

## Synthesis and Characterization of Green Novel Solvents

**KEYWORDS:** Ethyl lactate; Ionic liquids; Green novel solvents; Thermophysical characterisation; DSC; VPO.

The thermophysical characterisation (density, viscosity and refractive index) of binary mixtures containing novel ionic liquids was successfully performed. Moreover, the osmotic coefficients and activity coefficients of mixtures composed of green solvents were determined using vapour pressure osmometry (VPO). Finally, to find less expensive refrigerant fluids, calorimetry measurements (transition temperatures and molar heat capacities) were conducted for binary mixtures of ionic liquids.

#### Objectives

The transition to more eco-friendly solvents in the chemical industry has been delayed by the lack of reliable thermophysical data for the so called green novel solvents. Properties such as density, viscosity and pH play an especially important role, for example, in extractive processes, so it is necessary to diversify the studied properties, increase the number of covered systems, expand the assessed conditions (pressure and temperature) and enlarge the composition range available in literature. Other crucial properties include the refractive indices, which are useful in the food and beverage industry, and the heat capacities, which allow to evaluate their potential as replacements to more pollutant refrigerant fluids.

On the other hand, liquid density and vapour pressure are the most considered properties in the parameterization of thermodynamic models (e.g., equations of state and excess Gibbs free energy models), for which accurate experimental determinations are essential for the correct description of systems. While liquid density data for mixtures containing green solvents is frequently found in literature, vapour-liquid equilibrium data is often unavailable and significantly contributes to the low maturity of the thermodynamic modelling of green solvents. Moreover, a proper characterisation of the solvents is of the utmost importance to promote industrial applications and ease process design.

#### Current Development

The ionic liquids cholinium alaninate, cholinium serinate, cholinium leucinate and cholinium glycinate were synthesized, at 318.15 K and 0.1 MPa, based on choline salts and amino acids. Their chemical structure was then validated by density and infrared (IR) spectra measurements. The experimental IR spectra determinations were also compared with the Fourier-transform IR spectra yielded by computational chemistry (Density Functional Theory, DFT), obtaining a very satisfactory agreement. In these studies, the B3LYP hybrid functional was applied with the 6-311++G\*\* basis set.

Moreover, the thermophysical characterisation of mixtures containing these ionic liquids, specifically to what concerns density, viscosity and refractive index, was copiously performed, and the experimental data were successfully fitted to classical empirical correlations, such as the Vogel–Fulcher–Tammann–Hesse equation for dynamic viscosities.

Additionally, the degree of dissociation (or ionicity) of these choline-amino acid ionic liquids (CAAILs), which is essential for an accurate thermodynamic modelling of electrolytes, was experimentally assessed in aqueous and alcoholic mixtures at 298.15 K and 0.1 MPa using the Walden plot methodology.

To couple the removal of active pharmaceutical ingredients (APIs) with the need for solvents with lower environmental impact, choline-based ionic liquids were synthesized after the extraction of pharmaceutical pollutants (e.g., salicylic acid) in

Aqueous Two-Phase Systems (ATPS). This way, a commonly found pollutant in residual waters was converted to a greener solvent with high potential for application in research. Following, similarly to what was performed to other choline-based ionic liquids, the chemical structure was validated by density and infrared (IR) spectra measurements, and the latter were compared with predictions from DFT calculations.

The vapour pressure osmometry (VPO) technique was used to determine vapour pressures of mixtures containing green solvents at 303.15 K and 0.1 MPa and the obtained osmotic coefficients and activity coefficients were satisfactorily modelled using the extended Pitzer model of Archer. Moreover, the density of these mixtures was assessed at 293.15, 298.15 or 303.15 K and 0.1 MPa and successfully fitted to second-degree polynomial functions, as Fig. 1 shows for the case of water, ethanol or propan-1-ol and cholinium alaninate ([Ch][Ala]).

