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The NADES glyceline as a potential Green Solvent: A comprehensive study of its thermophysical properties and effect of water inclusion

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ABSTRACT

In this paper, two Natural Deep Eutectic Solvents, glyceline (Gly) and glyceline-water (GlyW), containing choline chloride as acceptor H-bond compound and glycerol as donor H-bond group are studied. For glyceline the mole relation is 1 (choline chloride): 2 (glycerol) and for glyceline-water the mole relation is 1 (choline chloride): 1.99 (glycerol): 1.02 water. The ternary NADES has been synthetized and characterized chemically by NMR techniques for this work. Several thermophysical properties in a wide range of temperature (278.15–338.15) K and at atmospheric pressure (0.1 MPa) have been measured for both compounds: density, ρ, speed of sound, u, refractive index, n_D, surface tension,σ, isobaric molar heat capacity, $C_{p,m}$, kinematic viscosity, ν, and electric conductivity,κ. Furthermore, some related properties have been also calculated: isobaric expansibility, α_p, isentropic compressibility, κ_S, molar refraction, R_m, entropy and enthalpy of surface formationper unit surface area (ΔS_s and ΔH_s), and dynamic viscosity, η, and viscous flow and electrical conductivity activation energies. The results have been discussed in terms of the effect of temperature and the inclusion of water. We conclude that the compound containing water into the structure has a higher molar volume and a higher fluidity. The binary NADES (Gly) is a more structured liquid than ternary one (GlyW).

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1. Introduction

Over the past two decades, the ionic liquids have been considered as the green alternative to volatile organic compounds (VOCs) due to their special properties (low volatility, high solvent capacity, and others). However, the sustainability properties of a number of ILs is not suitable from the point of view of Green Chemistry [1]. In 2004, Abbott et al. [2] showed that: "the principle of creating an ionic fluid by complexing a halide salts can be applied to mixtures of quaternary ammonium salts with a range of amides" (and others hydrogen bond donors). As a consequence of the moiety process, a hydrogen-bonding network is established and the melting point decreased drastically. Relevant differences between both type of fluids, such as the synthesis method and the reactivity to water, was found and a new term, Deep Eutectic Solvent (DES), was introduced. This concept does not imply that the mixture composition corresponds to the system eutectic point. To highlight, a supramolecular structure has been detected from FT-IR, NOESY, and DOSY experiments showing that DESs are singular compounds [3–7].

If the raw materials of DESs come from natural sources, such as sugars, organic acids or amino acids, the compound is called Natural Deep Eutectic Solvent (NADES) and are supposed to be renewable. Taking into account the similarity of properties and applications, NADESs have been described by some authors as a subclass (or analogues) of ILs [8–10]. Nevertheless, a greater future in the "Green Chemistry" field is predicted for NADESs due to their chemical nature. These compounds are being used in synthesis and shape control of metallic nanoparticles, electroplating, for gas and liquid adsorption processes or as intermediate for organic chemicals synthesis, among many others uses [11].

Water in DESs can be intentionally added in order to modulate the solvent properties as absorption capacity, CO_2 solubility, and viscosity improving its potential services or applications [12,13]. Furthermore, the presence of water profoundly affects the molecular structure of the system; a structure transition from the water-NADES mixture to a type aqueous solution structure of solvated components is found when increasing the water content [14–17]. Water, at low quantity, contributes to the hydrogen-bonding network strengthens. Increasing water content, the DESs structure remains but is weakened. A significant dilution (upper than 50% water mole fraction for reline, glyceline or ethaline [16] provokes the full loss of the clusters. Besides, the water content at which this

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transition occurs depends strongly on the molecules and compositions of the NADESs and thus, experimentation is needed to get this information [17].

One of the most promising NADES is glyceline (Gly). This moiety is formed by choline chloride (HBA) and glycerol (HBD) in proportion, mole relation 1:2, very close to the eutectic point of the mixture ($x_{glycerol} \cong 0.7, T_f \cong 230$ K) [18]. Glyceline can be used in many applications. For instance, in catalytic reactions of compounds with therapeutic properties, such as N-phenyl phthalimide derivatives, which are used as anticonvulsants and anti-inflammatory drugs [19] or extraction [20] and enzyme stabilization agent [21]. Other applications are related with the purification of (bio)fuels [22–23] or absorption processes of CO_2 and SO_2 [24] Besides, different studies about the (eco)toxicity of Gly have shown that it is relatively safe for human health and environment [25]. For instance, cytotoxicity of Gly in several line cells such as CCO or MCF-7 is quite low (EC_{50} values higher than 2000 mg·dm^3) [26] as well as its toxicity towards fungi *Aspergillus niger* and fishes *Cyprinus carpio* [27,28]. Another important finding is the relationship between the toxicity of several NADESs, including Gly, and several physicochemical properties such as viscosity [29]. This type of connections has also been mathematically described for some ILs and the toxicity exhibited by environmental biomodels such as *Vibrio fischeri* and *Daphnia magna* [30]. Regarding biodegradability, Gly exhibits >90% of biodegradation at the test conditions measured, thus, this NADES can be referred to as "readily biodegradable" [25,27].

