ FT-IR (NaCl): 3433, 2938, 2875, 2875, 2801, 2558, 2801, 1381, 1645, 1234, 1041, 853, 740, 582 cm⁻¹. ¹H-NMR (400MHz, DMSO-*d*₆): δ 7.11 (s, 1H), 2.99 (t, 6H, J=7.6, CH₂), 1.59 (m, 6H, CH₂), 1.27 (m, 6H, CH₂), 0.87 (m, 9H, CH₃) ppm.

[Bu₃NH]NO₃. FT-IR (NaCl): 3463, 2962, 2875, 2740, 2561, 1742, 1633, 1469, 1294, 1035, 1159, 926, 826, 738, cm⁻¹. ¹H-NMR (400MHz, DMSO-*d*₆): δ 7.00 (s, 1H, NH), 3.02 (t, 6H, J=7.6, CH₂), 1.56 (m, 6H, CH₂), 1.34 (m, 6H, CH₂), 0.89 (m, 9H, CH₃) ppm.

[Bu₃NH]Cl. FT-IR (NaCl): 3434, 2960, 2524, 1631, 1379, 1105, 1034, 926, 739, 580, 563, cm⁻¹. ¹H-NMR (400MHz, DMSO-*d*₆): δ 9.85 (s, 1H, NH), 2.85 (t, J=7.2, 6H, CH₂), 1.57 (m, 6H, CH₂), 1.29 (m, 6H, CH₂), 0.89 (m, 9H, CH₃) ppm.

Results and Discussion

Determination of water content

Before their use, the ionic liquids samples were dried and degassed under vacuum (10⁻³bar) at 85 °C during 3 h. After this treatment, the mass fraction of water determined by coulometric Karl-Fischer titration using a Metrohm 756 KFCoulometer with a Hydranal® Coulomat AG reagent. Defined water content (45 ± 10) 10⁻⁵w/w that were revealed very low levels of water.

Density

Density was measured by a 25 ml pycnometer. In general, density precisions are ±0.0005 g cm⁻³. The temperature was maintained using a thermostatic bath with a precision of ±0.01 K. All density measurements were repeated at least three times. Densities of the ILs as a function of temperature are shown in Fig. 1. As expected, densities decrease linearly with increasing temperature, and can be well correlated by the linear regression (r² > 0.999).

The temperature-dependent densities (ρ), refractive indices (n_D), surface tension (σ) and thermal conductivity (λ) values were fitted by the method of least squares using the following equations (1) [9].

$$z = A_0 + A_1 T(K) + A_2 T^2(K)^2 \quad (1)$$

Where fitting parameters A₀ (gcm⁻³), A₁ (gcm⁻³ K⁻¹) and A₂ (gcm⁻³ K⁻²) are related to temperature and extrapolated density at 0K, respectively and T is the temperature (K). The adjustable parameters of Eq. (2) for the density of these ILs are summarized in Table 1.

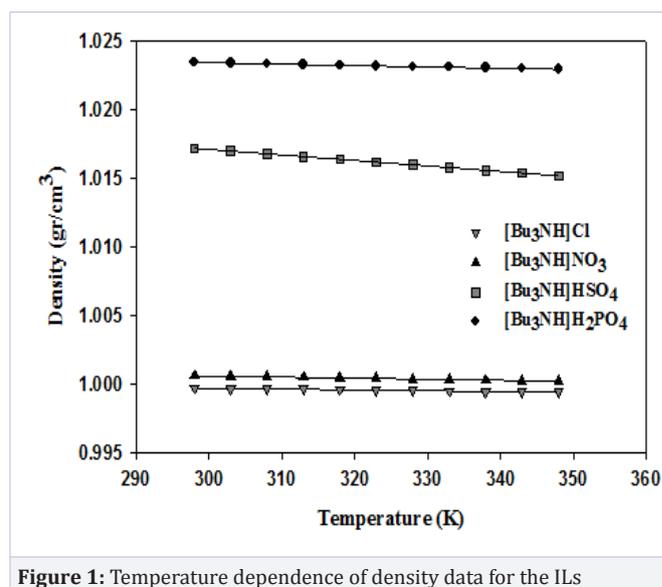


Table 1: Fitting Parameters of Equation 1 and Standard Deviations, SD, of the Density (ρ) ILs