Finally, differential scanning calorimetry (DSC) was used to determine the molar heat capacities ( $C_p$ ) and characteristic

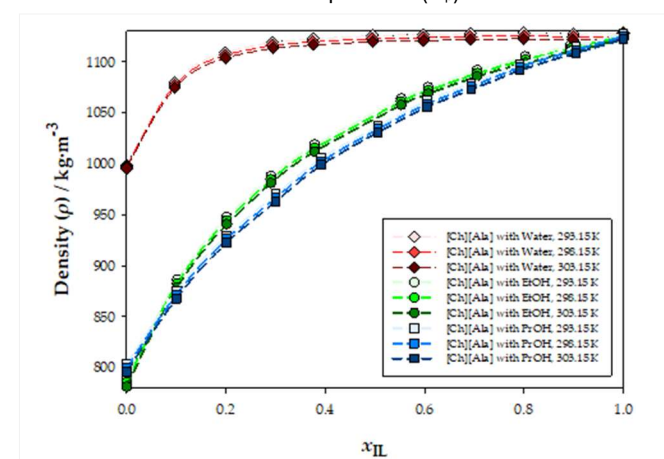


Fig 1. Experimental densities with the mole fraction of ionic liquid for the binary mixtures composed of water, ethanol or propan-1-ol with cholinium alaninate ([Ch][Ala]) at 293.15, 298.15 or 303.15 K and 0.1 MPa.

temperatures (melting, freezing, cold crystallization and glass transition temperatures) for some common pyrrolidinium-based ionic liquids (e.g., 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate and 1-butyl-1-methylpyrrolidinium dicyanamide). It was noticed that the heat capacities of ionic liquids containing the  $[NTf_2]^-$  anion increased with the alkyl chain length of the cation, and that larger ionic liquids favoured higher heat capacities, for which these conclusions are expected to ease the search for greener refrigerant fluids.

#### Collaboration with the University of Vigo

To further explore the evaluation of ionic liquids as potential replacements of more pollutant solvents, a collaboration between the University of Porto and the University of Vigo (Spain) was promoted. It involved a research stay for the thermal analysis of five equimolar binary mixtures of nine common ionic liquids (e.g., 1-butyl-3-methylimidazolium trifluoromethanesulfonate and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide), as Fig. 2 shows.

The application of these solvents as refrigerant fluids is often hindered by their prohibitive cost, so the main objective was to evaluate the thermal efficiency of mixtures containing a more expensive ionic liquid (with higher thermal capacity) and a less

expensive one (with lower thermal capacity). The transition temperatures and molar heat capacities of these systems were determined using differential scanning calorimetry (DSC), and it was found that a favourable compromise between cost and efficiency could be achieved by using the studied binary mixtures of ionic liquids.

### Future Perspectives

Even though the synthesis of ionic liquids was deeply delved into, only choline-based ionic liquids were synthesized, which

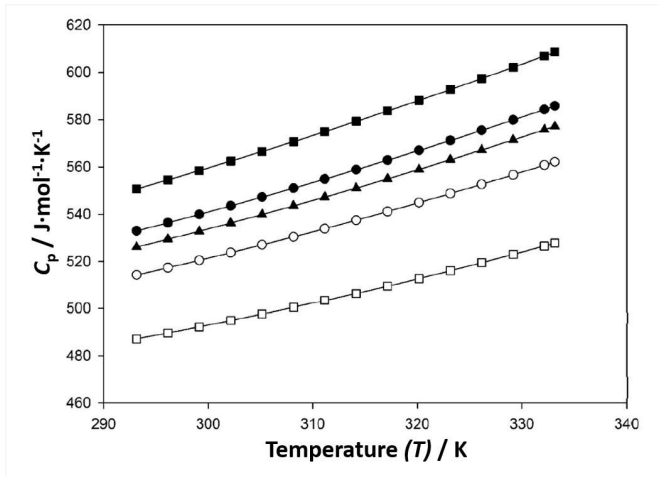


Fig 2. Experimental molar heat capacities ( $C_p$ ) for the binary mixtures: (○) (1,3) [BMim][TFO] + (1,3) [BMim][NTf<sub>2</sub>]; (□) (1,3) [BMim][DCA] + (1,3) [BMim][NTf<sub>2</sub>]; (▲) (1,3) [BMPy][TFO] + (1,3) [BMPy][NTf<sub>2</sub>]; (●) (1,1) [BMPy][TFO] + (1,1) [BMPy][NTf<sub>2</sub>] and (■) (1,1) [PMpip][TFO] + (1,1) [PMpip][NTf<sub>2</sub>].

traditionally possess pH values higher than 13, narrowing their practical application. Moreover, it was also noticed that most research on the thermophysical properties of ionic liquids lacks information on pH. Therefore, other families of green ionic liquids must be assessed, and future studies should report the pH of ionic liquids either in solution or in pure state.