To sum up, we can say that glyceline shows interesting properties from the Green Chemistry point of view; it can be used for interesting well-stablished applications and shows a great potential for many more to find out, comes from renewable resources, presents low VOC character, is biodegradable and although more study is required, first approximations to toxicity are promising and a low (eco)toxicity profile is expected. However, with the double aim of ensuring the greenness character of Gly and using it in any reliable cost-effective process chemical process, accurate information of its thermophysical behaviour in a wide range of temperature is needed. Furthermore, there are properties that provide information about the molecular behavior of this solvent when interacting with other substances which might be in the medium that are also of great importance in order to explore and understand its molecular behaviour and make available new and useful applications [31,32]. In the literature, several papers reporting thermophysical properties of pure glyceline [33–44] and its mixtures with water [16,42–46] or other NADESs [47,48] can be found. It is worth mentioning the recent work of Troter et al. [49], in this contribution, which reports the water content of compounds, density, dynamic viscosity, electrical conductivity and refractive index of some choline chloride-based deep eutectic solvents are presented. Thus, in general terms, the thermophysical information about glyceline is limited and disjointed.

For these reasons, in this manuscript we present a complete set of thermophysics properties of glyceline (Gly) over a wide range of temperature (278.15–338.15 K) at atmospheric pressure. In order to explore the changes in the behaviour caused by the inclusion of water, a new NADES, glyceline-water (GlyW) formed by choline chloride, glycerol and water (mole relation (1:1.99:1.02) has been synthesized and studied; this compound is not an aqueous solution. The properties of this NADES, whose T_f = 171.6 K [5], have been also measured and compared with glyceline. Concretely, information about density, isobaric expansibility, speed of sound, isentropic compressibility, refractive index, molar refraction, surface tension surface, entropy and enthalpy of surface formation, isobaric molar heat capacity, kinematic and dynamic viscosity and electric conductivity, has been provided.

2. Experimental

2.1. Materials

The chemical structures of the compounds used in this work are shown in Fig. S1 of the Supplementary material. The information about the chemicals is presented in Table 1. The solvent glyceline was dried under vacuum for 24 h before utilization. The water content was determined by Karl Fischer method (automatic titrator Crison KF 1S-2B). The ternary NADES, GlyW, was obtained from choline chloride, glycerol and distilled deionized water with resistivity less than 18.2 MΩ cm. The ternary eutectic mixture

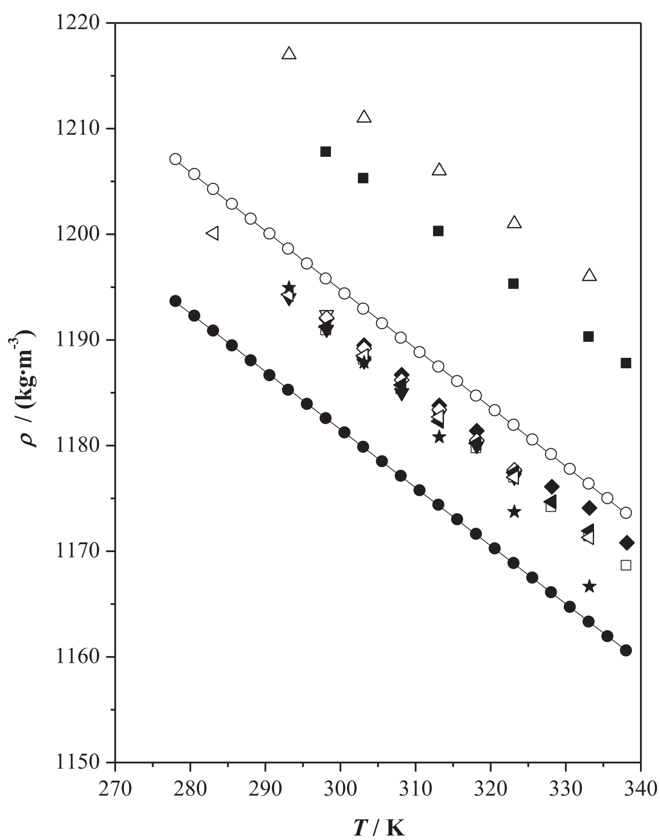

Fig. 1. Density, ρ, as a function of temperature, T, at p = 0.1 MPa for the studied compounds. Gly: (○) experimental; (▲) Ref. [16]; (△) Ref. [33]; (■) Ref. [35]; (□) Ref. [36]; (▼) Ref. [37]; (▽) Ref. [38]; (◆) Ref. [39]; (◇) Ref. [42]; (◄) Ref. [43]; (◁) Ref. [45]; (★) Ref. [48]; (☆) Ref. [49]. GlyW: (●) experimental.

Table 1
Sample table.

Chemical Name	Formula	CAS Number	Source	Purification method	MassFraction Purity [a]	Water content/ppm
Choline chloride	$C_5H_{14}ClNO$	67-48-1	Sigma-Aldrich		0.993	1250
Glycerol	$C_3H_8O_3$	56-81-5	Sigma-Aldrich		0.999	500
Glyceline			Scionix	Vacuum treatment	0.98	275

[a] As stated by the supplier.

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