ILs	$\rho = A_0 + A_1 T(K) + A_2 T^2(K)^2$				
	$A_0 (g\text{ cm}^{-3})$	$A_1 (g\text{ cm}^{-3} K^{-1}) \times 10^{-2}$	$SD \times 10^{-4}$	$A_2 (g\text{ cm}^{-3} K^{-2})$	$(\Delta\rho / \rho) \times 100$
[Bu ₃ NH]H ₂ PO ₄	1.0264	-1.0002	-5.7137	1.6583	1.0232
[Bu ₃ NH]HSO ₄	1.0291	-4.0000	2.8837	6.6332	1.0162
[Bu ₃ NH]NO ₃	1.0007	-6.1538	1.3916	1.0028	0.9996
[Bu ₃ NH]Cl	1.0030	-8.0000	5.1021	1.3266	1.0004

Viscosity

In our viscosity measurements, BAILs showed no deviation from Newtonian behavior in the investigated temperature range. Kinematic viscosities were obtained using a LVDV-I PRIME model viscometer made of Brookfield Co and capillary tube deeper in a thermostated bath with a precision of ±0.01 K. The dynamic viscosities were calculated from the densities with a precision equal to 0.03 mPa·s. All measurements were repeated two times. Sample viscosities were first determined as a function of the temperature during a heating cycle from (293.15 to 363.15) K. Data on viscosity and density for the ILs at temperatures ranging from (293.15 to 363.15) K are shown in Figs. 2. The temperature dependency of the dynamic viscosity values fit well to the Vogel–Tammann–Fulcher (VTF) equation (2) [10].

$$\eta = \eta_0 \exp \left[\frac{B}{(T - T_0)} \right] \quad (2)$$

Where T is the absolute temperature, η_0 , B and T_0 are adjustable parameters. The η_0 (cP), B (K), and T_0 (K) parameters are given in Table 2. Commonly used equation to correlate the variation of viscosity with temperature is the Arrhenius-like law Eq (3) [11].

$$\eta = \eta_0 \exp(-Ea / RT) \quad (3)$$

Viscosity at initial temperature and the activation energy (Ea) are characteristic parameters generally adjusted from experimental data. Table 3 lists the parameters for both equations with the standard relative deviation (S. D.) Eq (4):

$$S.D. = \left[\frac{\sum_i^n (z_{\text{exp}} - z_{\text{cal}})^2}{n} \right]^{1/2} \quad (4)$$

Where z_{exp} and z_{cal} are the values of the experimental and calculated property, n is the number of experimental data of parameters. Table 2 Table 3

Table 2: Fitting Parameters of Equation 2 and Standard Deviations, SD, of the Dynamic viscosity (η) ILs

ILs	$\eta = \eta_0 \exp \left[\frac{B}{(T - T_0)} \right]$				
	η_0 (mpas)	B (K)	T_0 (K)	SD	$(\Delta\eta / \eta) \times 100$
[Bu ₃ NH]H ₂ PO ₄	12.2363	-0.2302	0.0017	1.8248	2.5421
[Bu ₃ NH]HSO ₄	6.6842	-0.0963	0.0005	0.8500	3.0050
[Bu ₃ NH]NO ₃	12.2363	-0.2802	0.0017	0.7972	2.3257
[Bu ₃ NH]Cl	6.9168	-0.1565	0.0009	1.1275	1.3293

Table 3: Experimental value of dynamic viscosities (η), refractive indices (n_D), densities (ρ), surface tensions (σ), electrical conductivity (κ), thermal conductivity (λ) and pKa of the Acidic Brönsted ionic liquids at 25.0 °C

