

# CONDUCTIVITY STUDIES OF IMIDAZOLIUM-BASED IONIC LIQUIDS IN AQUEOUS SOLUTION

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**Abstract:** *The conductivity of aqueous solutions of nine types of imidazolium-based ionic liquids [ILs] has been studied analysing the influence of the length of the hydrocarbon chain attached to the imidazolium ring (ethyl, methyl, hexyl and dodecyl), the anion nature ( $Cl^-$ ,  $BF_4^-$  and  $FeCl_4^-$ ) and the solution concentration. It was determined that the concentration increase up to 40% IL, for all types of ILs in water, led to the solution conductivity increase after this, the aggregation phenomenon becomes dominating leading to the solution conductivity decrease. The longer the side chain is, the lower conductivity is. The major influence on the ILs solutions conductivity is that of the cation nature while that of the anion is negligible.*

**Key words:** *imidazolium-based ionic liquids, aqueous solutions, conductivity.*

## 1. Introduction

Ionic liquids (ILs) are organic salts consisting of an organic cation with an organic or inorganic anion, with melting points below that for water. They also have unusual properties including non-volatility, conductivity, chemical and electrochemical stability.

While liquids like water are predominantly made of electrically neutral molecules, ionic liquids [ILs] are largely made of ions and short-lived ion pairs. These substances are called liquid electrolytes. Ionic liquids have many applications, such as powerful solvents and electrically conducting fluids (electrolytes) [2].

Previously, ILs attracted special attention due to their very low vapour pressure and as consequence very low tendency to evaporate.

Nowadays, when environmental issues are very important, ILs seem to be a good solution for replacing volatile organic solvents in different technologies aiming to avoid atmospheric pollution.

Of course, their toxicity and effect in case of water or soil pollution has to be studied [12], [15], [17].

This includes ILs separation through membrane processes too. Taking into account that ILs are electrolytes, the diffusion monitoring could be made by conductometric method [8], [13]. So, the correlation between the ILs solution conductivity and their concentration has to be studied.

ILs can have wide electrochemical potential and good electrical conductivity.

Generally, it is expected that ILs possess very high conductivity, due to their entire

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ionic structure. Unfortunately, it is not the case. The conductivity of some classes of ionic liquids is similar with the best non-aqueous solvents-electrolyte solutions, being up to 10 mS/cm [18]. However, they are less conductive than the concentrated aqueous electrolytes solutions. This fact can be attributed to the decreased availability of the charge carriers due to ion pairing or ions aggregation, having as result a large ion size and consequently a reduced mobility.

The electrochemical potential of an ionic liquid is also influenced by the stability of the cation against electrochemical reduction-processes and the stability of the anion against oxidation-processes. [3], [7].

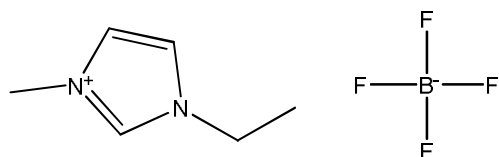
ILs can be used in a various applications [6], [9]: controlled modification of hydrogels morphology, controlled release of ILs, as antimicrobial agents [11], [16], [19], replacing water as the electrolyte in metal-air batteries [1], [4], controlling solutions or polymeric matrix conductivity due to their association in water [14] or through their interaction with polymers in films and gels by obtaining conductive systems [10], [11]. Hence it is very important to know ILs behaviour in aqueous solutions.

In respect to this, conductivity studies of some ILs aqueous solutions were made using four types of imidazolium-based ILs: 1-ethyl-3-methyl imidazolium [EMIM]<sup>+</sup>, 1-butyl-3-methyl imidazolium [BMIM]<sup>+</sup>, 1-hexyl-3-methyl imidazolium [HMIM]<sup>+</sup>, dodecyl-3-methyl imidazolium [DMIM]<sup>+</sup>, combined with three types of anions: tetrafluoroborate [BF<sub>4</sub><sup>-</sup>], chloride Cl<sup>-</sup>, and tetrachloroferrate [FeCl<sub>4</sub><sup>-</sup>].

