

Thermo Physical Properties of Lewis Acidic Ionic Liquids [Bu₃NBn] Cl-2(MClm), (MClm= AlCl₃, FeCl₃, CuCl₂, SnCl₄, ZnCl₂) binary mixtures with DMSO at Temperatures from (298.15 to 363.15) K

 Zeinab Heidari Pebdani^{*}, Abdol Reza Hajipour¹ and Yosofe Ghayeba¹
¹Pharmaceutical Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan 84156, IR Iran

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^{*}Corresponding author: Pharmaceutical Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan 84156, IR Iran, Email: zenabheydari.pebdani@yahoo.com

Abstract

In this article, we were investigated as a function of temperature, densities (ρ), dynamic viscosities (η), surface tension (σ), ionic conductivity (κ), refractive indices (nD), and thermal conductivity (λ) for the binary systems of the DMSO with ionic liquids (ILs) over the whole composition range at temperature from 298.15 to 363.15 Kelvin under atmospheric pressure. The ILs investigated in the present study included [Bu₃NBn]Cl-2(MClm), (MClm= AlCl₃, CuCl₂, FeCl₃, SnCl₄, ZnCl₂) that synthesis for the first one in our laboratory. At first, we investigated Biodegradation and Toxicity of the ILs as served for Green Solvent. Then, the influence of temperature on the thermo physical properties on the new series of room temperature ionic liquids (RTILs), have been prepared and characterized using TLC, CHNS, FT-IR and Mass Spectroscopy. Thermogravimetric analysis (TGA) confirmed that the heat stability of ILs in the temperature range of 400–800°C. A common and effective way to evaluate the Acidity of Lewis acids was the Hammett method (Ho) that we used them for RTILs. Also, Densities, dynamic viscosity, surface tension, ionic conductivity, refractive indices, thermal conductivity deviations, and dynamic viscosity deviations in for the binary systems with Di-Methyl Sulfoxide (DMSO) were fitted to a Vogel-Fulcher-Tammann (VFT) equation. In the end, we offer some useful applications and future perspectives for these new ILs. In comparison with the other ILs in that how do the thermo physical properties and the most advantages and the superiority of these systems when compared to the ones reported in the literature being easily produced and used in the various temperatures.

Abbreviations: (LAILs) Lewis Acidic Ionic Liquids; (RTILs) Room Temperature Ionic Liquids; (VOC) Volatile Organic Compounds; (DMSO) Di-Methyl Sulfoxide.

Introduction

Large attention is being strained towards Ionic Liquids (ILs) as alternatives for usual molecular solvents used in organic synthesis and catalytic reactions [1]. They complement the family of “green solvents” counting water and supercritical fluids. In order to check the biocompatibility of ILs, toxicity, eco-toxicity, and biodegradation studies have to be carried out. ILs is usually referred to as “Green” alternatives to Volatile Organic Compounds

(VOCs). Instead of the “Green” marker, ILs can be characterized in the arrangement of “Traffic Signal Lights” as debated at the BATIL (Biodegradation And Toxicity of Ionic Liquids) conference in DECHEMA, Frankfurt, 2009[2]. Biodegradation is one technique of investigation to define and calculate how Ionic Liquids interaction with the environment. Among these, room temperature ionic liquids are definite as materials containing only ionic species and having a melting point lower than 298 K. They display many interesting properties such as slight vapour pressure, low melting point, and large liquid range, only one of its kind salvation talents and generally, the flexibility of their physicochemical properties makes them really attractive. Most of the ILs studied is based on [Bu₃NBn] Cl-2(AlCl₃), [Bu₃NBn] Cl-2(CuCl₂), [Bu₃NBn] Cl-2(FeCl₃), [Bu₃NBn] Cl-2(SnCl₄) and [Bu₃NBn] Cl-2(ZnCl₂). They have been recently proposed as solvents in chemical reactions [3], multiphase bioprocess operations [4] and liquid-liquid separations [5] electrolytes for batteries and fuel cells [6] stationary phases in gas chromatography[7] mobile phase additives in liquid chromatography[8] and electrolyte additive in capillary electrophoresis (CE) [9]. However, the awareness of their physicochemical properties, which has been revealed to be directly related to their purity level, for instance, the temperature dependence of density, dynamic viscosity, conductivity, surface tension, refractive index, and thermal conductivity.

Among the known ionic liquids, those series having asymmetric quaternary ammonium cations are assumed to be one of the most promising for battery electrolyte use because they exhibit a wider electrochemical window, especially along a cathodic direction, and than imidazolium cation-based ionic liquids [10]. However, quaternary ammonium-based ionic liquids have the drawback of low ionic conductivity at 10⁻³ S cm⁻¹ or lower. Indeed, salts based on small quaternary ammonium cations are basically solid around room temperature. In contrast, an increase in cation size decreases cation mobility. The mixing of cations is expected to lower the melting point of the salt as reported by Sun ET al [12].