ILs	η (mPa.s)	n_D	ρ (g/cm ³)	σ (N/m)	κ (ms/m)	λ (W/KC)	pKa
[Bu ₃ NH]H ₂ PO ₄	6.25	1.3499	1.0235	0.0819	10.8000	0.6700	5.35, 3.35
[Bu ₃ NH]HSO ₄	4.59	1.3475	0.0172	0.0860	60.2000	0.5800	6.33, 2.26
[Bu ₃ NH]NO ₃	3.99	1.3402	0.9997	0.0968	14.1000	0.5500	2.55
[Bu ₃ NH]Cl	3.72	1.3395	1.0006	0.0885	27.4000	0.5100	1.95

A comparison between the experimental data for the physical properties of the studied ABILs at 25 °C has also been made in Table 3. To the best of our knowledge, no literature data on densities (ρ), dynamic viscosities (η), surface tension (σ), electrical conductivity (κ), refractive indices (n_D) and thermal conductivity (λ), were not previously available for four studied ILs. As is obvious from Table 3, the experimental data for [Bu₃NH]H₂PO₄, [Bu₃NH]HSO₄, [Bu₃NH]NO₃, and [Bu₃NH]Cl. Figure 2

Refractive Index

An Abbe Refractometer Model ATAGO-T3 programmable digital with a measuring accuracy of (4×10^{-5}) was used to measure the refractive index of various ILs in a temperature range of (298.15 to 363.15) K. The temperature was controlled with an accuracy of (0.05) K. The apparatus was calibrated and checked before each series of measurements using pure organic solvents (ethanol) with known refractive indices [12]. Refractive Indices can be well fitted by Eq (1). Table 4

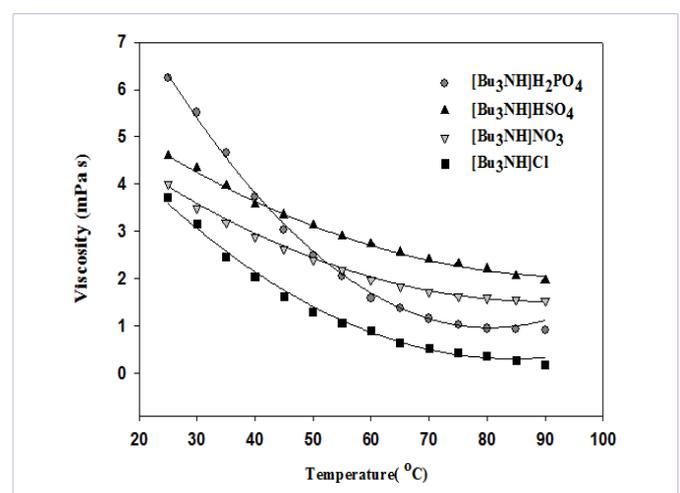


Figure 2: Dynamic viscosity (η) as a function of temperature for ILs

Table 4: Fitting Parameters of Equation 1 and Standard Deviations, SD, of the Refractive Index (n_D) ILs

ILs	$n_D = A_0 + A_1T (K) + A_2T^2 (K)^2$				$(\Delta n_D / n_D) \times 100$
	A_0	$A_1 (K^{-1}) \times 10^{-2}$	$SD \times 10^{-3}$	$A_2 (K^{-2})$	
[Bu ₃ NH]H ₂ PO ₄	1.3515	-6.5385	6.9930	9.8026	1.3487
[Bu ₃ NH]HSO ₄	1.3490	-6.0013	-4.6620	9.9590	1.3463
[Bu ₃ NH]NO ₃	1.3422	-8.0000	1.2472	1.3266	1.3386
[Bu ₃ NH]Cl	1.3410	-6.0000	2.6056	9.9499	1.3383

Figure 3 shows temperature dependence of refractive index for the studied ILs have refractive indices >1.4. As it can be seen from Fig3, for all three ILs, there refractive index decreases linearly with increasing temperature. Figure 3.

