

PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE ESCUELA DE INGENIERÍA

PHYSICAL PROPERTIES OF LOW VISCOSITY DEEP EUTECTIC SOLVENTS, AND ITS BINARY MIXTURES WITH 1-BUTANOL

NICOLÁS FELIPE GAJARDO PARRA

Thesis submitted to the Office of Research and Graduate Studies in partial fulfillment of the requirements for the degree of Master of Science in Engineering

Advisor: ROBERTO CANALES MUÑOZ

Santiago de Chile, October 2018

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Acuerdense de luchar por lo imposible porque lo posible se agotó.

ACKNOWLEDGEMENTS

First of all, I would like to thank Dr. Roberto Canales, my advisor, for his support, guidance, and the knowledge he transferred to me during the development of this research.

I would also like to express my gratitude to all the staff working at the Department of Chemical and Bioprocess Engineering, especially to Mrs. María Inés Valdebenito, for her invaluable help.

I would like to express my biggest gratitude to my family, Giovanna, Carlos, Matías, Benjamín and to Constanza, for their unconditional support, love and patience during this time.

I am very grateful with all my colleagues and friends in the CIAP research group. Specially, Christopher Lorca and Julián Arias for sharing this wonderful road, plenty of learning and knowledge.

Finally I would like to thank the financial support from Fondecyt de iniciación 2016 N° 11160882 and Conicyt International Networks Project REDI170207.

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ABSTRACT

Liquid-liquid extraction (LEE) and extractive distillation (ExD) are common unit operations for the separation of mixtures with a similar boiling point or presenting an azeotrope. Within these processes, ionic liquids (IL) and deep eutectic solvents (DES) have aroused interest as an alternative extractants for LEE and ExD, due to their low volatility and high selectivity. The DESs usually are biodegradable, non-toxic and low-cost alternative to ionic liquids because these compounds are obtained mainly from primary metabolites. DES are not extensively studied in literature, thus physicochemical data of the pure compound and equilibrium in the different phases are necessary to analyze the feasibility of use in separation operations. The hypothesis of this research is that it is possible to understand the effect on the thermodynamic and transport properties given by the intermolecular interactions between the constituent compounds of DES and the organic solvent through the addition of an organic compounds such as 1-butanol it is. To carry out the above, samples of three DES were synthesized and analyzed by different instrumental techniques.

Properties such as decomposition temperature, surface tension, density, viscosity were measured for pure DES and density, viscosity and enthalpy of mixture were measured for binary mixtures of DESs with 1-butanol. With this, the excess properties were calculated to understand the behavior of the DES in the mixture. The results indicate that DES are formed due to a strong intermolecular forces between their constitutens, and no reaction is present. This generates a greater thermal stability of the DESs compared to their constituent hydrogen bond donor. Also, with the addition of 1-butanol to the DESs, the mixture contracted due to the creation of new networks of hydrogen bonds and interstitial site accommodations. As a result of this, the excess properties show a negative deviation from ideality. The thermophysical properties were adjusted by different empirical and predictive models, obtaining errors of less than 5% for pure compounds. Experimental data and calculation of properties of the process allowed to understand the magnitude of

the interactions that occur when mixing a DES with an organic solvent. This contributes to having a better understanding of the effect of the electrostatic forces on the thermodynamic properties of the separation process. Subsequently, these data and parameters can be incorporated into models that are able to predict physicochemical properties for industrial applications.

Keywords: Deep eutectic solvents, excess properties, density, viscosity, enthalpy.

