Thermo Physical Properties of Lewis Acidic Ionic Liquids
[Bu$_3$NBn] Cl-2(MClm), (MClm= AlCl$_3$, FeCl$_3$, CuCl$_2$, SnCl$_4$, ZnCl$_2$) binary mixtures with DMSO at Temperatures from (298.15 to 363.15) K

Zeinab Heidari Pebdani$^1$, Abdol Reza Hajipour$^1$ and Yosofe Ghayeba$^1$

$^1$Pharmaceutical 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: zenabheidyari.pebdani@yahoo.com

Abstract

In this article, we were investigated as a function of temperature, densities ($\rho$), dynamic viscosities ($\eta$), surface tension ($\sigma$), ionic conductivity ($\kappa$), refractive indices (nD), and thermal conductivity ($\lambda$) 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 [Bu$_3$NBn]Cl-2(MClm), (MClm= AlCl$_3$, CuCl$_2$, FeCl$_3$, SnCl$_4$, ZnCl$_2$) that synthesis for the first time 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 TGC, CHNS, FT-IR and Mass Spectroscopy. Thermogravimetric analysis (TGA) confirmed that the heat stability of ILs in the temperature range of 400–800°C is common and effective way to evaluate the Activity of Lewis acids was the Hammett method (Ho) that we used for RTILs. Also, 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; (VOCs) 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 are based on [Bu$_3$NBn]Cl-2(AlCl$_3$), [Bu$_3$NBn]Cl-2(CuCl$_2$), [Bu$_3$NBn]Cl-2(FeCl$_3$), [Bu$_3$NBn]Cl-2(SnCl$_4$) and [Bu$_3$NBn]Cl-2(ZnCl$_2$). 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 sin 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, 11. In contrast, an increase in cation size decreases cation mobility. The cations are basically solid around room temperature. In general, ILs 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 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 \([\text{Bu}_3\text{NBn}]\text{Cl}^{-2}(\text{MCl}_m)\), \((\text{MCl}_m= \text{AlCl}_3, \text{FeCl}_3, \text{CuCl}_2, \text{SnCl}_4, \text{ZnCl}_2)\) binary mixtures with DMSO at Temperatures from (298.15 to 363.15) K.

### 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 \(\text{AlCl}_3\), \(\text{CuCl}_2\), \(\text{FeCl}_3\), \(\text{SnCl}_4\), \(\text{ZnCl}_2\) 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:** \([\text{Bu}_3\text{NBn}]\text{Cl}^{-2}(\text{AlCl}_3),\ [\text{Bu}_3\text{NBn}]\text{Cl}^{-2}(\text{CuCl}_2),\ [\text{Bu}_3\text{NBn}]\text{Cl}^{-2}(\text{FeCl}_3),\ [\text{Bu}_3\text{NBn}]\text{Cl}^{-2}(\text{SnCl}_4)^\text{a}\) and \([\text{Bu}_3\text{NBn}]\text{Cl}^{-2}(\text{ZnCl}_2)\). 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 \(\text{MCl}_m\) 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:** Two steps preparation of ionic liquids

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Thermo Physical Properties of Lewis Acidic Ionic Liquids \([\text{Bu}_3\text{NBn}]\text{Cl-2(MClm)}, (\text{MClm}=\text{AlCl}_3, \text{FeCl}_3, \text{CuCl}_2, \text{SnCl}_4, \text{ZnCl}_2)\) binary mixtures with DMSO at Temperatures from (298.15 to 363.15) K

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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 muscarinic paralysis and other medically significant nervous problems. A array of regularly used \([\text{Bu}_3\text{NBn}]\text{Cl-2(AlCl}_3\), \([\text{Bu}_3\text{NBn}]\text{Cl-2(CuCl}_2\), \([\text{Bu}_3\text{NBn}]\text{Cl-2(FeCl}_3\), \([\text{Bu}_3\text{NBn}]\text{Cl-2(SnCl}_4\), and \([\text{Bu}_3\text{NBn}]\text{Cl-2(ZnCl}_2\)ionic liquids were tested in this analyse. \([\text{Bu}_3\text{NBn}]\text{Cl-2(SnCl}_4\) liquid presented high toxicity to acetyl cholinesterase at very low absorptions, whereas \([\text{Bu}_3\text{NBn}]\text{Cl-2(FeCl}_3\) 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.