Surface Tension

We used Stalagmometer dope of falling for estimated surface tension ILs. The surface tension of the ILs has been measured as a function of temperature. The experimental data decrease with increase in temperature in Fig 4. These values were compared with those obtained with [Bu₃NH]NO₃ has high surface tension than ILs. Based on these data, it appears that the surface tension lowly decreases with increases temperature. The relationship between surface tension and temperature of can be fitting by the Eq (1). Table 5

The present synthesized ionic liquids show a weak temperature dependency on the surface tension Figure 4. Figure 4

Thermal conductivity

The thermal conductivity was measured by using a KD2 thermal property meter (decagon, Canada), which is based on the transient hot wire method. The KD2 meter has a probe with 60 mm length and 0.9 mm diameter, which integrates in its interior a heating element and a thermo-resistor and is connected to a microprocessor for controlling and conducting the measurements. The KD2 meter was calibrated by using distilled water and

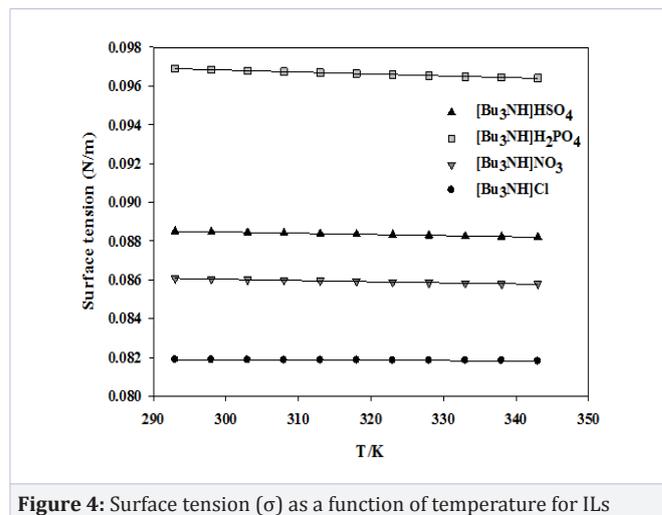


Figure 4: Surface tension (σ) as a function of temperature for ILs

standard ethylene glycol before any set of measurements. In order to study the effect of temperature, a thermostat bath was used, which was able to keep the temperature regularity within the range of ± 0.1 K. At least five measurements were taken for each temperature to make sure the uncertainty of measurements almost $\pm 2\%$.

Figure 5 shows the thermal conductivity of ILs as a function of temperature. Figure 5.

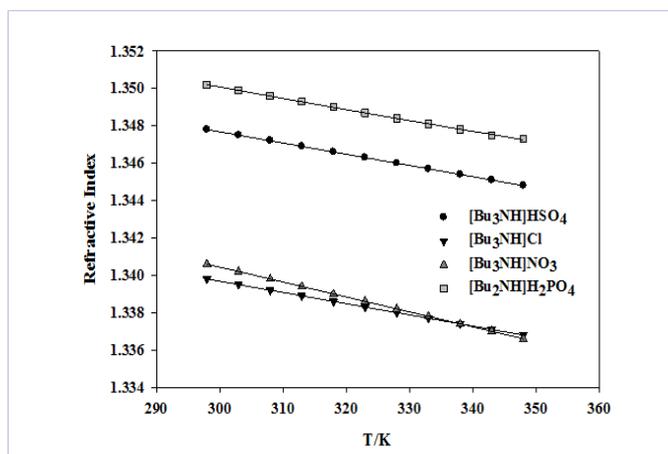


Figure 3: Refractive Index (n_D) as a function of temperature for ILs

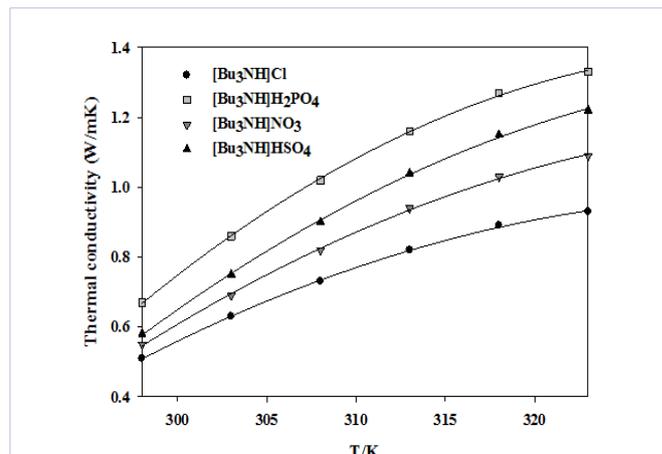


Figure 5: Thermal conductivity (λ) as a function of temperature for ILs

Table 5: Fitting Parameters of Equation 1 and Standard Deviations,SD, of the Surface tension (σ) ILS