RESUMEN

La extracción líquido-líquido (LLE) y la destilación extractiva (ExD) son operaciones unitarias comunes para la separación de mezclas con similar punto de ebullición o con presencia de azeótropo. Dentro de estos procesos, los líquidos iónicos (IL) y los "*Deep eutectic solvents*" (DES) han despertado interés como extractante alternativo debido a su baja volatilidad y alta selectividad. Los DESs son usualmente una alternativa biodegradable, no tóxica y de bajo costo a los líquidos iónicos debido a que estos compuestos se obtienen principalmente desde metabolitos primarios. Los DES no han sido estudiados extensivamente en la literatura, en consecuencia, las propiedades fisicomoquínicas de los compuestos puros y el equilibrio de las distintas fases son necesarios para analizar la factibilidad en el uso de operaciones de separación. La hipótesis de esta investigación es que es posible entender el efecto en las propiedades de transporte y termodinámicas que generan las interacciones moleculares entre los DES y sus componentes constituyentes a través de la adición de 1-butanol. Para llevar a cabo lo anterior, tres muestras de DES fueron sintetizadas y analizadas por distintas técnicas instrumentales.

Propiedades como temperatura de descomposción, tensión superficial, densidad, viscosidad fueron medidas para DES puros y, densidad, viscosidad y entapía de fueron medidas para mezclas binarias de DES con 1-butanol. Con esto, las propiedades de exceso fueron calculadas para entender el comportamiento de los DES en la mezcla. Los resultados indican que los DES se forman debido a fuertes fuerzas intermoleculares entre sus constituyentes y no se presenta ninguna reacción. Esto genera una mayor estabilidad térmica de los DESs frente a sus donadores de puentes de hidrógeno. Además, ante la adición de 1-butanol al DES, la mezcla se contrajo debido a la creación de nuevas redes de puentes de hidrgeno y acomodación de sitios intersticiales. Como resultado de esto, las propiedades de exceso muestran una desviación negativa de la idealidad. Las propiedades termofísicas fueron ajustadas por distintos modelos tanto empíricos como predictivos obteniendo errores menores al 5% para compuestos puros.

La obtención de datos experimentales y clculo de propiedades del proceso permitió entender la magnitud de las interacciones que ocurren al mezclar un DES con un solvente orgánico. Esto contribuye a tener una mejor compresión del efecto de las fuerzas electroestáticas sobre las propiedades termodinámicas en procesos de separación. Posteriormente, estos datos y parámetros pueden ser incorporados en modelos que sean capaces de predecir propiedades fisicoquímicas para aplicaciones industriales.

Palabras Claves: *Deep eutectic solvents*, propiedades de exceso, densidad, viscosidad, entalpía.

1. INTRODUCTION

Separations are essential for recovering high-value products in process industries but they are energy intensive, consuming up to 90% of the total energy of the plant. Also, they can represent more than a half of the capital cost. Advances in the production of novel separation techniques by using new materials or new processes are important to decrease the energy consumption and produce more economical procedures. To perform this change, understanding the experimental thermophysical properties and phase behavior is indispensable, not only to improve the experimental thermodynamic knowledge but to develop new models or enhance the application of the current theory that is useful to predict the performance through micro- and macroscopic simulations. The biggest challenge in separation processes as liquid-liquid extraction (LLEx) or extractive distillation (ExD) is the selection of an extraction or solvent with low vapor pressure for decreasing regeneration costs along with decreasing its emissions to the atmosphere, low toxicity and good selectivity and capacity for economically obtaining the valuable solutes. In this context, ionic liquids (ILs) and deep eutectic solvents (DESs) have captured attention as an option for separations processes (Tang, Zhang, & Row, 2015; Rodríguez, 2015; De Los Rios & Fernandez, 2014), due to their interesting thermophysical properties.

ILs are usually defined as molten salts below 373 K but a huge number of ILs synthesized present a melting point (T_m) below 298 K or even just present a low glass transition temperatures (T_g) (Crosthwaite, Muldoon, Dixon, Anderson, & Brennecke, 2005; Fredlake, Crosthwaite, Hert, Aki, & Brennecke, 2004). At the same time, ILs show a high thermal stability, allowing liquid ranges as low as 400 K and presenting low or negligible vapor pressure (Aschenbrenner, Supasitmongkol, Taylor, & Styring, 2009). This characteristic is very important in order to reduce gas emissions to the atmosphere, so ILs are an option to substitute the commonly used volatile organic solvents (VOCs). Another major advantage of ILs is the huge amount of possible anion/cation combinations; thus, physical and chemical properties of the IL can be adjusted by forming a task specific IL that satisfies the requirements of a specific process. The major weaknesses of ILs are their reported toxicity (Pham, Cho, & Yun, 2010; Zhao, Liao, & Zhang, 2007), their high cost and high viscosity.