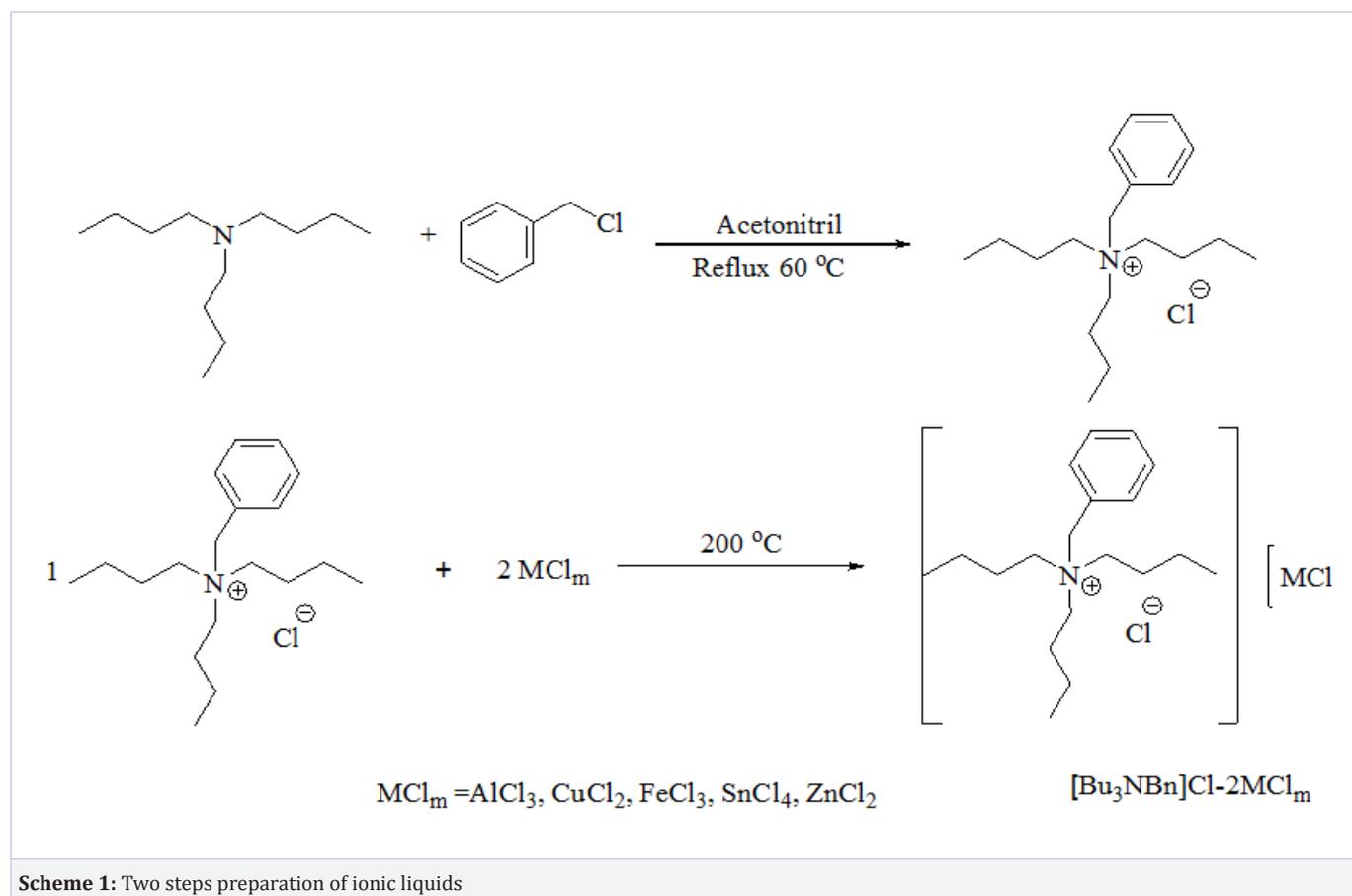
In spite of the interesting feature and practical importance of Isothere are limited literature reports on the accurate measurements of many of their fundamental physical and chemical properties at various temperatures [13]. Thus, in this paper we wish to report the results of our studies on the physical, electrochemical, thermodynamic and transport properties of [Bu₃NBn] Cl-2(AlCl₃), [Bu₃NBn] Cl-2(CuCl₂), [Bu₃NBn] Cl-2(FeCl₃) and [Bu₃NBn] Cl-2(SnCl₄), [Bu₃NBn] Cl-2(ZnCl₂). Molecular structures of the five ILs are shown in the scheme. 1. The properties physical of these five ILs, accurately measured at atmospheric pressure and several temperatures include density, viscosity, thermal stability, surface tension, refractive index, conductivity, and thermal conductivity. The measured densities as a function of the temperature from 298.15 to 363.15K, Also we measured the Hammett parameter (Ho) that a common and effective way to evaluate the acidity of Lewis acids we used them for RTILs [14].

Experimental Section

Preparation of ionic liquids

Materials: Chemicals of analytical grade were used for the synthesis of the ILs. Tributylamine and DMSO were purchased from the Sigma-Aldrich. (>99 % of purity), salts such as AlCl₃, CuCl₂, FeCl₃, SnCl₄, ZnCl₂, were purchased from Merck. The purity of the ILs was further confirmed by FT-IR and Mass- spectroscopy and elemental analysis. The RTILs were prepared from the corresponding chlorides according to the procedures reported in literature [15].

Synthesis of ILs: [Bu₃NBn] Cl-2(AlCl₃), [Bu₃NBn] Cl-2(CuCl₂), [Bu₃NBn] Cl-2(FeCl₃), [Bu₃NBn] Cl-2(SnCl₄) and [Bu₃NBn] Cl-2(ZnCl₂). Initially, tri-butyl Ammine Chloride and benzene chloride was added in 1:1 to a round-bottom flask, Acetonitrile were added and stirred thoroughly, and then anhydrous MCl_m was added in 1:2 molar ratio to an oil path under the protection of dry nitrogen in stages forming a liquid. The mixture was stirred at room temperature for 30 min and then was heated to 80°C. The Chloro metallic ionic liquid was required to be kept in desiccators because it easily reacts with moisture [16]. Yield reaction 68%, Scheme 1. Scheme 1



[Bu₃NBn]Cl-2(AlCl₃). FT-IR (NaCl): $\nu = 3325-3294, 2962-2534, 1638-1380, 843-610, \text{cm}^{-1}$. Mass Spectroscopy (T=230 °C, EI=70 eV): m/z=591, 552, 236, 185, 142, 100, 91, 57.

[Bu₃NBn]Cl-2(CuCl₂). FT-IR (NaCl): $\nu = 3036-3388, 2962-2874, 2309-2359, 1378-1478, \text{cm}^{-1}$. Mass Spectroscopy (T=230 °C, EI=70 eV): m/z=753, 677, 616, 571, 466, 447, 428, 409, 396, 360, 351, 332, 309, 285, 188, 126, 84, 57.

[Bu₃NBn]Cl-2(FeCl₃). FT-IR (NaCl): $\nu = 3782-3384, 2967-2874, 1998-1825, 1477-1370, 878-702, \text{cm}^{-1}$. Mass Spectroscopy (T=230 °C, EI=70 eV): m/z=474, 459, 369, 313, 285, 239, 210, 185, 176, 142, 91, 58.

[Bu₃NBn]Cl-2(SnCl₂). FT-IR (NaCl): $\nu = 3526-3420, 2965-2876, 2380-2309, 1679-1375, 846-701, \text{cm}^{-1}$. Mass Spectroscopy (T=230 °C, EI=70 eV): m/z=690, 573, 260, 225, 155, 142, 120, 91, 58.

[Bu₃NBn]Cl-2(ZnCl₂). FT-IR (NaCl): $\nu = 3092-3037, 2964-2742, 1969-1624, 1497-1348, 1031, 865-701, \text{cm}^{-1}$. Mass Spectroscopy (T=230 °C, EI=70 eV): m/z=654, 626, 598, 535, 507, 190, 176, 142, 100, 91, 57.