$\sigma = A_0 + A_1 T (K) + A_2 T^2 (K)^2$					
ILs	$A_0 (mN s^{-1})$	$A_1 \times 10^{-2} (mN s^{-1})$	$A_2 (mN s^{-1} K)$	$SD \times 10^{-3}$	$(\Delta\sigma / \sigma) \times 100$
[Bu ₃ NH]H ₂ PO ₄	1.3515	-6.5385	6.9930	2.1598	0.0818
[Bu ₃ NH]HSO ₄	1.3490	-6.0013	-4.6620	9.9982	0.0859
[Bu ₃ NH]NO ₃	1.3422	-8.0000	1.2472	1.6434	0.0966
[Bu ₃ NH]Cl	1.3410	-6.0000	2.6056	9.9500	0.0884

Table 6: Fitting Parameters of Equation 1 and Standard Deviations,SD, of the Thermal conductivity (λ) ILS

$\lambda = A_0 + A_1 T (K) + A_2 T^2 (K)^2$					
ILs	$A_0 (W / m K)$	$A_1 (W / m K) \times 10^{-2}$	$A_2 (W / m K)$	SD	$(\Delta\lambda / \lambda) \times 100$
[Bu ₃ NH]H ₂ PO ₄	-0.7557	0.0715	-0.0006	0.0125	0.2531
[Bu ₃ NH]HSO ₄	-0.6600	0.0609	-0.0005	0.2449	0.9400
[Bu ₃ NH]NO ₃	-0.4671	0.0495	-0.0004	0.2071	0.8533
[Bu ₃ NH]Cl	-0.3800	0.0448	-0.000	0.1608	0.7517

The relationship between thermal conductivity (λ) and temperature of can be fitting by the Eq (1) and fitting parameters listed in table 6. Table 6.

Electrical Conductivity

Electrical conductivity is one of the most main properties of ILS as electrolyte materials [13]. The electrical conductivity (κ) of the ionic liquids was analytically measured with a conductivity meter CTR80(ZAG-CHEMIE). Electrical conductivity was measured by means of the complex impedance method, using a thermometer, under atmosphere for determined temperature. The cell constant was determined by calibration after each sample measurement using an aqueous 0.02M KCl aqueous solution. The κ data for the considered aqueous RTIL systems were measured for temperatures ranging from (293.15 to

348.15) K at normal atmospheric pressure. Table 7 presented the obtained κ measurements. Molar conductivity of the ionic liquids Λ ($m^2 Smol^{-1}$) was calculated from the ionic conductivity σ (Sm^{-1}) and the molar concentration C ($kmolm^{-3}$) according to the Eq (5).

$$\Lambda = 1000 \left(\frac{\kappa}{C} \right) \quad (5)$$

The electrical conductivity presents linearly behaviour with temperature for all ILS measured. Electrical conductivity (κ) values were fitted by the method of least squares using the following equations (6) [14].

$$\Lambda = \Lambda_0 + AT(K) + BT^2(K)^2 + CT^3(K)^3 \quad (6)$$

Table 7: Fitting Parameters of Equation 5 and Standard Deviations,SD, of the Electrical conductivity