Deep eutectic solvents (DESs) are a biodegradable and low cost alternatives to ILs since their constituents are obtained from relatively inexpensive natural sources. DESs share some properties with ILs as tunability and a number of them have low vapor pressures, (T_m) below room conditions and acceptable thermal stability (E. L. Smith, Abbott, & Ryder, 2014). DESs are the combination of a halide salt used as a hydrogen bond acceptor (HBA), normally a tetraalkylammonium or phosphonium cation, and a hydrogen bond donor (HBD) as an alcohol, carboxylic acid, amide or sugar. The major disadvantages of using DESs are their high viscosity, not all the mixtures produce a T_m below room conditions and there are some cases with detectable vapor pressure and low thermal stability (Francisco, van den Bruinhorst, & Kroon, 2012). These compounds have shown promising results in the aromatics separation industry (Tang et al., 2015; Kareem et al., 2012; Mulyono et al., 2014; Kareem et al., 2013), however, the literature is still poor in equilibrium data and how DESs interact with other solvents. It is interesting to know the behavior of the DESs in a mixture with an alcohol because they are used in a large number of industrial applications, the presence of the OH group generates a strong dependence on hydrogen bond and how the temperature affect the hydrogen bonds (Sun, Wick, Siepmann, & Schure, 2005). Specifically 1-butanol was chosen to perform the experiments due to its wide use in the separation industry in applications such as biodiesel (Merza, Fawzy, Al-Nashef, Al-Zuhair, & Taher, 2018; Homan, Shahbaz, & Farid, 2017) o biobutanol (Verma & Banerjee, 2018; Sander, Rogošić, Slivar, & Žuteg, 2016).

1.1. Hypothesis

A proper understanding of the intermolecular interactions in the formation of DES and its binary mixtures with alcohols is of critical importance to evaluate the potential of DES as a solvent in the separation industry. The characterization of the structure after the synthesis is essential to demonstrate that the DES are formed by molecular interactions of the hydrogen bond type and not due to a reaction Also, properties such as density, viscosity and decomposition temperature are important to define the limits of decomposition and operation for DES in extraction process. Binary mixtures with 1-butanol can be used to improve our knowledge about the effect in the physical properties of DES due to the addition of an organic compound. Specifically, it is expected to observe a contraction of the physical properties, due to the creation of a new network of hydrogen bonds between 1-butanol and DES.

1.2. Objectives

Accordingly, the main objective of this thesis was to study the effect in the DES physical properties with the addition of an organic compound together with increase the amount of data on the physical properties of DES in the literature, using different analytic methods and measurement equipment. To achieve this objective, the specific aims of this thesis are:

- (i) To understand the intermolecular forces involved in the formation of the DES, for each of the different hydrogen bond donor and how this affects the stability of DES.
- (ii) To understand the effect on thermal stability and surface properties due to the formation of the DES. Understand how these parameters change from the values of the precursors.
- (iii) To understand the effect of the addition of 1-butanol in the physical properties of the mixture with excess properties. Excess volume, viscosity and enthalpy could shown the behaviour that help to understand the nature of the interactions that occur in the mixture.

This thesis is organized as follows: Section 2, literature review, describes the state of arts introducing the reader to deep eutectic solvents and their thermophysical properties. Sections 3 to 4 are materials and methods, results and discussion, following a classical

journal article scheme. Finally, Section 6 collects the principal conclusions of this research and poses the state of the future work on the topic.

2. LITERATURE REVIEW

The following section is structured as follows. Subsection 2.1 introduces the reader to eutectic mixtures, their constitutive components, and their classification. Subsection 2.2 briefly reviews the type of DES used in this work and their advantages. Subsection 2.3 covers pure eutectic mixtures reviewing the most important properties that describe them. Subsection 2.4 report the binary systems between eutectic mixtures and organic compounds; reviewing the important properties of the system and their relevance to the industrial applications. Finally, the Subsection 2.5 briefly cover the main predictive models for the calculation of viscosity.