Results and Discussion

Toxicity and Eco (toxicity) of Ionic Liquids

Over the last decade, although a single toxicological test yields valuable, regardless of restricted information, plenty of publications have established a wide variety of 'biological test systems' for toxicity testing of ionic liquids [17], [18]. This contains fungi, bacteria, algae, enzymes, rat cell line, fish, and so forth.

Stock and colleagues highlighted that the consequence of ionic liquids on acetyl cholinesterase [19]. Enzymes are a vital fragment of the human nervous system. Acetyl cholinesterase is recognized to catalyze the hydrolysis of the neurotransmitter acetylcholine, to acetate and choline. Inhibition of acetyl cholinesterase results in muscular paralysis and other medically significant nervous problems. A array of regularly used [Bu₃NBn] Cl-2(AlCl₃), [Bu₃NBn]Cl-2(CuCl₂), [Bu₃NBn]Cl-2(FeCl₃), [Bu₃NBn] Cl-2(SnCl₄) and [Bu₃NBn]Cl-2(ZnCl₂) ionic liquids were tested in this analyse. [Bu₃NBn]Cl-2(SnCl₄) ionic liquid presented high toxicity to acetyl cholinesterase at very low absorptions, while [Bu₃NBn] Cl-2(FeCl₃) ionic liquid was non-toxic within the test limits. This testing revealed that toxicity of these ionic liquids lies in the cationic part and tri-butyl Ammine Benzen on the side chain and not in the anionic part.

Another significant result of this assessment was that growing the length of alkyl side chains rises the toxicity. This can be clarified as long alkyl chain increases lipophilic nature of the ionic liquids, which can then simply combine within the biological membrane of nerve cell synapses [20]. Comparable trends between the toxicity and length of alkyl chain on luminescence inhibition of *Vibrio fischeri* and promyelocytic leukaemia rat cell line IPC-81 were reported by Ranke and co-workers [21].

Leukemia rat cell line IPC-81 was also used to detect the cytotoxic effect of commercially accessible anions [22]. The major anion effect was found under the test system as following respectively.

[Bu₃NBn][Cu₂Cl₅] > [Bu₃NBn][Fe₂Cl₇] > [Bu₃NBn][Al₂Cl₇] > [Bu₃NBn][Sn₂Cl₉] > [Bu₃NBn][Zn₂Cl₅].

Bernot and associates confirmed that severe toxicity of certain 1-butyl-3-methyl imidazolium ionic liquids on *Daphnia Magna* was mostly due to the cationic part [23]. *Daphnia Magna* has been widely used for ecotoxicological assessment of chemicals in invertebrates. Ionic liquids were found to impact of the duplicate of *Daphnia Magna*. [Bu₃NBn][Zn₂Cl₅] was found to be the most toxic in the test system (LC₅₀: 3.05 mg/L). This study revealed that the toxicity of ionic liquids was influenced by the cation component, which was established by high LC₅₀ values for sodium salts of analogous anions. Yu and co-workers testified the toxicity study of tributyl-Ammine-Benzenchloridionic liquid towards the antioxidant defense system of *Daphnia Magna* [24]. Swelling the length of alkyl side chain with a difference of metal was found again to surge toxicity. Toxicity of ionic liquids, in this case, was owed to oxidative strain in *Daphnia Magna*, which was evaluated by measuring the activity of antioxidant defense enzymes, levels of the antioxidant [Bu₃NBn] and metal i.e. per oxidation by-product of lipid. [Bu₃NBn][Sn₂Cl₉] presented very high toxicity with an LC₅₀ of 0.03 mg/L less than 48 h incubation times.

In work to evaluate the eco (toxicity) of ionic liquids, Yun and associates informed evaluate of freshwater microalgae *Selenastrum capricornutum* [25]. Thechloride salts of commonly used [Bu₃NBn][Cu₂Cl₅] > [Bu₃NBn][Fe₂Cl₇] > [Bu₃NBn][Al₂Cl₇] > [Bu₃NBn][Sn₂Cl₉] > [Bu₃NBn][Zn₂Cl₅] ILs were tested against the *S. capricornutum* and compared with traditional water-miscible organic solvents such as methanol, 2-propanol, and dimethylformamide. Increase in the toxicity of imidazolium cations was observed with an increase in incubation time, whereas the opposite trend was found in the case of tetrabutylammonium ILs. The growth inhibition of *S. capricornutum* was higher in ionic liquids than organic solvents. A similar test system was applied to investigate the toxicological effect of anions [26]. Toxicity of various anions incorporated with tributyl-Ammine-Benzenchlorid cation was compared with their respective sodium and potassium salts. The anions were found to inhibit the growth of freshwater algae *S. capricornutum*. The clear trend in algae toxicity was observed as chlorid (Cl⁻). Toxicity studies (in fish, aquatic plants/invertebrates) on anionic surfactants have shown that toxicity is dependent on a number of factors such as alkyl chain length, solubility, and stability in water [27]. As the length of alkyl chain increases, toxicity increases until certain limits. Further increase in chain length can decrease the hydrophilic nature of these materials, reducing the bioavailability of compound which results in a general decrease in the toxicity [28].

In order for how do the thermo physical properties compare with the new design ILs of these systems when compared to the ones reported in the literature, reference for data demonstration

of toxicity of ionic liquids and regularly used organic solvents [2,29].

Benzene- Dichloromethane- Carbon Tetrachloride- Hexane> Cyclohexane- Tleptane- Ethylene Glycol- Toluene> Water- Acetone- Etheanol- 2-Propanol

[OMIM][Cl]- [FMIM][NO₃]- [EMIM][Lactate] [HMIM][Sacch]> [bmpy][Cl]-[BMIM] [N(CN)₂]- [EMIM][OctOSO₃]-[BMIM][OAc]> [EMIM][Cl]- [BMIM][EtOSO₃]- [bmpy][(MeO)2PO₃]- [EMIM][OTs]

Biodegradation of Ionic Liquids

Biodegradation is an essential parameter to investigate in ILs, supporting the design of safer analogs where requisite, decreasing environmentally persistent molecules in ecosystems. Biodegradation – standardized tests the following section delivers an overview of the biodegradation tests which are of attention and accessible to ILs scientists. The research zone of biodegradation is regarded as into the following terms:(I) Primary biodegradation – the defeat of a precise physical moiety, example hydrolysis of an ester bond (II) Naturally biodegradable – if a composite biodegrades B20% then the likelihood of supplementary degradation is implicit (III) Readily biodegradable – biodegrades a explicit % inside a specified timeframe (IV) Ultimately biodegradable – comprehensive collapse of a

composite(V) Mineralisation – decomposition of a complex into fragments accessible to plants [30].

