Fundamental studies on natural deep eutectic solvents: physico-chemical, thermal and rheological properties

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Abstract/Introduction

When combined at particular molar fractions, sugars, aminoacids or organic acids a present a high melting point depression, becoming liquids at room temperature. These are called Natural Deep Eutectic Solvents – NADES and are envisaged to play a major role on the chemical engineering processes of the future. Nonetheless, there is a significant lack of knowledge of its fundamental and basic properties, which is hindering their industrial applications. For this reason it is important to extend the knowledge on these systems, boosting their application development [1].

In this work, we have developed and characterized NADES based on choline chloride, organic acids, amino acids and sugars. Their density, thermal behavior, conductivity and polarity were assessed for different compositions. The conductivity was measured from 0 to 40 °C and the temperature effect was well described by the Vogel-Fulcher-Tammann equation. The morphological characterization of the crystallizable materials was done by polarized optical microscopy that provided also evidence of homogeneity/phase separation. Additionally, the rheological and thermodynamic properties of the NADES and the effect of water content were also studied. The results show these systems have Newtonian behavior and present significant viscosity decrease with temperature and water content, due to increase on the molecular mobility. The anhydrous systems present viscosities that range from higher than 1000Pa.s at 20°C to less than 1Pa.s at 70°C. DSC characterization confirms that for water content as high as 1:1:1 molar ratio, the mixture retains its single phase behavior.

The results obtained demonstrate that the NADES properties can be finely tunned by careful selection of its constituents. NADES present the necessary properties for use as extraction solvents. They can be prepared from inexpensive raw materials and tailored for the selective extraction of target molecules. The data produced in this work is hereafter importance for the selection of the most promising candidates avoiding a time consuming and expensive trial and error phase providing also data for the development of models able to predict their properties and the mechanisms that allow the formation of the deep eutectic mixtures.

Experimental

Preparation of NADES mixtures

The mixtures were prepared by mixing choline chloride or betaine with xylose, glucose, sucrose, citric acid and tartaric acid. The combinations of the different molecules were mixed, in the required amounts, to obtain molar ratios of 4:1, 3:1, 2:1, 1:1, 1:2, 1:3 and 1:4. Table 1 presents the NADES combinations which resulted in a liquid mixture at room temperature. For each mixture, the constituents were transferred to a tightly closed glass flask and heated to 90°C with constant stirring, for the time required until the formation of a clear liquid. For the mixtures which did not form a liquid, the process was considered concluded after 16 hours.

Rheological measurements

Rheological measurements were performed on a Malvern rheometer, model kinexus Prot, equipped with a cone-plate geometry (diameter of 4 cm) and a protective hood. During measurement, a stream of N_2 gas was maintained in order to avoid water absorption.

Results and Discussion

NADES preparation

The different mixtures were obtained by direct mixing of the solid components. The formation of liquid mixtures was assessed by differential scanning calorimetry (DSC) and polarized optical microscopy (POM) (Table 1).

The preparation of Bet based NADES was found to be more difficult than those based on CC, requiring the inclusion of water to promote the formation of the liquid

mixture. Therefore, the mixtures between Bet and CA or Tart were prepared as three component systems, of equal molarity, with water as the third component.

Table 1 – Nomenclature and molar ratios of the NADES that are liquid at room temperature.

NADES designation	Component 1, molar ratio X1	Component 2, molar ratio X2	Molar ratios found to be liquids*
[CC:Xyl; X1:X2]	Choline Chloride (CC)	Xylose (Xyl)	1:1
[CC:Glu; X1:X2]	CC	Glucose (Glu)	1:1
[CC:Suc; X1:X2]	CC	Sucrose (Suc)	1:1
[CC:CA; X1:X2]	CC	Citric acid (CA)	2:1; 1:1; 1:2
[CC:Tart; X1:X2]	CC	Tartaric acid (Tart)	2:1; 1:1; 1:2
[Bet:CA:H_2O; X1:X2:X3]**	Betaine (Bet)	CA	1:1:1
[Bet:Tart:H_2O; X1:X2:X3]**	Bet	Tart	1:1:1

*classified after POM and DSC characterization results.   ** Betaine based mixtures were prepared as three component mixtures of equal molarity, with water (X3) as the third component.

Rheological Properties

The rheological properties were assessed by obtaining flow curves. The effect of temperature and water content on the NADES viscosity was determined. The characterization of the CC based NADES was performed for the mixtures of molar ratio 1:1. The mixtures with glucose, xylose and sucrose were characterized in the presence of diferent water contents, namely of 0, 1, 3 and 5 % wt. %.Citric acid and tartaric acid NADES were characterized in the presence of 0, 1 and 5 % wt. % water content. Betaine based NADES were characterized for the mixtures [Bet:CA:H_2O; 1:1:1] and [Bet:Tart:H_2O; 1:1:1].