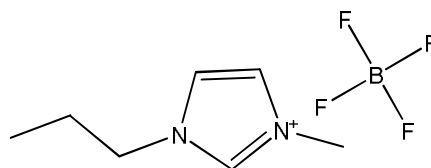
## 2. Experimental

### 2.1. Materials

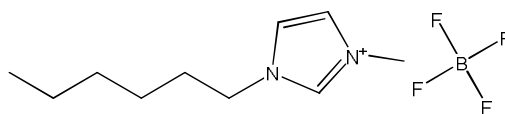
• 1-Ethyl-3-methyl imidazolium tetrafluoroborate (EMIMBF<sub>4</sub>) ionic liquid with a purity >98%:



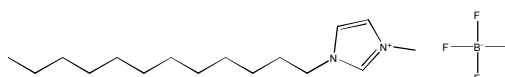
• 1-butyl-3-methyl imidazolium tetrafluoroborate (BMIMBF<sub>4</sub>) ionic liquid with a purity >99%:



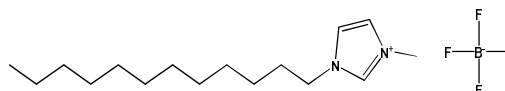
• 1-hexyl-3-methyl imidazolium tetrafluoroborate (HMIMBF<sub>4</sub>) ionic liquid with a purity >99%:



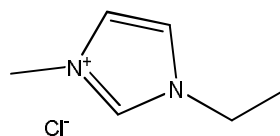
• 1-dodecyl-3-methyl imidazolium tetrafluoroborate (DMIMBF<sub>4</sub>) ionic liquid with a purity >99%:



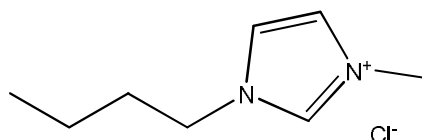
• 1-butyl-3-methyl imidazolium tetrachloroferrate [BMIMFeCl<sub>4</sub>] ionic liquid with a purity >97% has been purchased from Sigma-Aldrich (Germany):



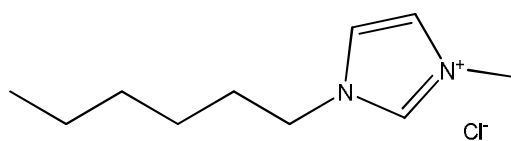
• 1-Ethyl-3-methyl imidazolium chloride [EMIMCl] with a purity >99%:



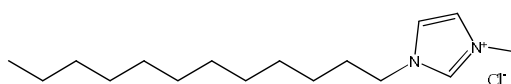
- 1-butyl-3-methyl imidazolium chloride [BMIMCl] with a purity >99%:



- 1-hexyl-3-methyl imidazolium chloride [HMIMCl] with a purity >99%:



- 1-dodecyl-3-methyl imidazolium chloride [DMIMCl] with a purity >98%:



All ILs, excepting  $\text{BMIMFeCl}_4$  were purchased from IoLiTech GmbH, Germany, and used without further purification.

- Aqueous solutions, covering the whole concentration range, were prepared for all ILs. The limits of ILs solubility in water as well as the possibility to enlarge the solubility range by temperature increase were considered.

## 2.2. Characterization of IL's Solution through Conductometric Method

The electrical conductivity is the physical measure which characterizes the ability of a material to allow transport of electrical charges when placed in an electric field. Aqueous solutions of acids, bases and salts are known as electrolytes and they are second order electrical conductors.

The introduction of two electrodes made of noble metal (Au, Ag, Pt etc.) in an electrolyte solution by connecting them to an outside

source of alternating current, the electrolyte solution will behave similarly to a metal conductor, in compliance with Ohm's law. Voltage and current are proportional as long as the solution composition, electrolyte-electrode geometry and temperature are kept constant.

Conductivity measurements were carried out using a Conductometer Radelkis OK-112. The instrument conductivity ranges from 0 to 1000 mS with a reproducibility of 1% and an accuracy of  $\pm 1.5\%$ . Before and after measurements, the instrument was calibrated with KCl solution. Each measurement was repeated three times and the average values were calculated. The conductivity of ILs aqueous solutions were determined at  $T = 25^\circ\text{C}$ . For the mixtures forming heterogeneous system at  $25^\circ\text{C}$  the conductivity was determined at the mixing temperature of the superior critical point.

## 3. Results and Discussions

The charge carriers in ILs aqueous solutions are ions. In aqueous solutions, the ILs dissociation occurs, and ions dissociation degree, their concentration and mobility are influencing the system conductivity. The charge carriers' mobility is influenced by the ions dimension. Increasing the charge carriers' concentration is increasing the conductivity [5].

Changes in conductivity of *chloride ILs* solutions depending on the concentration and the nature of the cation is shown in Figure 1.

It can be observed that all systems show an increase in the conductivity of up to 40% IL with the solution concentration increase. This could be due to the increasing number of the charge carriers (ions) in solution.