Freshwater

Because of the bigger size of the oxygen tank in the circumstance of the ISO 10708 bottle equalled to the technique defined by the OECD 301D, Table 1, a higher test material absorptions can be used in the ISO 10708 test as the total of oxygen in the bottle was fewer of a limiting issue. Table 1

Seawater

The biodegradation in seawater test OECD Table 1, differs from the standard 31 experiments in that the only microorganisms existent were those set up indeed in the seawater test means. The container was not charged with further inocula, while it was complemented with nutrients. This test was not projected to characterize a marine situation but rather evaluate biodegradation in seawater means. Table 2

Table 1: OECD testing guidelines [31].

Test	Pass level after 10 days
Biodegradability in seawater (TG 306)	>50% DOC removal
Shake flask and closed bottle variants	>45% ThOD

Table 2: OECD testing guidelines

Test/ ILs	[Bu ₃ NBn]				
Pass level after 5 days	[Al ₂ Cl ₇]	[Cu ₂ Cl ₅]	[Fe ₂ Cl ₇]	[Sn ₂ Cl ₉]	[Zn ₂ Cl ₅]
Dissolved Organic Carbon (DOC)	43% DOC-removal	40%	60%	37%	50%
CO ₂ Evolution Test (TG301B)	50% ThCO ₂	45%	50%	40%	33%
Manometric respirometry test (TG 301F)	40% ThOD	50%	45%	50%	60%

Soil, sediment, and water

Owing to the natural complications of consuming a solid standard for biodegradation and the use of Radiolabeled atoms, there are a number of factors recommended by the OECD that can be used to display the fate of chemical complexes in soil or sedimentary environment.

- Major direction or pseudo-first command rate constant for biodegradation kinetics.
- Degradation half-life (DT50)
- Half-saturation constant
- The maximum exact growth rate [31].

One other arranged test for inherent biodegradation of chemical compounds in the soil exists for ILs is in the OECD TG, Table 1.

Biodegradation in soil

Biodegradation of imidazolium-based [Bu₃NBn][Cu₂Cl₅]

[Bu₃NBn][Fe₂Cl₇], [Bu₃NBn][Al₂Cl₇], [Bu₃NBn][Sn₂Cl₉], [Bu₃NBn][Zn₂Cl₅] ILs in soil were scrutinized for their biodegradability. In this test, a pass spot is not given and biodegradation is only detected. Below the test circumstances, the test composite is mixed with soil and sited in a great beaker vessel with CO growth commonly dignified. Soil can be a species-rich blend but it is predictable that the action will be less than a stimulated sludge so the test is run over a 5 days period. In this particular study, it was found that the linear alkyl [Bu₃NBn][Fe₂Cl₇] example undertook degradation of 35.1 ± 5.6% with the N(CN) derivative being less biodegradable than other halides, producing 14.0 ± 1.6% degradation.

Determination of water content

Before their use, the ionic liquids samples were dried and degassed under vacuum (10⁻³ bar) 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 (50 ± 10) 10⁻³ w/w that was revealed very low levels of water.

Density

Density was measured in a 25 ml pycnometer. In general, density precisions are $\pm 0.0005 \text{ g cm}^{-3}$. The temperature was maintained using a thermostatic bath with a precision of $\pm 0.01 \text{ K}$. 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 ($r^2 > 0.999$).

The temperature-dependent densities (ρ), refractive indices (n_D), surface tension (σ) and thermal conductivity (K) values were fitted by the method of least squares using the following equations (1) [32].

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

Where fitting parameter B and A are related to the coefficient of volume expansion ($\text{gcm}^{-3} \text{ K}^{-1}$) and extrapolated density at 0K (gcm^{-3}), respectively and T is the temperature (K). The adjustable parameters of Eq. (2) for the density of these ILs are summarized in Table 1.

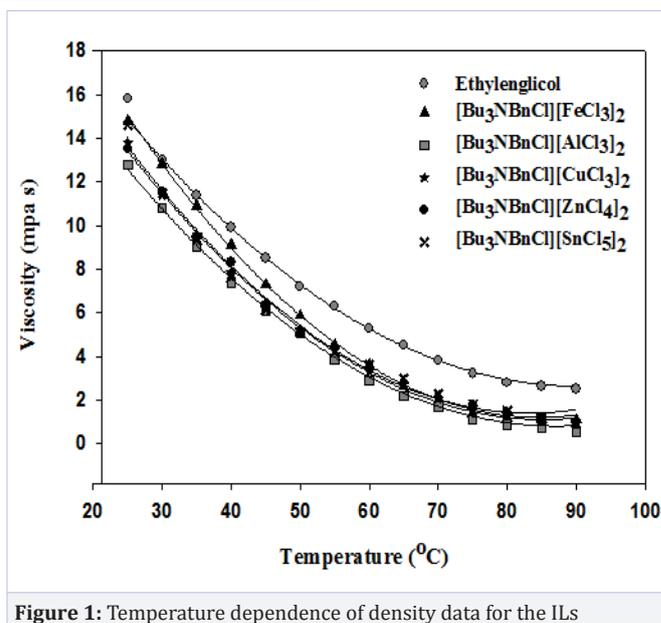


Figure 1: Temperature dependence of density data for the ILs

Table 3: Fitting Parameters of Equation 1 and Standard Deviations, SD, of the Density (ρ) ILs

ILs	$\rho = A_0 + A_1 T (K) + A_2 T^2 (K)^2$				$(\Delta\rho / \rho) \times 100$
	$A_0 (\text{g cm}^{-3})$	$A_1 (\text{g cm}^{-3} \text{ K}^{-1}) \times 10^{-2}$	$A_2 (\text{g cm}^{-3} \text{ K}^{-2})$	$SD \times 10^{-4}$	
[Bu ₃ NBn][Al ₂ Cl ₇]	1.0073	-2.2000	1.5701	1.6583	1.0232
[Bu ₃ NBn][Cu ₂ Cl ₅]	1.0117	-2.6000	-6.7742	6.6332	1.0033
[Bu ₃ NBn][Fe ₂ Cl ₇]	1.0028	-3.1773	-4.1119	3.8799	0.9995
[Bu ₃ NBn][Sn ₂ Cl ₆]	1.0118	-2.3716	-4.6620	4.4374	1.0037
[Bu ₃ NBn][Zn ₂ Cl ₅]	1.0022	-2.6000	-8.6318	4.3116	1.0014

Viscosity

In our viscosity measurements, ILs showed no deviation from Newtonian behaviour in the investigated temperature range. Kinematic viscosities were obtained using an LVDV-IPRIME model viscometer made of Brookfield Co and capillary tube deep in athermostated bath with a precision of $\pm 0.01 \text{ K}$. The dynamic viscosities were calculated from the densities with a precision equal to $0.03 \text{ mPa}\cdot\text{s}$. All measurements were repeated two times. Sample viscosities were first determined as a function of the temperature during a heating cycle from (298.15 to 363.15) K. Data on viscosity for the ILs at temperatures ranging from (298.15 to 363.15) K. are shown in Fig 2.