The rheological characterization results have shown that these liquids behave as Newtonian fluids. For a given system, temperature and water content, the viscosity is constant and independent of the shear rate applied.
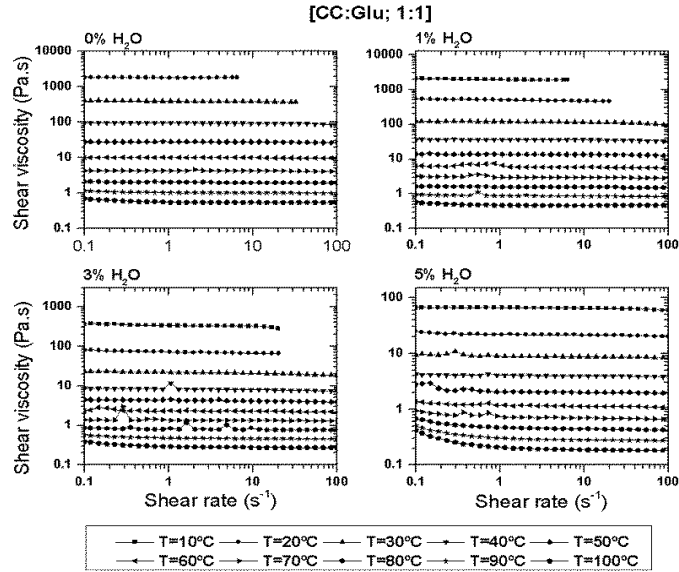

Figure 1 - Viscosity-shear rate curves for [CC:Glu; 1:1] with water content of 0, 1, 3 and 5% wt.%.

The NADES viscosities vary greatly with the nature of the constituting components, the temperature and the water content. In general, these are highly viscous liquids, with typical viscosities higher than 1000Pa.s at 20°C. The viscosity decreases significantly with both temperature and water content, as it can be observed in figure 1 for the system CC:Glu; 1:1.

Considering the choline based NADES, the viscosity is higher for [CC:Suc; 1:1], followed by [CC:CA; 1:1], [CCTtart; 1:1], [CC:Glu; 1:1] and [CC:Xyl; 1:1]. This trend is maintained for the range of temperatures considered and for the mixtures with different water contents. The bet based nades present similar viscosity.

The variation of viscosity with temperature can be represented by the Arrhenius equation:

$$\eta_0 = Ae^{E\eta/RT} \qquad (1)$$

and by representing the ln of shear viscosity as function of the reciprocal of temperature (T), it is possible to determine the flow activation energy, E_η, which represent the energy necessary to provide to the system to achieve the desired flow, respectively (where R is the ideal gas constant and A a constant for each system).

Representing the logaritm of shear viscosity as function of the reciprocal of temperature, it is possible to determine the flow activation energy, E_η, which represents the energy necessary to provide to the system to achieve the desired flow respectively. The calculated values for **E_η** are presented on Table 2.
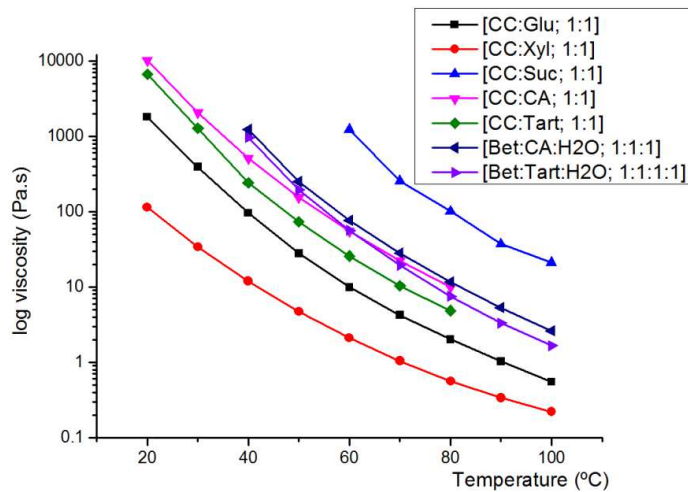
Figure 2 – Variation of viscosity with temperature, for selected NADES

Conclusions

The formation of liquid mixtures only occurs for specific components molar ratios. The NADES are highly viscous liquids, following a Newtonian behavior. Furthermore, the viscosity decreases significantly with temperature and water content. The finding of this work contribute to the enhancement of the state of the art and to the future design of processing technologies based on NADES.

Table 2 – Flow activation energy, E_η, calculated from the Arrhenius plots.

NADES	Water content			
	0%	1%	3%	5%
	E_η, kJ/mol			
[CC:Glu; 1:1]	91.7	77.0	61.0	50.1
[CC:Xyl; 1:1]	71.0	68.5	56.3	47.9
[CC:Suc; 1:1]	104.5	85.2	42.1	32.2
[CC:CA; 1:1]	96.1	89.4	---	70.6
[CC:Tart; 1:1]	103.6	93.7	---	74.4
[Bet:CA;H_2O; 1:1:1]	101.9			
[Bet:Tart;H_2O; 1:1:1]	97.8			

Acknowledgments

References

1.   Paiva, A., et al., *Natural Deep Eutectic Solvents - Solvents for the 21st Century.* Acs Sustainable Chemistry & Engineering, 2014. **2**(5): p. 1063-1071.