\([\text{Bu}_3\text{NBn}]\text{CuCl}_2\rangle>[\text{Bu}_3\text{NBn}]\text{FeCl}_3\rangle>[\text{Bu}_3\text{NBn}]\text{AlCl}_3\rangle>[\text{Bu}_3\text{NBn}]\text{SnCl}_4\rangle>[\text{Bu}_3\text{NBn}]\text{ZnCl}_2\).

Berner and associates confirmed that severe toxicity of certain 1-butyl-3-methyl imidazolium liquid ions 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. \([\text{Bu}_3\text{NBn}]\text{ZnCl}_2\) 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-Benzencholoridionic 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 \([\text{Bu}_3\text{NBn}]\text{SnCl}_4\) and metal i.e. per oxidation by-product of lipid. \([\text{Bu}_3\text{NBn}]\text{SnCl}_4\) 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 microalge Selenastrum capricornutum [25]. Thechloride salts of commonly used \([\text{Bu}_3\text{NBn}]\text{CuCl}_2\rangle>[\text{Bu}_3\text{NBn}]\text{FeCl}_3\rangle>[\text{Bu}_3\text{NBn}]\text{AlCl}_3\rangle>[\text{Bu}_3\text{NBn}]\text{SnCl}_4\rangle>[\text{Bu}_3\text{NBn}]\text{ZnCl}_2\). 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 chloride (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- Diclorom ethane- Carbon Tetrachloride- Hexane-
Cyclohexane- Tleptane- Ethylene Glycol- Toluene> Water- Acetone- Ethanol- 2-Propanol

\[
\begin{align*}
[OMIM][Cl]-[FMIM][N03]-[EMIM][Lactate]-[HMIM][Sacch]-
[bmpy][Cl]-[BMIM][N(CN)2]-[EMIM][OctOSO3]-[BMIM][OAc]-
[EMIM][Cl]-[BMIM][EtOSO3]-[bmpy][{(Me)2PO3}]-[EMIM][OTs]
\end{align*}
\]

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 preciophysicscalmoiety, example hydrolysis of an ester bond(N) Naturally biodegradable – if a composite biodegrades B20% then the likelihood of supplementary degradation is implicit(II) Readily biodegradable – biodegrades a explicit % insidea 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 inthe bottle was fewer of a limiting issue. Table 1

Seawater

The biodegradation in seawater test OECD Table 1, differsfrom the standard experimentsin 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].

<table>
<thead>
<tr>
<th>Test</th>
<th>Pass level after 10 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biodegradability in seawater</td>
<td>&gt;50% DOC removal</td>
</tr>
<tr>
<td>(TG 306)</td>
<td></td>
</tr>
<tr>
<td>Shake flask and closed bottle</td>
<td>&gt;45% ThOD</td>
</tr>
<tr>
<td>variants</td>
<td></td>
</tr>
</tbody>
</table>

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 \([\text{Bu}_2\text{NBn}][\text{Cu} Cl_2]\)
Density

Density was measured in a 25 ml pyknometer. 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 ($r^2 > 0.999$).

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

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

(1)

Where fitting parameter $B$ and $A$ are related to the coefficient of volume expansion ($g$ cm⁻³ K⁻¹) and extrapolated density at 0K ($g$ cm⁻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.

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 ±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 (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–Tammann–Fulcher (VTF) equation (2) [32].

$$η = η_0 \exp \left[ B / (T - T_0) \right]$$  

(2)

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

<table>
<thead>
<tr>
<th>ILs</th>
<th>$A_0$ ($g$ cm⁻³)</th>
<th>$A_1$ ($g$ cm⁻³ K⁻¹) × 10⁻²</th>
<th>$A_2$ ($g$ cm⁻³ K⁻²)</th>
<th>$SD × 10^{-4}$</th>
<th>$(Δ\rho / ρ)×100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Bu₃NBn][Al₂Cl₇]</td>
<td>1.0073</td>
<td>-2.2000</td>
<td>1.5701</td>
<td>1.6583</td>
<td>1.0232</td>
</tr>
<tr>
<td>[Bu₃NBn][Cu₂Cl₅]</td>
<td>1.1017</td>
<td>-2.6000</td>
<td>-6.7742</td>
<td>6.6332</td>
<td>1.0033</td>
</tr>
<tr>
<td>[Bu₃NBn][Fe₂Cl₇]</td>
<td>1.0028</td>
<td>-3.1773</td>
<td>-4.1119</td>
<td>3.8799</td>
<td>0.9995</td>
</tr>
<tr>
<td>[Bu₃NBn][Sn₂Cl₉]</td>
<td>1.1118</td>
<td>-2.3716</td>
<td>-4.6620</td>
<td>4.4374</td>
<td>1.0037</td>
</tr>
<tr>
<td>[Bu₃NBn][Zn₂Cl₅]</td>
<td>1.0022</td>
<td>-2.6000</td>
<td>-8.6318</td>
<td>4.3116</td>
<td>1.0014</td>
</tr>
</tbody>
</table>

