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Density, conductivity, viscosity, and excess properties of (pyrrolidinium nitrate-based Protic Ionic Liquid + propylene carbonate) binary mixture

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ABSTRACT

Density, ρ, viscosity, η, and conductivity, σ, measurements of binary mixtures containing the pyrrolidinium nitrate Protic Ionic Liquid (PIL) and propylene carbonate (PC), are determined at the atmospheric pressure as a function of the temperature from (283.15 to 353.15) K and within the whole composition range. The temperature dependence of both the viscosity and conductivity of each mixture exhibits a non-Arrhenius behaviour, but is correctly fitted by using the Vogel–Tamman–Fulcher (VTF) equation. In each case, the best-fit parameters, such as the pseudo activation energy, E_a^* and ideal glass transition temperature, T_0 are then extracted. The excess molar volumes V^E, and viscosity deviations from the ideality, $\Delta\eta$, of each investigated mixture were then deduced from the experimental results, as well as, their apparent molar volumes, V_ϕ, thermal expansion coefficients α_p, and excess Gibbs free energies (ΔG^{*E}) of activation of viscous flow. The V^E, $\alpha_p{}^E$, $\Delta\eta$ values are negative over the whole composition range for each studied temperature therein. According to the Walden rule, the ionicity of each mixture was then evaluated as a function of the temperature from (283.15 to 353.15) K and of the composition. Results have been then discussed in terms of molecular interactions and molecular structures in this binary mixture.

1. Introduction

Ionic liquids (ILs) are a class of chemicals composed entirely of ions having melting points below $T = 373$ K. Due to their unique physicochemical properties, ILs are rapidly gaining interest as greener replacements for traditional volatile organic solvents (VOCs). Other benefits are their large liquid temperature ranges driven by low melting temperatures and high decomposition temperatures, favourable solvation behaviour, high stability in air, high ionic conductivity, and modification of selectivity in chemical reactions, which open new possibilities in various industrial fields as catalysis, separation techniques, and electrochemical devices applications [1–13]. However, any industrial development requires reliable reference data on the thermodynamic properties of pure ILs and their mixtures with other solvents. In spite of extensive applications little information on their thermodynamic properties are published [14–23].

Most ILs are based on heterocyclic compounds, particularly the alkylimidazolium, alkyl pyrrolidinium, or alkylpyridinium cations. They can be broadly classified into two groups, protic and aprotic ILs [24,25]. Protic Ionic Liquids (PILs) are synthesized by proton transfer from a Brønsted acid to a Brønsted base, which creates proton donor and acceptor sites and can lead to the formation of hydrogen bonds [25]. The research concerning PILs has generally focused on surfactant self-assembly [26–32], and their physical properties [23,24,33–34]. Due to their excellent catalytic effects and other advantages such as easy preparation, cheap cost, and low toxicity, theirs physicochemical properties have also attracted researcher's attention [35–38]. For example, recently, Nakamoto *et al.* have reported that PILs are processing candidates as electrolyte for electrochemical storage and conversion devices [39,40]. Indeed, our group has recently shown that the labile proton on PILs structure participates to the pseudo capacitance on the fast redox reactions at the electrode/electrolyte interface in the case of activated carbon-based super capacitors [41,42]. However, despite the exceptional properties of these promising electrolytes, very few study concerning the physical properties of pure PILs as well as their mixtures with classical solvents for batteries or super capacitors has been reported in the literature. Previously, our group has presented a series of thermodynamic properties (such as specific heat capacities, volumetric and, rheological properties) for different PILs in mixtures with molecular solvents, such as acetonitrile, water, and alcohols [43,44]. Nevertheless, classical batteries electrolytes are generally composed of salt (*e.g.* lithium salt or an IL) dissolved in an alkylcarbonate solvents mixture. To the best

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of our knowledge, no thermodynamic data of electrolyte based on an alkylcarbonate mixed with any PIL is, up-to date, available in the literature.

Herein, we report a thermodynamic study of pyrrolidinium nitrate-based PIL, [Pyrr][NO_3], in mixture with the propylene carbonate, PC. Their volumetric, thermal and transport properties are presented as the function of temperature and composition, and then discussed in order to understand the molecular interactions between (individual ion–PC), (cation–anion), and (PILs ions pair–PC) in solution. Finally, all thermodynamics properties of the ([Pyrr][NO_3] + PC) binary mixture presented in this paper are then compared with those already reported by our group in the case of the ([Pyrr][NO_3] + water) mixture [43].