The temperature dependency of the dynamic viscosity values fit well to the Vogel- Tamman -Fulcher (VTF) equation (2) [32].

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

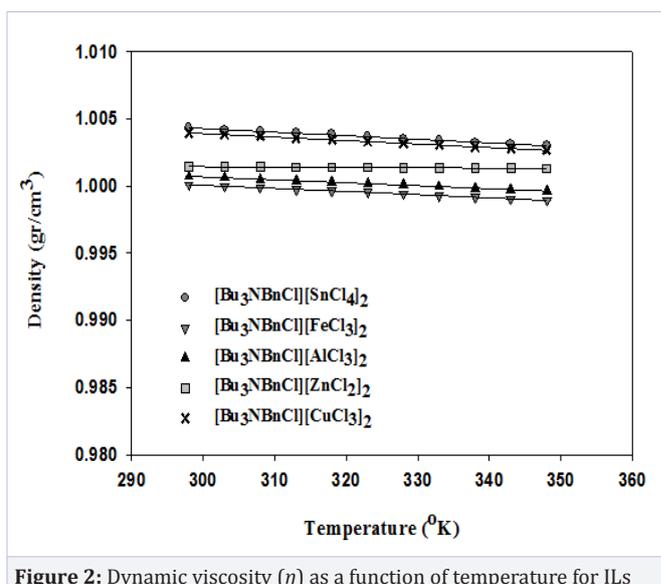


Figure 2: Dynamic viscosity (η) as a function of temperature for ILs

Where T is the absolute temperature, η_0 , and T_0 is adjustable parameters. Then η_0 (cP), B, and T_0 (K) parameters are given in Table 2. Commonly used an equation to correlate the variation of viscosity with temperature is the Arrhenius-like law Eq (3) [34].

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

Viscosity at initial temperature η_0 and the activation energy (Ea) are characteristics parameters generally adjusted

from experimental data. Table 3 lists the parameters for both equations with the standard relative deviation (S. D.) Eq (4):

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

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 4

Table 4: Fitting Parameters of Equation 2 and Standard Deviations, SD, of the Dynamic viscosity (η) ILs

ILs	$\eta = \eta_0 \exp \left[B / (T - T_0) \right]$				SD	$(\Delta\eta / \eta) \times 100$
	η_0 (mpas)	B (K)	T_0 (K)			
[Bu ₃ NBn][Al ₂ Cl ₇]	23.9420	-0.5309	0.0030	4.0284	4.6514	
[Bu ₃ NBn][Cu ₂ Cl ₅]	25.7803	-0.5791	0.0034	4.1442	5.1007	
[Bu ₃ NBn][Fe ₂ Cl ₇]	29.0771	-0.6586	0.0039	4.6741	5.6021	
[Bu ₃ NBn][Sn ₂ Cl ₉]	26.3494	-0.5989	0.0036	4.1831	5.2036	
[Bu ₃ NBn][Zn ₂ Cl ₅]	25.9771	-0.6586	1.4286	4.0827	5.1629	

Refractive Index

An Abbe Refractometry 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. 35 Refractive Indices can be well fitted by Eq (1). Table 5 Figure 3

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

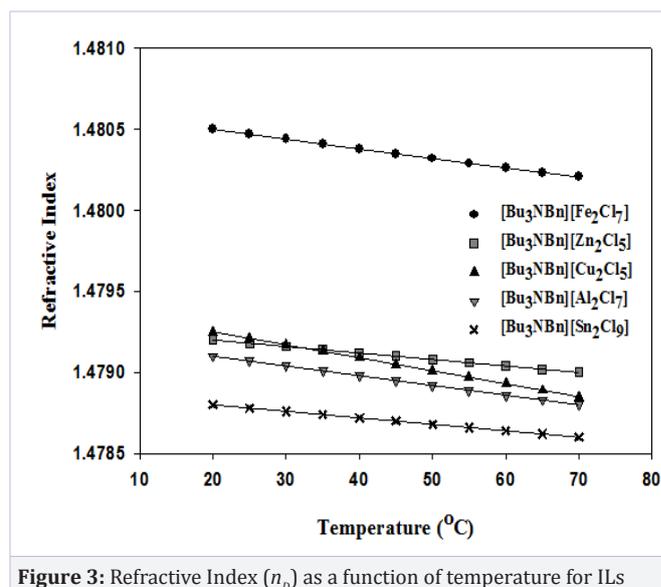


Figure 3: Refractive Index (n_D) as a function of temperature for ILs

Table 5: Fitting Parameters of Equation 1 and Standard Deviations, SD, of the Refractive Index (n_D) ILs

ILs	$n_D = A_0 + A_1 T (K) + A_2 T^2 (K)^2$				SD $\times 10^{-4}$	$(\Delta n_D / n_D) \times 100$
	A_0	$A_1 (C^{-1}) \times 10^{-2}$	$A_2 (C^{-2})$			
[Bu ₃ NBn][Al ₂ Cl ₇]	1.4792	-6.0000	-1.4293	9.9499	1.4790	
[Bu ₃ NBn][Cu ₂ Cl ₅]	1.4794	-8.0000	-6.0984	1.3226	1.4791	
[Bu ₃ NBn][Fe ₂ Cl ₇]	1.4806	-6.5385	-6.9930	9.8026	1.4804	
[Bu ₃ NBn][Sn ₂ Cl ₉]	1.4789	-4.0000	-7.3833	6.6333	1.4787	
[Bu ₃ NBn][Zn ₂ Cl ₅]	1.4793	-4.0000	-6.7560	6.6333	1.4791	

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 [Bu₃NBn][Fe₂Cl₇] has high surface tension than Lewis ILs. Based on these data, it appears that the surface tension lowly decreases with increases temperature. The relationship between surface tension and temperature can be fitting by the Eq (1). Table 6