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

Where T is the absolute temperature, ηₒ, B, and Tₒ are adjustable parameters. Then ηₒ (cP), B, and Tₒ(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].

$$\eta = \eta_o \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

Viscosity at initial temperature ηₒ 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):

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

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

<table>
<thead>
<tr>
<th>ILs</th>
<th>ηₒ (cP)</th>
<th>B (K)</th>
<th>Tₒ (K)</th>
<th>SD</th>
<th>(Δη/η)×100</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BuNBN][AlCl3]</td>
<td>23.9420</td>
<td>-0.5309</td>
<td>0.0030</td>
<td>4.0284</td>
<td>4.6514</td>
</tr>
<tr>
<td>[BuNBN][FeCl3]</td>
<td>25.7803</td>
<td>-0.5791</td>
<td>0.0034</td>
<td>4.1442</td>
<td>5.1007</td>
</tr>
<tr>
<td>[BuNBN][CuCl2]</td>
<td>29.0771</td>
<td>-0.6586</td>
<td>0.0039</td>
<td>4.6741</td>
<td>5.6021</td>
</tr>
<tr>
<td>[BuNBN][SnCl4]</td>
<td>26.3494</td>
<td>-0.5989</td>
<td>0.0036</td>
<td>4.1831</td>
<td>5.2036</td>
</tr>
<tr>
<td>[BuNBN][ZnCl2]</td>
<td>25.9771</td>
<td>-0.6586</td>
<td>1.4286</td>
<td>4.0827</td>
<td>5.1629</td>
</tr>
</tbody>
</table>

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. Refractive Indices can be well fitted by Eq (1). Table 5

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

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

<table>
<thead>
<tr>
<th>ILs</th>
<th>Aₒ</th>
<th>A₁ (C⁻¹) × 10⁻²</th>
<th>A₂ (C⁻²)</th>
<th>SD × 10⁻⁴</th>
<th>(ΔnD / nD) ×100</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BuNBN][AlCl3]</td>
<td>1.4792</td>
<td>-6.0000</td>
<td>-1.4293</td>
<td>9.9499</td>
<td>1.4790</td>
</tr>
<tr>
<td>[BuNBN][FeCl3]</td>
<td>1.4794</td>
<td>-8.0000</td>
<td>-6.9084</td>
<td>1.3226</td>
<td>1.4791</td>
</tr>
<tr>
<td>[BuNBN][SnCl4]</td>
<td>1.4789</td>
<td>-4.0000</td>
<td>-7.3833</td>
<td>6.6333</td>
<td>1.4787</td>
</tr>
<tr>
<td>[BuNBN][ZnCl2]</td>
<td>1.4793</td>
<td>-4.0000</td>
<td>-6.7560</td>
<td>6.6333</td>
<td>1.4791</td>
</tr>
</tbody>
</table>
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.

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±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
Thermo Physical Properties of Lewis Acidic Ionic Liquids \([\text{Bu}_3\text{NBn}] \text{Cl-2(MClm)}, \) (MClm= AlCl\(_3\), FeCl\(_3\), CuCl\(_2\), SnCl\(_4\), ZnCl\(_2\)) binary mixtures with DMSO at Temperatures from (298.15 to 363.15) K

Table 7: Fitting Parameters of Equation 1 and Standard Deviations, SD, of the Thermal conductivity (\(\lambda\)) IILs