Although Density Functional Theory (DFT) calculations were found to be particularly useful for chemical synthesis evaluation, they were only used to predict the infrared (IR) spectra of the studied components. For that reason, further work should be directed towards the calculation of physicochemical properties of ionic liquids such as density, activation energy of viscosity and electrochemical stability, and, if possible, compare them with the experimental results.

Concerning vapour pressure osmometry (VPO) measurements, illustrated in Fig. 3, it is still important to enlarge the number of studied green solvents and evaluated temperatures since the performed assays were limited to 303.15 K and 0.1 MPa.

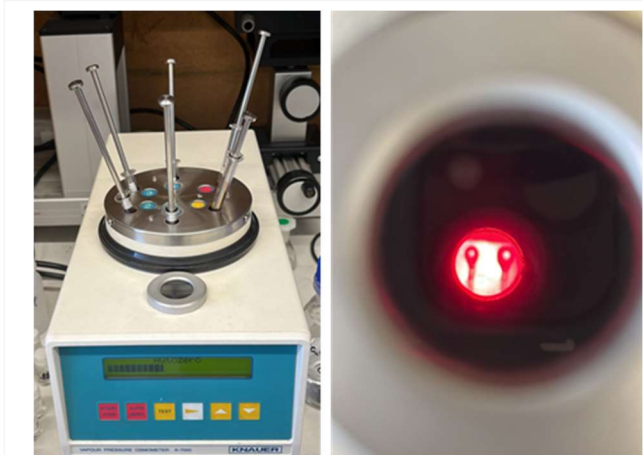


Fig 3. Vapour pressure osmometer (VPO) during calibration.

Moreover, it would be very useful to include the determination of vapour pressures, osmotic coefficients and activity coefficients in binary and ternary systems containing green novel solvents and salts, as widely observed in Aqueous Two-Phase Systems (ATPS). In these systems, some other thermodynamic models specifically developed for electrolytes could be applied, such as the electrolyte-Non-Random Two-Liquid (eNRTL) model.

Additionally to the determination of molar capacities and transition temperatures, vapour pressure, viscosity, biodegradability and toxicity experiments could also help evaluate the suitability of ionic liquid-based refrigerants. Furthermore, to allow a more complete assessment of the impact of the studied ionic liquids in the case of a large-scale adoption as substitutes to less eco-friendly components, a new collaboration could be initiated with other research groups to perform a complete life cycle assessment (LCA) of their implementation in industry.

Finally, the thermophysical properties of other green solvents such as the Deep Eutectic Solvents (DES) were not evaluated even though they are being increasingly studied for their low cost, low volatility, high biodegradability and non-toxicity. Conversely to ionic liquids, DES are easy to synthesize since they only require mixing the components. To make usage of the available chemicals, DES based on choline, glycerol or urea could be studied in future works.

### Related Sustainable Development Goals



### Outputs

#### Master Dissertations

[1] L.R. Barroca, Partition of Pharmaceutical Pollutants using Aqueous Two-Phase Systems based on Choline, MEQ, FEUP, 2023.

#### Selected Publications

- [1] E. Gómez et al., Fluid Phase Equilib. 470, 51-59 (2018)
- [2] E. Gómez et al., Fluid Phase Equilib. 519, 112658 (2020)
- [3] E. Gómez et al., Molecules 26, 6383 (2021)
- [4] P. Velho et al., J. Chem. Eng. Data (2023)
- [5] L. Barroca et al., J. Chem. Eng. Data (2023)
- [6] P. Velho et al., J. Chem. Eng. Data (2023)

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