$\Lambda = \Lambda_0 + AT(K) + BT^2(K)^2 + CT^3(K)^3$						
ILs	$\Lambda_0 (ms cm^{-1})$	$A (ms cm^{-1} K^{-1})$	$B (ms cm^{-1} K^{-2})$	$C (ms cm^{-1} K^{-3})$	SD	$(\Delta\Lambda / \Lambda) \times 100$
[Bu ₃ NH]H ₂ PO ₄	0.7212	0.5210	-0.0068	4.6309	3.4696	14.4000
[Bu ₃ NH]HSO ₄	48.7594	0.5213	-0.0031	1.2121	5.2367	66.7891
[Bu ₃ NH]NO ₃	-3.6261	1.0933	-0.0194	0.0001	4.9628	19.6182
[Bu ₃ NH]Cl	11.6469	0.6826	-0.0027	3.8850	7.6316	36.5000

The plots showing the behaviour of the present κ data for the studied solvent systems: [Bu₃NH][H₂PO₄] + H₂O, [Bu₃NH][HSO₄] + H₂O, [Bu₃NH][NO₃] + H₂O, [Bu₃NH][Cl] + H₂O are shown in Figure 6. Figure 6

Acidity

The acidic scale of the RTILs was measured using a titration pH- metre with volume of NaOH indicator and the pKa data of RTILs listed on table 8. Table 8

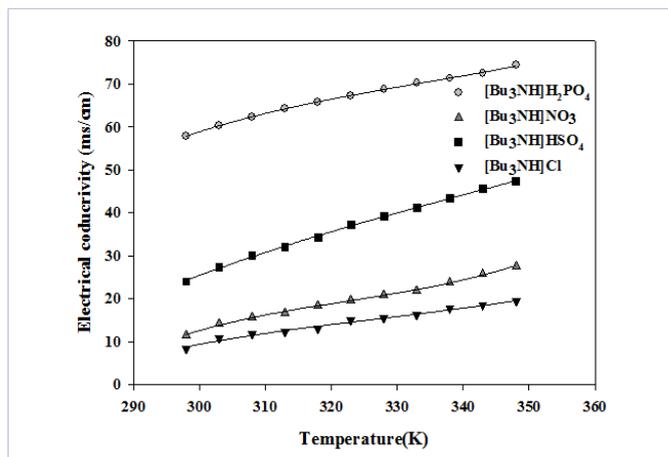


Figure 6: Electrical conductivity (κ) as a function of temperature for ILs

Table 8: The pKa data of RTILs at 25°C

ILs	[Bu ₃ NH]H ₂ PO ₄	[Bu ₃ NH]HSO ₄	[Bu ₃ NH]NO ₃	[Bu ₃ NH]Cl
pKa ₁	3.35	2.26	2.55	1.95
pKa ₂	5.35	6.33	-	-

This value was regarded as the relative acidity of the IL. [8] Where $pK(I)_{aq}$ was the pKa value of the indicator, [I] and [HI] were, respectively, the molar concentrations of the unprotonated and protonated forms of the indicator, determined by UV-visible spectroscopy.

Determination of H₀ values of Brönsted acidic ILs

A common and effective way to evaluate the acidity of Brönsted acids was the Hammett method [15]. In reported papers, the measurement of the acidic scale of these acidic Brönsted ILs was conducted on a UV-Vis spectrophotometer with a basic indicator (para-nitroaniline). Increasing the acidic scale of the acidic IL, the absorbance of the unprotonated form of the basic indicator was decreased, whereas the protonated form of the indicator was not observed because of its small molar absorptivity and its wavelength. Thus $[I]/[HI]$ (I represents the indicator) ratio was determined from the measured absorbance differences after addition of an acidic Brönsted IL, and then the Hammett function, H_0 , was calculated by using Eq 7.

$$H_0 = pK(I)_{aq} + \log([I]/[HI]) \quad (7)$$

When an acidic IL was added, the absorbance of the unprotonated form of the indicator decreased. The acidities of the four ionic liquids were examined using 4-nitroaniline as indicator in dichloromethane. We obtained the acidity order of several ILs with the H_0 values that are shown in Table 9. Table 9