<table>
<thead>
<tr>
<th>IILs</th>
<th>(A_0 (W/\text{mK}))</th>
<th>(A_1 (W/\text{mK}) \times 10^{-2})</th>
<th>(A_2 (W/\text{mK}))</th>
<th>SD</th>
<th>((\Delta\lambda/\lambda) \times 100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Bu}_3\text{NBn}]\text{[AlCl_3]})</td>
<td>1.057</td>
<td>0.0268</td>
<td>-0.0002</td>
<td>0.1405</td>
<td>0.8767</td>
</tr>
<tr>
<td>([\text{Bu}_3\text{NBn}]\text{[CuCl_2]})</td>
<td>-0.1686</td>
<td>-0.0144</td>
<td>6.4286</td>
<td>0.1663</td>
<td>0.7950</td>
</tr>
<tr>
<td>([\text{Bu}_3\text{NBn}]\text{[FeCl_3]})</td>
<td>-0.0186</td>
<td>0.0222</td>
<td>-2.8571</td>
<td>0.1776</td>
<td>0.7633</td>
</tr>
<tr>
<td>([\text{Bu}_3\text{NBn}]\text{[SnCl_4]})</td>
<td>-0.3271</td>
<td>0.0368</td>
<td>-0.0002</td>
<td>0.1799</td>
<td>0.7050</td>
</tr>
<tr>
<td>([\text{Bu}_3\text{NBn}]\text{[ZnCl_2]})</td>
<td>0.1877</td>
<td>0.01714</td>
<td>-1.4286</td>
<td>0.1545</td>
<td>0.8331</td>
</tr>
</tbody>
</table>

Electrical Conductivity

Electrical conductivity is one of the most main properties of IILs as electrolyte materials.\(^{36}\) The electrical conductivity (\(\kappa\)) 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 \(\kappa\) 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 \(\kappa\) Table 8 Measurements: Molar conductivity of the ionic liquids \((\Lambda \text{m}^2\text{Smol}^{-1})\) was calculated from the ionic conductivity \(\sigma \text{ (Sm}^{-1})\) and the molar concentration \(C \text{ (kmolm}^{-3})\) according to the Eq (5).

\[
\Lambda = \frac{1000 C \kappa}{\sigma} \quad (5)
\]

Table 8: Fitting Parameters of Equation 5 and Standard Deviations, SD, of the Electrical conductivity (\(\Lambda\)) IILs

<table>
<thead>
<tr>
<th>IILs</th>
<th>(\Lambda_0 (\text{m}^2\text{Smol}^{-1}))</th>
<th>(\Lambda_1 (\text{m}^2\text{Smol}^{-1} \text{K}^{-1}))</th>
<th>(\Lambda_2 (\text{m}^2\text{Smol}^{-1} \text{K}^{-2}))</th>
<th>(\Lambda_3 (\text{m}^2\text{Smol}^{-1} \text{K}^{-3}))</th>
<th>SD</th>
<th>((\Delta\Lambda/\Lambda) \times 100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Bu}_3\text{NBn}]\text{[AlCl_3]})</td>
<td>6.0371</td>
<td>-0.1120</td>
<td>0.0005</td>
<td>-0.8415</td>
<td>0.6588</td>
<td>2.4027</td>
</tr>
<tr>
<td>([\text{Bu}_3\text{NBn}]\text{[CuCl_2]})</td>
<td>-79.6589</td>
<td>0.7109</td>
<td>-0.0022</td>
<td>2.3140</td>
<td>0.5930</td>
<td>1.8082</td>
</tr>
<tr>
<td>([\text{Bu}_3\text{NBn}]\text{[FeCl_3]})</td>
<td>-10.0573</td>
<td>0.0176</td>
<td>0.0001</td>
<td>-2.1875</td>
<td>0.6966</td>
<td>3.0625</td>
</tr>
<tr>
<td>([\text{Bu}_3\text{NBn}]\text{[SnCl_4]})</td>
<td>-43.4523</td>
<td>0.3440</td>
<td>-0.0009</td>
<td>9.6830</td>
<td>0.6545</td>
<td>2.0055</td>
</tr>
<tr>
<td>([\text{Bu}_3\text{NBn}]\text{[ZnCl_2]})</td>
<td>-33.5008</td>
<td>0.2711</td>
<td>-0.0007</td>
<td>7.1673</td>
<td>0.3435</td>
<td>1.3901</td>
</tr>
</tbody>
</table>

The electrical conductivity presents linear behaviour with temperature for all IILs measured. Electrical conductivity (\(\kappa\)) values were fitted by the method of least squares using the following equations (6).\(^{14}\)

\[
\Lambda = \Lambda\_0 + \Lambda\_1 \text{AT} (K) + \Lambda\_2 \text{BT}^2 (K) + \Lambda\_3 \text{CT}^3 (K) \quad (6)
\]