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

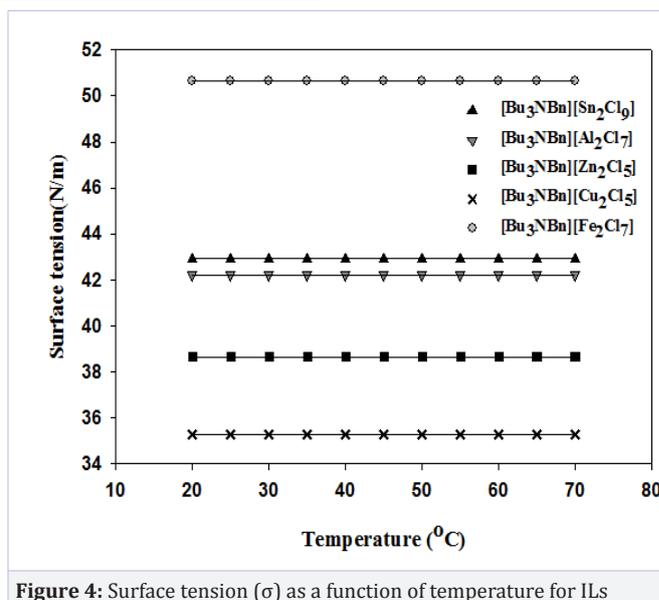


Figure 4: Surface tension (σ) as a function of temperature for ILs

Table 6: Fitting Parameters of Equation 1 and Standard Deviations,SD, of the Surface tension (σ) ILs

ILs	$\sigma = A_0 + A_1 T (K) + A_2 T^2 (K)^2$				$(\Delta\sigma / \sigma) \times 100$
	$A_0 (mN s^{-1})$	$A_1 \times 10^{-2} (mN s^{-1})$	$A_2 (mN s^{-1} K)$	$SD \times 10^{-4}$	
[Bu ₃ NBn][Al ₂ Cl ₇]	42.2259	-4.0000	3.5157	6.6332	4.2241
[Bu ₃ NBn][Cu ₂ Cl ₅]	25.2757	-5.2825	-9.7902	1.0226	3.2731
[Bu ₃ NBn][Fe ₂ Cl ₇]	50.6445	-6.8420	6.5268	1.0376	5.6415
[Bu ₃ NBn][Sn ₂ Cl ₉]	42.918	-5.2420	1.8648	5.9391	4.9161
[Bu ₃ NBn][Zn ₂ Cl ₅]	38.6589	-0.0448	9.7902	1.0226	3.6559

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 into 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 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 gularity within the range of ± 0.1 K. At least five measurements were taken for each temperature to make sure the uncertainty of measurements almost $\pm 2\%$.

The relationship between thermal conductivity (λ) and temperature of can be fitting by the Eq (1) and fitting parameters listed in table 5. Table 7

Fig5 shows the thermal conductivity of ILs as a function of temperature. Figure 5

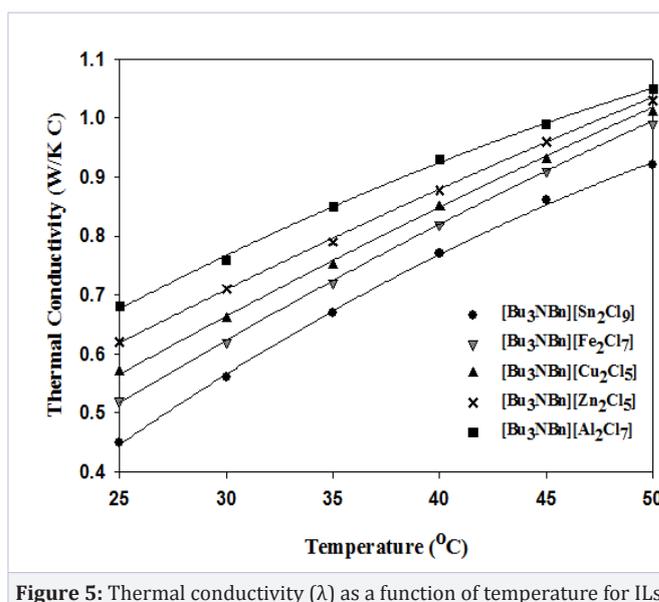


Figure 5: Thermal conductivity (λ) as a function of temperature for ILs

Table 7: Fitting Parameters of Equation 1 and Standard Deviations, SD, of the Thermal conductivity (λ) ILs

ILs	$\lambda = A_0 + A_1 T (K) + A_2 T^2 (K)^2$				SD	$(\Delta\lambda / \lambda) \times 100$
	$A_0 (W / m K)$	$A_1 (W / m K) \times 10^{-2}$	$A_2 (W / m K)$			
[Bu ₃ NBn][Al ₂ Cl ₇]	0.1057	0.0268	-0.0002	0.1405	0.8767	
[Bu ₃ NBn][Cu ₂ Cl ₅]	-0.1686	-0.0144	6.4286	0.1663	0.7950	
[Bu ₃ NBn][Fe ₂ Cl ₇]	-0.0186	0.0222	-2.8571	0.1776	0.7633	
[Bu ₃ NBn][Sn ₂ Cl ₉]	-0.3271	0.0368	-0.0002	0.1799	0.7050	
[Bu ₃ NBn][Zn ₂ Cl ₅]	0.1877	0.01714	-1.4286	0.1545	0.8331	

Electrical Conductivity

Electrical conductivity is one of the most main properties of ILs as electrolyte materials. 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 0.02 M KCl aqueous solution. The data for the considered aqueous RTIL systems were measured

for temperatures ranging from (298.15 to 348.15) K at normal atmospheric pressure. Table 6 presented the obtained κ Table 8

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 ($kmol m^{-3}$) according to the Eq (5).