Table 9: H_0 Values of Ionic Liquids in CH₂Cl₂ at Room Temperature

ILs	A _{max}	[I]%	[HI]%	H ₀
Para-nitro aniline	1.602	100	-	-
[Bu ₃ NH]H ₂ PO ₄	1.409	87.95	12.05	1.85
[Bu ₃ NH]HSO ₄	1.467	91.57	8.43	2.03
[Bu ₃ NH]NO ₃	1.433	89.45	10.85	1.92
[Bu ₃ NH]Cl	1.558	97.25	2.75	2.54

Under the same concentration of 4-nitroaniline (10 mg/L, $pK(I)_{aq} = p_{Ka} = 0.99$) and BAILs (0.1 mmol/L) in dichloromethane, H_0 values of all BAILs were determined. The maximal absorbance of the unprotonated form of the indicator was observed at 350 nm in dichloromethane. When the BAIL was added, the absorbance of the unprotonated form of the basic indicator decreased (Figure 7 and Table 9). Figure 7

Hammett acidity (H_0) of these BAILs was calculated using equations (7). As shown in Figure 7. Calculations suggest that the Hammett acidity (H_0) of these ionic liquids follows the order: [Bu₃NH][H₂PO₄] > [Bu₃NH][NO₃] > [Bu₃NH][HSO₄] > [Bu₃NH][Cl].

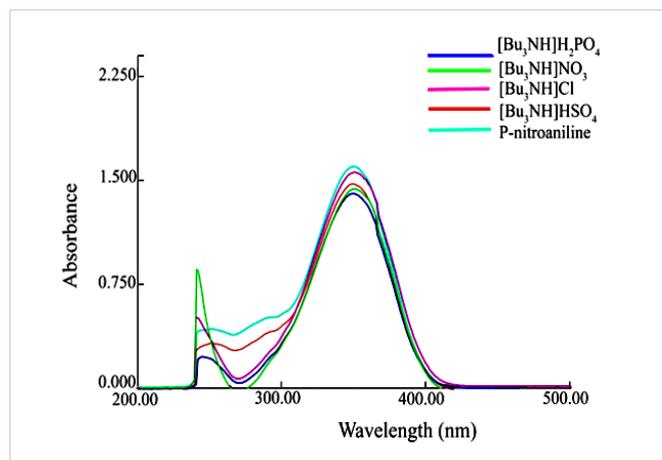


Figure 7: UV-Vis absorption spectra of ILs

Conclusions

Due to the development of green chemistry in recent years, researchers have been interested in the application of ionic liquids can apply as green catalysts, Room temperature ionic liquids (RTILs). Regard to these unique features, In spite of the interesting feature and practical importance of ILs, there are limited literature reports on the accurate measurements of many of their fundamental physical and chemical properties at various temperatures.

- Size particle affected on properties physical chemistry of ILs.
- Weight particle influenced on properties physical chemistry of ILs.
- Structure ILs impacted on properties physical chemistry of ILs.
- Hydrogen bonding internal molecular inclined on properties physical chemistry of ILs.
- Electrical charge particle subjective on properties physical chemistry of ILs.
- Temperature affected on properties physical chemistry of ILs.
- Principle HARD and SAFT influenced on properties physical chemistry of ILs.

The data of physical properties on ionic liquids are necessary for both theoretical research and industrial application. The establishment of the databases in this respect will certainly support the study and advance of ionic liquids. Thus, in this work, we have carefully measured several significant physical properties of ionic liquids: tri-butyl ammonium chloride $[\text{Bu}_3\text{NH}][\text{Cl}]$, tri-butyl ammonium nitrate $[\text{Bu}_3\text{NH}][\text{NO}_3]$, tri-butyl ammonium hydrogen sulfate $[\text{Bu}_3\text{NH}][\text{HSO}_4]$ and tri-butyl ammonium di-hydrogen phosphate $[\text{Bu}_3\text{NH}][\text{H}_2\text{PO}_4]$ over a wide range of temperature from (293.15 to 363.15 K). Clearly, much more attention should be paid on the measurement of physicochemical properties of ionic liquids.

