# Determination of Thermophysical Properties of the Protic Ionic Liquid EIM NO₃, Pure and Doped with Lithium Nitrate Salt †

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† Presented at the 24th International Electronic Conference on Synthetic Organic Chemistry, 15 November–15 December 2020; Available online: https://ecsoc-24.sciforum.net/.

**Abstract:** In this work, viscosity, density and electrical conductivity of the ionic liquid, Ethylimidazolium Nitrate pure and doped with lithium nitrate salt were determined in order to check the properties improvement of the ionic liquid with the salt addition to consider these mixtures as potential electrolytes. Viscosity decreases exponentially as temperature increases, and increases with salt content, as expected. Density values decrease linearly as temperature increases and also increases with salt content. From electrical studies an increase of conductivity with temperature and a decrease with salt concentration were observed. No significant differences between pure and doped sample were observed on Walden plots.

**Keywords:** Ionic liquid; density; ionic conductivity; viscosity; Walden plot

## 1. Introduction

Ionic liquids (ILs) are compound with organic cation and organic or inorganic anion which are liquid in a large temperature range, including room temperature (RTILs). This characteristic can be explained in terms of the weak coulombic anion-cation interactions of asymmetric anions. Other properties that make ILs good candidates to replace traditional materials are their non-flammability and non-volatility. Another interesting feature of these systems is that can be tuned by appropriately choosing a combination of cation and anion from the large number of currently known IL moieties [1,2].

Recently, the research in this field has been focused, mostly, on the potential application of these materials as electrolytes for electrochemical devices, with the aim to improve the performance, the safety and the cost of traditional lithium battery technology. For this reason, the knowledge of some properties such as density, viscosity, electrical conductivity, electrochemical window, thermal stability… is essential. The origin of the Walden rule [3] was based on the observation of the behavior of the molar conductivity and the viscosity for dilute aqueous solutions. This rule essentially states that the product of the molar conductivity of an electrolyte and the pure solvent's viscosity is constant.

Many studies have proved that this empirical Walden rule can be applied to non-aqueous electrolyte solutions and molten salts [4] The graphic representation of this rule is done on the Walden plot, where the log of molar conductivity is depicted versus log of viscosity. In this plot there is also presented an ideal line, which corresponds to the behaviour of a 0.01 M KCl solution. In case of a liquid could be represented as a group of independent ions, the corresponding data should be placed close to this ideal line. In most of the cases, ionic liquids are placed below the ideal line, that are categorized by "poor ionic liquids" [5].
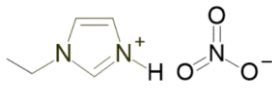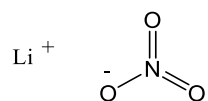
In this work some thermophysical properties, namely the density, viscosity and ionic conductivity of the protic ionic liquid, Ethylimidazolium Nitrate ([EIm] [NO$_3$]) pure and doped with lithium nitrate salt, were determined in order to check the possible improvement of these properties with the salt addition and to consider the potential of these systems as electrolyte good candidates [6,7].

## 2. Materials and Methods

*Chemicals*

Ethylimidazolium Nitrate ([EIm] [NO3]) and lithium nitrate salt (LiNO$_3$) were purchased from IOLITEC and SIGMA ALDRICH, respectively. Solutions IL+salt via stirring mixing at three different concentrations (0.5, 1 and 3 mol of LiNO$_3$ per kg of [EIm] [NO$_3$]) were prepared as described elsewhere in a previous work [6]. Chemical Structure and further identification (CAS Number, Molecular Weight, and abbreviation) can be found in Table 1. [EIm][NO$_3$] pure and mixtures with Lithium Salt were dried via vacuum procedure for 24–48 h in order to remove water content. The residual quantity of water was measured using a Karl Fisher titrator and quantities of water lower than 100 ppm were obtained.