2. Experimental

2.1. Materials

Nitric acid solution (68% in water), pyrrolidine, propylene carbonate (PC) and 1,2-dichloroethane, (DCE), used in this study are commercially available from Fluka within a molecular purity >99% and were used without further purification. Pyrrolidinium nitrate was prepared according to the methodology previously described by our group [45]. Briefly, the amine was placed in a triple necked flask equipped with a reflux condenser; nitric acid was added drop wise to the flask stirring with a magnetic bar. After reaction, 120 cm^3 of DCE was then added to obtained aqueous solution. Subsequently, in order to remove the water, the mixture was distilled under normal pressure until the water–DCE heteroazeotropic boiling point temperature was reached (*e.g.* 346.15 K). DCE was then evaporated from the mixture under reduced pressure enabling a pale yellow and viscous liquid to be collected within a yield close to 93–98%. Finally pyrrolidinium nitrate was dried overnight at $T = 343$ K under high vacuum (0.1 Pa) prior to use. Solid pale yellow crystals, containing less than 100×10^{-6} of residual water measured by using a Coulometric Karl–Ficher titrator, were then obtained, and stored at ambient temperature for a few weeks. It should be important to notify that this PIL is then liquid within a water content close to 2000×10^{-6}. Since pure PIL with this residual quantity of water was used during each measurement reported herein, such purity state was defined into this paper as the pure PIL, The water content in PC was quantified as below 10×0^{-6}. Information (*i.e.* source, abbreviation, purity, and water content) for each chemical sample studied in this paper are summarized in table 1.

2.2. Methods

Binary mixtures containing pyrrolidinium nitrate, [Pyrr][NO_3], and propylene carbonate, PC, were prepared by mass with an accuracy of $\pm 1 \times 10^{-4}$ g using a Sartorius 1602 MP balance.

The density of the pure components and their mixtures was determined by using an Anton Parr digital vibrating tube densitometer (model 60/602, Anton Parr, France) from (283.15 to 353.15) K. The densitometer was firstly calibrated at all temperatures with degassed water and dehumidified air at atmospheric pressure as recommended by the constructor. More than five readings were taken for each density measurement reported therein. The uncertainty of the density, and of excess volume values were better than 5×10^{-5} $g \cdot cm^{-3}$ and 0.007 $cm^3 \cdot mol^{-1}$, respectively.

A TA Instruments rheometer AR 1000 was used to determine the rheological behaviour and the viscosity (η) of the pure [Pyrr][NO_3] by using a conical geometry. The temperature in the cell was regulated within ±0.01 K with a solid-state thermostat. After ensuring that the studied ionic liquid presented a Newtonian behaviour, rheograms were recorded at atmospheric pressure as a function of temperature from (283.15 to 353.15) K for the pure [Pyrr][NO_3], as well as, their mixtures with PC, within an operating speed of 50 $rad \cdot s^{-1}$. The viscosity standard (Brookfield, 12700 $mPa \cdot s$ at 25 °C) and water were used to calibrate the rheometer. From this study, the uncertainty of viscosity measurements did not exceed ±1%.

Conductivity measurements were performed by using a Crison GLP31 digital multi-frequencies conductometer between (1000 and 5000) Hz. The temperature control from (258.15 to 363.15) K is ensured within ±0.01 K by means of a JULABO thermostatted bath. The conductometer was first calibrated with standard solutions of known conductivity (*i.e.* (0.1 and 0.02) $mol \cdot dm^{-3}$ KCl aqueous solutions), the uncertainty of reported conductivities did not exceed ± 2%. The conductivity measurements of the ([Pyrr][NO_3] + PC) solutions were carried-out by continuous addition of pure [Pyrr][NO_3] into PC. Each conductivity was recorded when its stability was better than 1% within 2 min.

3. Results and discussion

3.1. Effect of propylene carbonate on volumetric properties of the pyrrolidinium nitrate

3.1.1. Density data and excess molar volumes

The density of pure components and of ([Pyrr][NO_3] + PC) mixtures was measured as a function of the temperature from (283.15 to 353.15) K and the results are listed herein in table 2, shown in figure 1 and in figure S1 providing supporting information . From these as expected, it can be seen that the density decreases linearly with temperature and increases with the mole fraction of PIL in the binary mixture. In other words, the [Pyrr][NO_3] is denser than the PC (and its mixture with PC) over the whole temperature range studied. For example, the density values of pure PC and [Pyrr][NO_3] are close to (1.263 and 1.2350) $g \cdot cm^{-3}$ and to (1.1416 and 1.1820) $g \cdot cm^{-3}$ at $T = (283.15$ and $353.15)$ K, respectively. The density data were then fitted by using a linear relationship as a function of temperature and by using a cubic polynomial function

TABLE 1
Source, abbreviation, purity, and water content for each chemical sample reported during this work.

Chemical name	Source	Abbreviation	Mole fraction Purity	Water content10^{-6}
Propylene carbonate	Fluka	PC	0.9999	<10[b]
pyrrolidine			0.99	
1,2-dichloroethane		DCE	0.99	
Nitric acid solution, 68% in water		HNO_3		
Dried Pyrrolidinium nitrate (solid state) at 298 K	Synthesized in-house	[Pyrr][NO_3]	>0.98[a]	<100[b]
Pyrrolidinium nitrate (liquid state) at $T = 298$ K		[Pyrr][NO_3]	>0.98[a]	2000[b,c]

[a] Determined by NMR analysis.
[b] Precision and accuracy of the reported experimental data are close to (5 and 10)%, respectively.
[c] This purity state was defined into this paper as the pure PIL.