Also, it could be noted that the increase of the side chain length attached to imidazolium ring, leads to the lower values

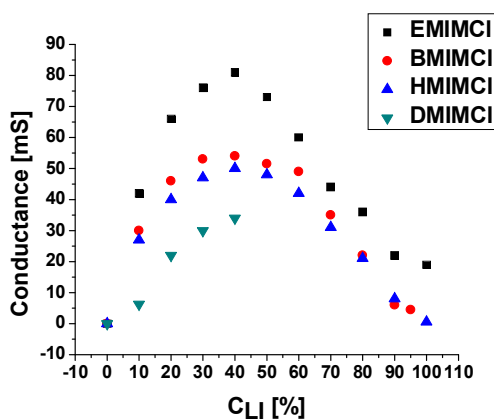


Fig. 1. The influence of the hydrocarbon chain attached to the imidazolium ring length on the binary system conductivity

of solution conductivity. This behaviour of long side chain cations could be attributed both to their mobility decrease, due to the mass increase, and to their higher tendency to agglomerate due to hydrophobic interaction between the hydrocarbon chains.

After its maximum, the conductivity is decreasing both with concentration increase and with the increase of the hydrocarbon chain attached to the imidazolium ring length. The differences between solution conductivity of different chloride ILs is lower in higher solution concentration range by comparing to the lower concentration range, suggesting cations associations with approximately same size. The lowering of higher solution concentration conductivity can be due also to the increase of solution viscosity that influences the ions mobility.

The conductivity variation with the ILs concentration for  $BF_4^-$  series follows the same trend as for chloride ILs evidencing the agglomeration tendency of ions in ILs solution (Figure 2).

The conductivity for EMIMBF<sub>4</sub> and BMIMBF<sub>4</sub> aqueous solution was measured at 25 °C, while for HMIMBF<sub>4</sub> and DMIMBF<sub>4</sub> aqueous solution conductivity,

was measured at 70 °C and 60 °C, respectively, due to the ILs solubility limits. It was observed that, at high temperatures the agglomeration tendency for  $BF_4^-$  series of ILs was maintained.

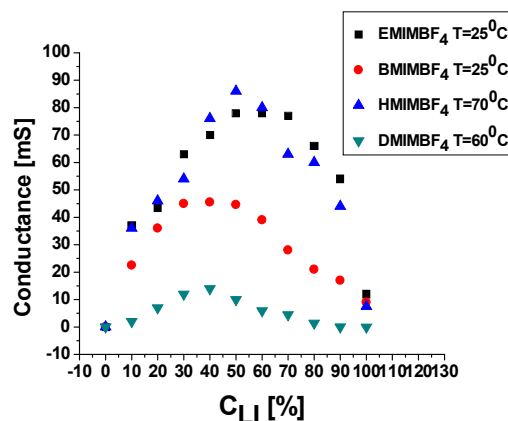


Fig. 2. The influence of the IL hydrocarbon chain length on the system conductivity

The conductivity of BMIMFeCl<sub>4</sub> aqueous solution was measured at 25 °C. The binary system has its solubility limit at 30 %IL towards water.

The conductivity obtained for BMIMFeCl<sub>4</sub>/H<sub>2</sub>O systems was the highest. This could be due to the anion hydrolysis that determines HCl formation which dissociate in H<sup>+</sup> and Cl<sup>-</sup> ions and this resulting in a higher conductivity (Figure 3).

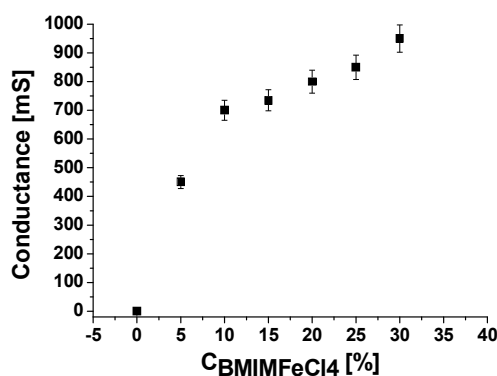


Fig. 3. BMIMFeCl<sub>4</sub>/water binary system conductivity

#### 4. Conclusions

Conductivity measurement of nine types of ionic liquid in water were made. Both tetrafluoroborates and chloride based ionic liquids aqueous solutions showed similar behaviour.

The electrical conductivity of the ILs aqueous solution increased with the decrease in length of the hydrocarbon chain attached to the imidazolium ring.

The non-linear variation of the solution conductivity versus IL concentration evidenced the tendency of cations to agglomerate. This phenomenon became dominant starting from concentrations higher than 40%.

The major influence on the ILs solutions conductivity is that of the cation nature while that of the anion is negligible.

The anion hydrolysis as well as the impurities from the IL strongly influence the conductivity value of the IL solution.

#### Acknowledgements

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