**Table 1.** Identification of Chemicals used in this work.

| Name | Molecular Weight (g·mol$^{-1}$) | Structure | Abbreviation CAS Number |
|---|---|---|---|
| Ethylimidazolium Nitrate | 159.14 | | [EIm][NO$_3$] 501693-38-5 |
| Lithium Nitrate | 68.946 | | LiNO$_3$ 7790-69-4 |

3. Experimental

*3.1. Density*

Density was continuously and automatically measured between (278.15 and 338.15) K using a DSA 5000 Anton Paar density analyzer. Density measurements were obtained with a resolution of $\pm 10^{-6}$ g cm$^{-3}$. The temperature was controlled to within $\pm 10^{-3}$ K by means of a Peltier module. The reproducibility of density measurements was $\pm 10^{-6}$ g cm$^{-3}$. The density meter was calibrated with dry air and distilled water at known pressure and temperature [8].

*3.2. Viscosity*

The viscosity of the pure [EIm][NO$_3$] and doped samples was measured in a temperature range between (278.15 and 338.1) K, under air atmosphere using a TA Instruments AR2000 stress control, with a Peltier cooling device that controls the temperature value. Geometry of cone and plate with a diameter of 60 mm, an angle of 1° and a truncation of 28 μm was employed. Both, the sample and the geometry, were covered with a lid to avoid the exchange of atmospheric water with the environment.

Viscosity values were obtained through temperature sweep stepped tests with a temperature increment of 5 °C and 3 min of equilibration time before each measurement, 10 Pa of oscillatory stress and 1 Hz of frequency.

### 3.3. Electrical Conductivity

Electrical conductivity ($\sigma$) has been measured using a conductivity meter from CRISON, model GLP31 being the resolution better than 1% of the measured value (with a minimum resolution of $2 \cdot 10^{-6}$ mS cm$^{-1}$). The measuring cell is formed by two parallel plane plates covered with platinum oxide, and was used to measure conductivities in both phases, liquid and solid. The temperature of the samples was controlled using a Julabo thermostat calibrated with an external Pt100 sensor connection, which provided a precision better than 0.1 K in the range of temperature (243.15 to 338.15) K.

## 4. Results

Figure 1 shows the density of the liquid samples versus temperature. As it was expected, density increases with molality. In all cases, a linear decrease with temperature was observed.
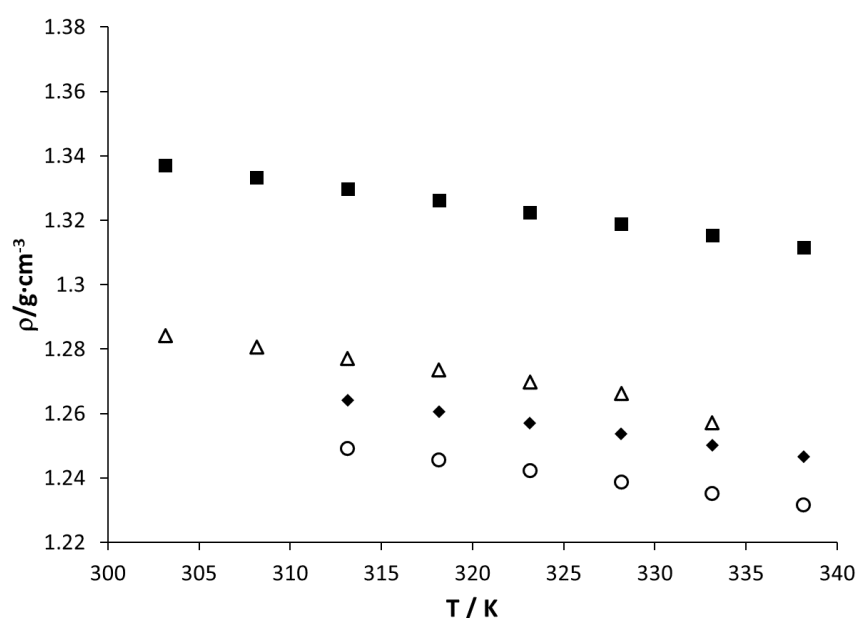


**Figure 1.** Density values versus temperature in heating ramp for pure (o), 0.5 m ($\blacklozenge$), 1 m ($\triangle$) and 3 m ($\blacksquare$) [EIm][NO$_3$] LiNO$_3$ samples.

In Figure 2 temperature dependence of viscosity values for pure and doped samples is presented. As it can be seen, an exponential decrease of viscosity with temperature is observed for all samples. On the other hand, a clear increase of viscosity with the salt concentration is also detected.