The plots showing the behaviour of the present \(\kappa\) data for the studied solvent systems: \([\text{Bu}_3\text{NBn}]\text{[AlCl_3]}\) + DMSO, \([\text{Bu}_3\text{NBn}]\text{[CuCl_2]}\) + DMSO, \([\text{Bu}_3\text{NBn}]\text{[FeCl_3]}\) + DMSO, \([\text{Bu}_3\text{NBn}]\text{[SnCl_4]}\) + DMSO, \([\text{Bu}_3\text{NBn}]\text{[ZnCl_2]}\) + DMSO are shown in Fig 6 Figure 6

Figure 6: Electrical conductivity (\(\kappa\)) as a function of temperature for IILs
Determination of $H_o$ values of Lewis acidic ILs

A common and effective way to evaluate the acidity of Brønsted acids was the Hammett method. In reported papers, the measurement of the acidic scale of these acidic Brønsted ILs was conducted on a UV-Vis spectrophotometer with a basic indicator (para-nitroaniline). Increasing the acidic scale of the 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 $[I]/[HI]$ ratio was determined from the measured absorbance differences after addition of an acidic Brønsted 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.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. Figure 7.

![UV-Vis absorption spectra of ILs](image)

Table 9: $H_o$ Values of Ionic Liquids in CH$_2$Cl$_2$ at Room Temperature

<table>
<thead>
<tr>
<th>ILs</th>
<th>$A_{max}$</th>
<th>$[I]$%</th>
<th>$[HI]$%</th>
<th>$H_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Para-nitro aniline</td>
<td>0.858</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Bu$_3$NBn][AlCl$_3$]</td>
<td>0.642</td>
<td>74.83</td>
<td>25.18</td>
<td>1.46</td>
</tr>
<tr>
<td>[Bu$_3$NBn][CuCl$_3$]</td>
<td>0.456</td>
<td>53.15</td>
<td>46.85</td>
<td>1.044</td>
</tr>
<tr>
<td>[Bu$_3$NBn][FeCl$_3$]</td>
<td>0.772</td>
<td>89.98</td>
<td>10.02</td>
<td>1.94</td>
</tr>
<tr>
<td>[Bu$_3$NBn][SnCl$_3$]</td>
<td>0.630</td>
<td>73.43</td>
<td>26.57</td>
<td>1.43</td>
</tr>
<tr>
<td>[Bu$_3$NBn][ZnCl$_3$]</td>
<td>0.735</td>
<td>85.66</td>
<td>14.33</td>
<td>1.76</td>
</tr>
</tbody>
</table>

Under the same concentration of 4-nitroaniline (10 mg/L, $pK(I)_{aq}=pK_a = 0.99$) 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).

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: [Bu$_3$NBn][CuCl$_3$]>[Bu$_3$NBn][SnCl$_3$]>[Bu$_3$NBn][ZnCl$_3$]>[Bu$_3$NBn][AlCl$_3$]>[Bu$_3$NBn][FeCl$_3$].

A comparison between the experimental data for the physical properties of the studied Lewis ILs at 25 °C has also made in Table 8. To the best of our knowledge, no literature data on densities ($\rho$), dynamic viscosities ($\eta$), surface tension ($\sigma$), electrical conductivity ($\kappa$), refractive indices (nD) and thermal conductivity ($\lambda$), were not previously available for five studied ILs. As is obvious from Table 8, the experimental data for [Bu$_3$NBn][AlCl$_3$], [Bu$_3$NBn][CuCl$_3$], [Bu$_3$NBn][SnCl$_3$], [Bu$_3$NBn][FeCl$_3$], [Bu$_3$NBn][ZnCl$_3$] and [Bu$_3$NBn][ZnCl$_3$] in Table 10.

Table 10: The experimental value of dynamic viscosities ($\eta$), refractive indices (nD), densities ($\rho$), surface tension ($\sigma$), electrical conductivity ($\kappa$), thermal conductivity ($\lambda$), and thermal decomposition ($\lambda_d$) of the Lewis ionic liquids at 25.0 °C