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

Table 8: Fitting Parameters of Equation 5 and Standard Deviations, SD, of the Electrical conductivity (Λ) ILs

ILs	$\Lambda = \Lambda_0 + AT(K) + BT^2(K)^2 + CT^3(K)^3$				SD	$(\Delta\Lambda / \Lambda) \times 100$
	$\Lambda_0 (ms cm^{-1})$	$A (ms cm^{-1} K^{-1})$	$B (ms cm^{-1} K^{-2})$	$C (ms cm^{-1} K^{-3})$		
[Bu ₃ NBn][Al ₂ Cl ₇]	6.0371	-0.1120	0.0005	-04.8415	0.6588	2.4027
[Bu ₃ NBn][Cu ₂ Cl ₅]	-79.6589	0.7109	-0.0022	2.3140	0.5930	1.8082
[Bu ₃ NBn][Fe ₂ Cl ₇]	-10.0573	0.0176	0.0001	-2.1875	0.6966	3.0625
[Bu ₃ NBn][Sn ₂ Cl ₉]	-43.4523	0.3440	-0.0009	9.6830	0.6545	2.0055
[Bu ₃ NBn][Zn ₂ Cl ₅]	-33.5008	0.2711	-0.0007	7.1673	0.3435	1.3901

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

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

The plots showing the behaviour of the present κ data for the studied solvent systems: [Bu₃NBn][Al₂Cl₇] + DMSO, [Bu₃NBn][Cu₂Cl₅] + DMSO, [Bu₃NBn][Fe₂Cl₇] + DMSO, [Bu₃NBn][Sn₂Cl₉] + DMSO, [Bu₃NBn][Zn₂Cl₅] + DMSO are shown in Fig 6. Figure 6

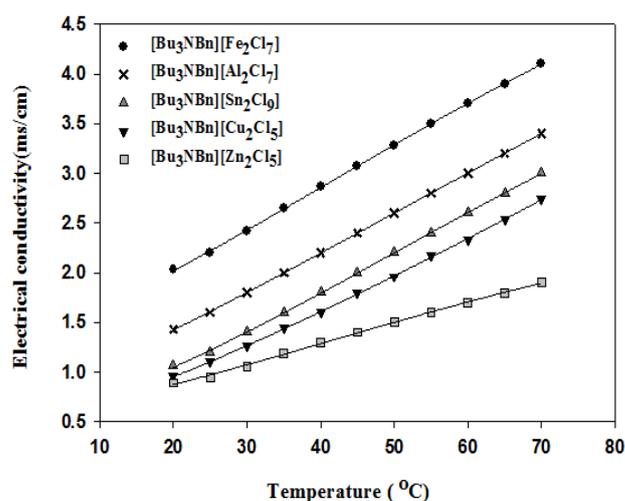


Figure 6: Electrical conductivity (κ) as a function of temperature for ILs

Determination of H_o values of Lewis acidic ILs

A common and effective way to evaluate the acidity of Brönsted acids was the Hammett method.³⁷ 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 absorptive 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_o, was calculated by using Eq 7

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

This value was regarded as the relative acidity of the IL. 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. Figure 7

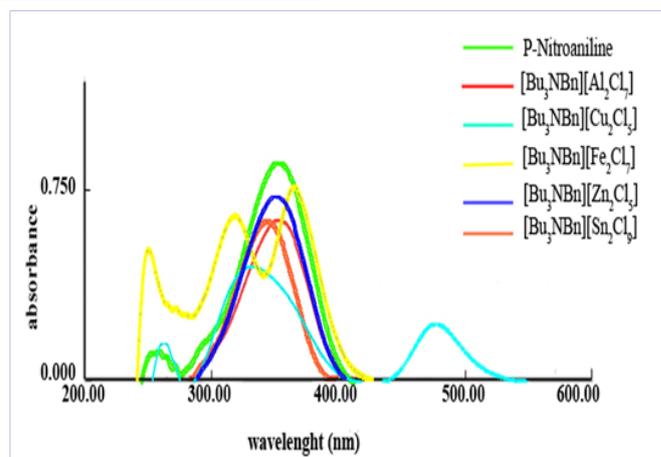


Figure 7: UV-Vis absorption spectra of ILs

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

ILs	A _{max}	[I]%	[HI]%	H _o
Para-nitro aniline	0.858	100	-	-
[Bu ₃ NBn][Al ₂ Cl ₇]	0.642	74.83	25.18	1.46
[Bu ₃ NBn][Cu ₂ Cl ₅]	0.456	53.15	46.85	1.044
[Bu ₃ NBn][Fe ₂ Cl ₇]	0.772	89.98	10.02	1.94
[Bu ₃ NBn][Sn ₂ Cl ₉]	0.630	73.43	26.57	1.43
[Bu ₃ NBn][Zn ₂ Cl ₅]	0.735	85.66	14.33	1.76

Under the same concentration of 4-nitroaniline (10 mg/L, Pk(I)_{aq}=pKa = 0.99) and Lewis ILs (0.1 mmol/L) in dichloromethane, H_o values of all Lewis ILs were determined. The maximal absorbance of the unprotonated form of the indicator was observed at 350 nm in dichloromethane. When Lewis IL was added, the absorbance of the unprotonated form of the basic indicator decreased (Figure 7 and Table 7). Table 10

Hammett acidity (H_o) of these Lewis ILs was calculated using equations (7). As shown in Figure 7. Calculations suggest that the Hammett acidity (H_o) of these ionic liquids follows the order:

[Bu₃NBn][Cu₂Cl₅] > [Bu₃NBn][Sn₂Cl₉] > [Bu₃NBn][Al₂Cl₇] > [Bu₃NBn][Zn₂Cl₅] > [Bu₃NBn][Fe₂Cl₇].

A comparison between the experimental data for the physical properties of the studied Lewis ILs at 25 °C has also been made in Table 8. 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 five studied ILs. As is obvious from Table 8, the experimental data for [Bu₃NBn][Al₂Cl₇], [Bu₃NBn][Cu₂Cl₅], [Bu₃NBn][Fe₂Cl₇], [Bu₃NBn][Sn₂Cl₉] and [Bu₃NBn][Zn₂Cl₅].

Table 10: The experimental value of dynamic viscosities (η), refractive indices (n_D), densities (ρ), surface tensions (σ), electrical conductivity (κ), thermal conductivity (λ) and thermal decomposition (td) of the Lewis 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)	t _d (°C)
[Bu ₃ NBn][Al ₂ Cl ₇]	12.8	1.4791	1.0007	42.2249	1.6000	0.6800	129.37
[Bu ₃ NBn][Cu ₂ Cl ₅]	13.8	1.4792	0.0039	35.2743	1.1000	0.5700	240.32
[Bu ₃ NBn][Fe ₂ Cl ₇]	14.8	1.4805	0.0001	50.6428	2.2000	0.5200	310.59
[Bu ₃ NBn][Sn ₂ Cl ₉]	14.6	1.4788	1.0043	42.9167	1.2000	0.4500	147.52
[Bu ₃ NBn][Zn ₂ Cl ₅]	13.5	1.4792	1.0014	38.6572	0.9500	0.6200	116.17