The temperature dependence of ionic conductivity for the pure and doped samples is presented in Figure 3. As it can be seen, an exponential increase of conductivity with temperature is observed for all the samples. On the other hand, the effect of salt concentration in this property is reflected in a clear decrease of conductivity values, probably due to the reduced mobility of ions as the number of salt ions increases.
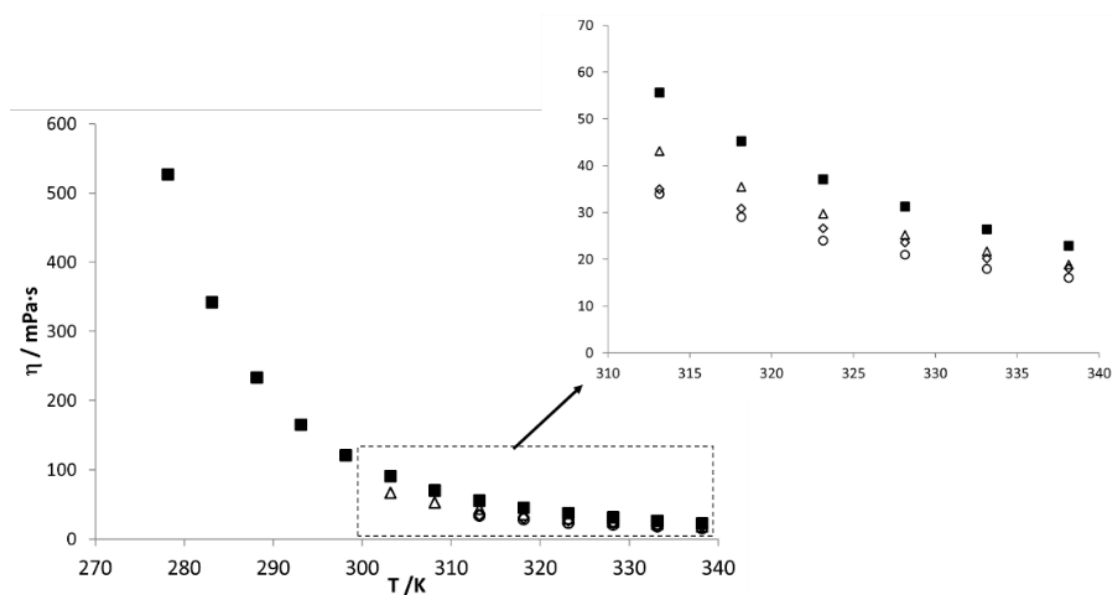
**Figure 2.** Viscosity values versus temperature in heating for pure (o), 0.5 m (♦), 1 m (Δ) and 3 m (■) [EIm][NO₃] LiNO₃ samples.
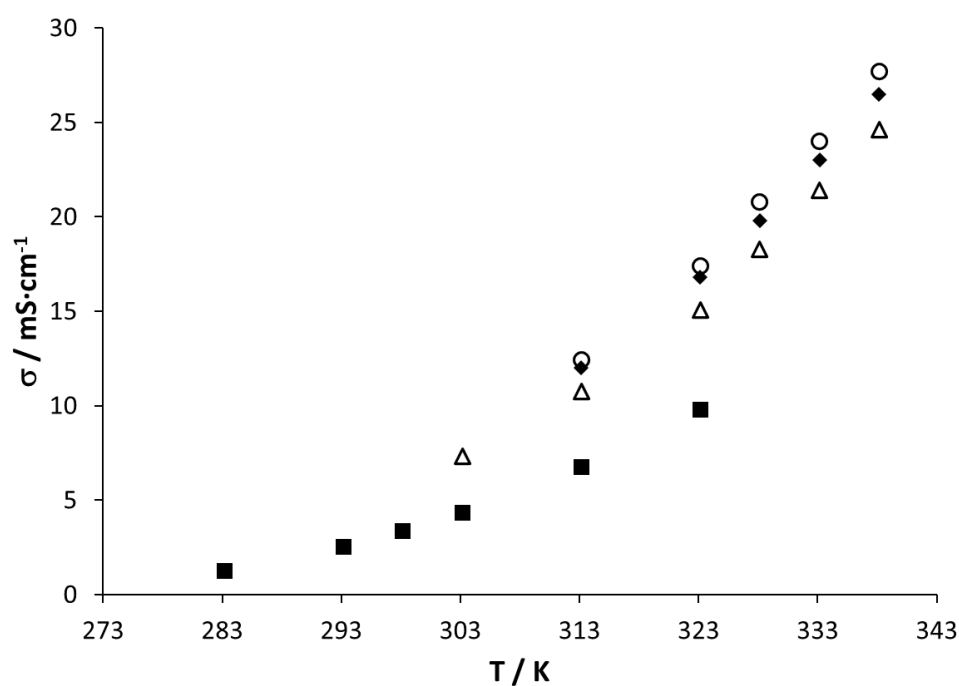