<table>
<thead>
<tr>
<th>ILs</th>
<th>$\eta$ (mPa.s)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$\sigma$ (N/m)</th>
<th>$\kappa$ (ms/m)</th>
<th>$\lambda$ (W/K cm)</th>
<th>$\lambda_d$ (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Bu$_3$NBn][AlCl$_3$]</td>
<td>12.8</td>
<td>1.4791</td>
<td>1.0007</td>
<td>42.2249</td>
<td>1.6000</td>
<td>0.6800</td>
</tr>
<tr>
<td>[Bu$_3$NBn][CuCl$_3$]</td>
<td>13.8</td>
<td>1.4792</td>
<td>0.0039</td>
<td>35.2743</td>
<td>1.1000</td>
<td>0.5700</td>
</tr>
<tr>
<td>[Bu$_3$NBn][FeCl$_3$]</td>
<td>14.8</td>
<td>1.4805</td>
<td>0.0001</td>
<td>50.6428</td>
<td>2.2000</td>
<td>0.5200</td>
</tr>
<tr>
<td>[Bu$_3$NBn][SnCl$_3$]</td>
<td>14.6</td>
<td>1.4788</td>
<td>1.0043</td>
<td>42.9167</td>
<td>1.2000</td>
<td>0.4500</td>
</tr>
<tr>
<td>[Bu$_3$NBn][ZnCl$_3$]</td>
<td>13.5</td>
<td>1.4792</td>
<td>1.0014</td>
<td>38.6572</td>
<td>0.9500</td>
<td>0.6200</td>
</tr>
</tbody>
</table>
Thermo Physical Properties of Lewis Acidic Ionic Liquids [Bu,NBn]Cl-2(MClm), (MClm= AlCl3, FeCl3, CuCl2, SnCl4, ZnCl2) binary mixtures with DMSO at Temperatures from (298.15 to 363.15) K

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 Hoftyzer equation (Equation (8)) is summarized in Table 9 [17].

\[
LOI = 17.5 + 0.4CR \quad (8)
\]

From these data, it is clear that the [Bu,NBn][FeCl3] is stable to 300°C and introduction of inorganic particles in IL matrix induced the thermal properties to rise. Table 11

<table>
<thead>
<tr>
<th>ILs</th>
<th>Decomposition temperature (°C)</th>
<th>Char Yield[%]</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Bu,NBn][AlCl3]</td>
<td>128.24</td>
<td>15.5</td>
<td>23.7</td>
</tr>
<tr>
<td>[Bu,NBn][CuCl2]</td>
<td>176.05</td>
<td>23.8</td>
<td>26.62</td>
</tr>
<tr>
<td>[Bu,NBn][FeCl3]</td>
<td>329.69</td>
<td>19.53</td>
<td>25.32</td>
</tr>
<tr>
<td>[Bu,Nb][SnCl4]</td>
<td>156.15</td>
<td>6.8</td>
<td>20.22</td>
</tr>
<tr>
<td>[Bu,NBn][ZnCl2]</td>
<td>143.29</td>
<td>5.95</td>
<td>19.88</td>
</tr>
</tbody>
</table>

\(a\) Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10°C/min under a nitrogen atmosphere.

\(b\) Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C/min under a nitrogen atmosphere.

\(c\) Weight percentage of material left undecomposed after TGA analysis at a temperature of 800°C under a nitrogen atmosphere.

\(d\) Limiting 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 RTILs. However, there is limited information on the accurate measurements 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: [Bu,NBn][AlCl3], [Bu,NBn][CuCl2], [Bu,NBn][FeCl3], [Bu,NBn][SnCl4] and [Bu,NBn][Zn2Cl4] 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.

\[
\begin{align*}
[Bu,NBn][CuCl2] & > [Bu,NBn][FeCl3] > [Bu,NBn][AlCl3] > [Bu,NBn][SnCl4] > [Bu,NBn][Zn2Cl4] \\
\end{align*}
\]

The measured densities, \(\rho\), and the dynamic viscosities, \(\eta\), for the binary mixtures of [Bu,NBn][FeCl3] 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 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 agreement with the very scarce data from the literature and are well represented by the VTF equation. At the same temperature, [BuNBn][FeCl₂] have high very significantly the viscosity of other Five ILs. Precisemetal 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 metal atoms, DMSOon the physical properties of [Bu3NBn][FeCl₂]. It has been shown that the presence of even low concentrations of chloride in the [BuNBn][FeCl₂] 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 [BuNBn][AlCl₃] is 0.68 W m⁻¹°C⁻¹. This indicates that [BuNBn][AlCl₃] 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:
  \[ \rho_v = \frac{1}{\rho} \frac{\partial \rho}{\partial T} \]
- 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 liquid ionic 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.

Acknowledgments

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References

Thermo Physical Properties of Lewis Acidic Ionic Liquids [Bu$_3$NBn] Cl-2(MClm), (MClm= AlCl$_3$, FeCl$_3$, CuCl$_2$, SnCl$_4$, ZnCl$_2$) binary mixtures with DMSO at Temperatures from (298.15 to 363.15) K