Thermal properties

Thermo gravimetric analysis was applied to evaluate the thermal properties of the Lewis IL sat a heating rate of 10°C/min, under a nitrogen atmosphere. Figure 8 demonstrates the respective TGA profiles and the corresponding thermo analysis data, including the temperatures at which 5% (T₅) and 10% (T₁₀) degradation occur. Char yield at 800°C and also limiting oxygen index(LOI) based on Van Krevelen and Hoftzyer equation(Equation (8)) is summarized in Table 9 [17].

$$LOI = 17.5 + 0.4CR \quad (8)$$

From these data, it is clear that the [Bu₃NBn][Fe₂Cl₇] is stable to 300°C and introduction of inorganic particles in IL matrix induced the thermal properties to rise. Table 11

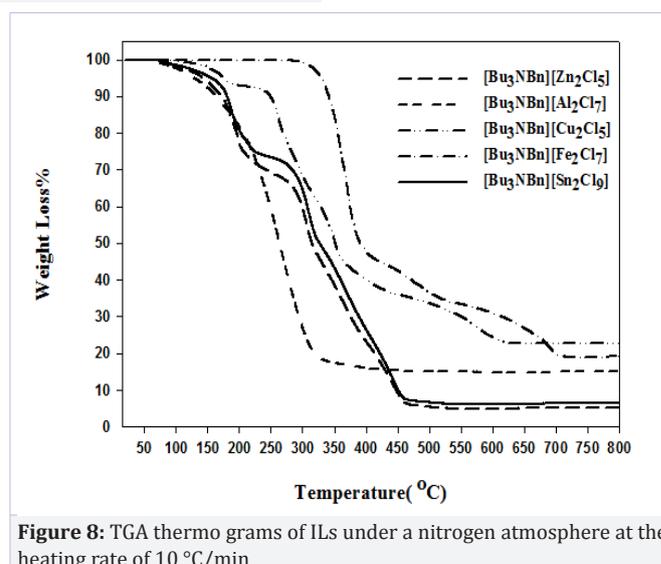


Figure 8: TGA thermo grams of ILs under a nitrogen atmosphere at the heating rate of 10 °C/min

Table 11: Thermal properties of ILs

ILs	Decomposition temperature (°C)		Char Yield[%] ^c	LOI ^d
	T ₅ ^a	T ₁₀ ^b		
[Bu ₃ NBn][Al ₂ Cl ₇]	128.24	158.54	15.5	23.7
[Bu ₃ NBn][Cu ₂ Cl ₅]	176.05	244.33	22.8	26.62
[Bu ₃ NBn][Fe ₂ Cl ₇]	329.69	339.9	19.53	25.32
[Bu ₃ NBn][Sn ₂ Cl ₉]	156.15	180.92	6.8	20.22
[Bu ₃ NBn][Zn ₂ Cl ₅]	143.29	172.26	5.95	19.88

^aTemperature at which 5% weight loss was recorded by TGA at a heating rate of 10°C/min under a nitrogen atmosphere.

^bTemperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C/min under a nitrogen atmosphere.

^cweight percentage of material left undecomposed after TGA analysis at a temperature of 800°C under a nitrogen atmosphere.

^dLimiting oxygen index (LOI) evaluating char yield at 800°C.

Conclusions

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. 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 physical chemistry properties of ILs. The weight particle influenced on physical chemistry properties of ILs. Structure ILs affected on properties physical chemistry of

ILs. Hydrogen bonding internal molecular influenced on physical chemistry properties of ILs. Electrical charge particle influenced on physical chemistry properties of ILs. Temperature affected on properties physical chemistry of ILs. Principle HARD and SAFT influenced on properties physical chemistry of ILs.

Thus, in this work, we have carefully measured several important physical properties of Lewis ionic liquids: [Bu₃NBn][Al₂Cl₇], [Bu₃NBn][Cu₂Cl₅], [Bu₃NBn][Fe₂Cl₇], [Bu₃NBn][Sn₂Cl₉] and [Bu₃NBn][Zn₂Cl₅] over a wide range of temperature from (298.15 to 363.15 K). Clearly, much more attention should be paid on the measurement of physicochemical properties of Lewis ionic liquids.

$Bu_3NBn][Cu_2Cl_5] > [Bu_3NBn][Fe_2Cl_7] > [Bu_3NBn][Al_2Cl_7] > [Bu_3NBn][Sn_2Cl_9] > [Bu_3NBn][Zn_2Cl_5]$

The measured densities, ρ , and the dynamic viscosities, η , for the binary mixtures of [Bu₃NBn][Fe₂Cl₇] with water at T = (298.15 to 363.15) K over the whole composition range are listed in Tables 1 and 2. As can be seen, the density of all of the mixtures with DMSO always decreases with temperature. A very good linear correlation is observed for all compositions ($r = 1$), this linear behavior with temperature.

The experimental viscosity results of Lewis ILs from this study are in good agreement with the very scarce data from the literature and are well represented by the VTF equation. At the same temperature, [Bu₃NBn][Fe₂Cl₇] have high very significantly the viscosity of other Five ILs. Presencemetal atoms perhaps make up high viscosity this IL than other ILs. Since the viscosities of ILs are essentially effective by the van derWaals interactions and H bonding, have reported the influence of metal atoms, DMSO on the physical properties of [Bu₃NBn][Fe₂Cl₇]. It has been shown that the presence of even low concentrations of chloride in the [Bu₃NBn][Fe₂Cl₇] substantially increases the viscosity.

Figure 5 shows the thermal conductivity of Lewis ILs as a function of temperature. It can be seen that the thermal conductivity of [Bu₃NBn][Al₂Cl₇] is 0.68 Wm⁻¹C⁻¹. This indicates that [Bu₃NBn][Al₂Cl₇] is a relatively poor thermal conductor with the thermal conductivity approximately of that of water at the room temperature. Electrically conductive Lewis ILs is influence of temperature. Besides, Thermo gravimetric analysis was demonstrated to evaluate the thermal properties of the Lewis ILs.

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: $\alpha_{\rho} = 1 / \rho (\partial \rho / \partial T)_{-p}$.
- Brönsted Lewis acidic ionic liquids were used as solvents and catalysts in many organic reactions such as esterification, polymerization, alkylation, acylation, carbonylation, aldol condensation, pinacol rearrangement, nitration, Koch reaction, oxidation of alcohols.
- Acidic Brönsted 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.
- Self-diffusion coefficient of cation and anion in ionic liquid (D).
- Cyclic voltammograms.
- Chronoamperograms for ferrocene.
- Excess Molar Volumes V E.

To recap, in comparison with the other ILs in that how do the thermo physical properties and the most advantages and the superiority of these system when compared to the ones reported in the literature being easily produced and used in the various temperature.

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