**Figure 3.** Electrical conductivity vs temperature measured in cooling ramp for pure (o), 0.5 m (♦), 1 m (Δ) and 3 m (■) [EIm][NO₃] LiNO₃ samples.

The Walden rule [5] was used for estimating the ionicity of the pure and dopped ionic liquid samples, as it is shown in Figure 4. As it can be seen, all analysed samples lie close to each other and all of them are below the "ideal KCl line". According to the classification diagram proposed by Angell et al. [9] for ionic liquids and based on the Walden rule, all the analysed samples are in the region of poor ionic liquids.
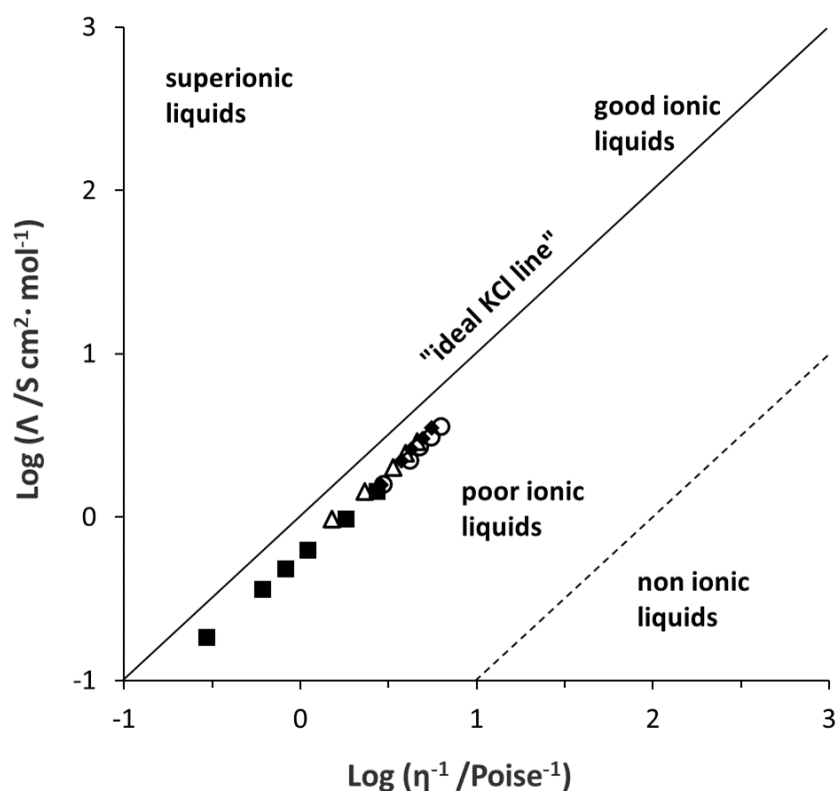
**Figure 4.** Walden plot for pure (o), 0.5 m (♦), 1 m (Δ) and 3 m (■) [EIm][NO₃] LiNO₃ samples. The straight solid line through the origin with slope 1 is the "ideal KCl line" [9].

## 5. Conclusions

Density, viscosity and electrical conductivity of Ethylimidazolium Nitrate ([EIm][NO₃]) pure and doped with lithium nitrate salt were determined in order to check the promising improvement of the properties of the IL with the salt addition.

The three properties above mentioned show the expected behaviors specifically, density values decrease linearly as temperature increases, and increases with salt content; viscosity decreases exponentially with temperature, and increases with salt content and ionic conductivity increases with temperature and a decreases with salt concentration.

No significative differences in the degree of ionicity were observed with the addition of the different concentrations of salt with respect to the pure ionic liquid. All the analysed samples, pure and dopped ones, lie below the "ideal KCl" line in the poor ionic liquids' region.

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