The measured densities, ρ , and the dynamic viscosities, η , for the binary mixtures of $[\text{Bu}_3\text{NH}][\text{H}_2\text{PO}_4]$ with water at $T = (293.15 \text{ to } 363.15)$ Cover the whole composition range are listed in Tables 1 and 2. As can be seen, the density of all of the mixtures always decreases with temperature. A very decent linear correlation is observed for all compositions ($r = 1$), this linear behavior with temperature.

The experimental viscosity results of $[\text{Bu}_3\text{NH}][\text{Cl}]$, $[\text{Bu}_3\text{NH}][\text{NO}_3]$, $[\text{Bu}_3\text{NH}][\text{HSO}_4]$, $[\text{Bu}_3\text{NH}][\text{H}_2\text{PO}_4]$ from this study are in respectable agreement with the very scarce data from the literature and are well represented by the VTF equation. At the same temperature, $[\text{Bu}_3\text{NH}][\text{H}_2\text{PO}_4]$ have high very significantly the viscosity of other tri ILs. Presence oxygen atoms perhaps make up high viscosity this IL than other ILs. Since the viscosities of ILs are essentially effective by the van der Waals interactions and H bonding, have reported the influence of oxygen, water on

the physical properties of $[\text{Bu}_3\text{NH}][\text{H}_2\text{PO}_4]$. It has been shown that the presence of even low concentrations of oxygen in the $[\text{Bu}_3\text{NH}][\text{H}_2\text{PO}_4]$ substantially increases the viscosity.

Figure 5 shows the thermal conductivity of ILs as a function of temperature. It can be seen that the thermal conductivity of $[\text{Bu}_3\text{NH}][\text{H}_2\text{PO}_4]$ is $0.67 \text{ Wm}^{-1} \text{ K}^{-1}$. This indicates that $[\text{Bu}_3\text{NH}][\text{H}_2\text{PO}_4]$ is a relatively poor thermal conductor with the thermal conductivity approximately of that of water at the room temperature. Initially, the temperature-independent thermal conductivity of the $[\text{Bu}_3\text{NH}][\text{H}_2\text{PO}_4]$ was thought to be due to the inappropriate method of measurements as both the thermal probe and the liquid are electrically conductive. It was also hypothesised that the temperature-independent behaviour is associated with the high viscosity of the ionic liquids.

Future Prospective of this work is following:

- Application as specific lubricants for engineering fluids.
- Electrochemical Applications Ionic liquids, as possible replacements for organic solvents in lithium ion rechargeable batteries for laptops, mobile phones, biosensors, actuators, solvents for electrochemical devices, super capacitors fuel cells, dye-sensitized solar cells, and polymer electrolytes.
- Coefficients of thermal expansion are defined by the following equation: $\alpha_p = -1/\rho(\partial\rho/\partial T)_p$.
- Brønsted Lewis acidic ionic liquids were used as solvents and catalysts in many organic reactions such as etherification, polymerization, alkylation, acylation, carbonylation, aldol condensation, pinacol rearrangement, nitration, Koch reaction, oxidation of alcohols.
- Acidic Brønsted ionic liquids as environmental-friendly solvents and catalysts with high activity and selectivity and easily recovered were used to replace traditional liquid acids, such as sulphuric acid and hydrochloric acid, in chemical processes, especially acid catalysed.
- Speeds of Sound (u).
- Cyclic voltammograms.
- Chronoamperograms for ferrocene.
- Excess Molar Volumes VE.
- Self-diffusion coefficient of Cation and anion in ionic liquid (D).

To recap, in comparison with the other BAILs in that how do the thermo physical properties and the most benefits and the dominance of these classifications when compared to the ones conveyed in the literature being easily made and recycled in the various temperature, and the structure effect of the ILs on the physical properties, the quality of this study would be substantially promoted as followed:

$[\text{Bu}_3\text{NH}][\text{H}_2\text{PO}_4] > [\text{Bu}_3\text{NH}][\text{H}_5\text{O}_4] > [\text{Bu}_3\text{NH}][\text{NO}_3] > [\text{Bu}_3\text{NH}][\text{Cl}]$.

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