2.1. History of Deep Eutectic Solvents

An eutectic system is a mixture of chemical compounds or elements that exhibit a single composition that freezes at a lower temperature than any other composition(Atkins & De Paula, 2006; W. F. Smith & Hashemi, 2011).



Figure 2.1. Diagrammatic representation of the theory behind eutectic mixtures (E. L. Smith et al., 2014)

The reason of the name Deep Eutectic Solvents is because when the two components are added together in a specific molar ratio an eutectic point can be seen. The eutectic point of a mixture is the molar ratio of two components which provide the lowest melting point possible. An schematic representation can be seen in the Figure 2.1. Systems with extremely large depression of the melting point, around 200 K, can be called Deep Eutectic Solvents (Zhang, Vigier, Royer, & Jérôme, 2012).

Although low-melting salts mixtures are known for quite a long time, the group of Professor Andrew Abbott of the University of Leicester (Abbott, Capper, Davies, Rasheed, & Tambyrajah, 2003; Abbott, Harris, & Ryder, 2007; Abbott, Barron, Ryder, & Wilson, 2007) was the first group to coin the term Deep Eutectic Solvent. The work of the Abbott's group was focused, initially, in the mixtures of choline chloride (ChCl) and urea, then they changed their interest to study the possible types of DESs and generating a classification (E. L. Smith et al., 2014). The Table 2.1 shows the four types of DESs described in the literature.

Table 2.1. Types of DESs, their general formula, terms and examples. Adapted from (E. L. Smith et al., 2014)

Types	General formula	Terms	Formula
Type I	$Cat^+X^- + zMCl_x$	M = Zn, In, Sn, Al, Fe	$ChCl + ZnCl_2$
Type II	$Cat^+X^- + zMCl_x \cdot yH_2O$	$M = Cr^{13}$, Co, Cu, Ni, Fe	$ChCl + CoCl_2 \cdot 6H_2O$
Type III	$Cat^+X^- + zRZ$	$Z = OH$, COOH, $CONH_2$	ChCl + Urea
Type IV	$MCl_x + zRZ$	M = Zn, Al and Z = OH, $CONH_2$	ZnCl ₂ + Urea

The present work will focus in type III because, as mentioned in Chapter 1, they are easy to prepare, nontoxic and biodegradable. In addition, they are a low cost alternative to ILs since their constituents are obtained from relatively inexpensive natural sources and share some interesting properties as tunability, low vapor pressures and melting points (T_m below room conditions (E. L. Smith et al., 2014).

2.2. Type III Deep Eutectic Solvents and their advantages

Type III eutectics solvents, formed from choline chloride ($T_m = 576$ K) as hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) like urea ($T_m = 407$ K), is the most common and studied DESs. Once both compounds are heated and mix, i.e at 1:2 mole ratio, the DES mixture has a T_m equal to 285 K (Abbott et al., 2003). However, the principle of DESs is not limited to urea. It can be also applied to a variety of other hydrogen bond donors such as carboxylic acids, glycols, amines and alcohols (Zhang et al., 2012).

In general, a significant reduction of T_m is observed comparing with the pure compound due to the internal interactions that create a highly non symmetric structure reducing the lattice energy. In addition, some HBA:HBD combinations have also low glass transition temperatures (T_g); this variant is usually called low transition temperature mixtures (LTTMs) (Francisco, van den Bruinhorst, & Kroon, 2013), but DESs is used as a generic name.

One of the great advantages of DESs is that choline chloride is biocompatible and known as constituent of vitamin B_4 (Blusztajn, 1998). Also, most of the HBDs are cheap and environmentally bening such as urea, glycerol, sugars and carboxilic acids. Figure 2.2 summarizes the different quaternary ammonium salts that are widely used in combination with various HBDs in DESs formation. There is no limit in the number of DESs that can be synthesized from the available chemicals because the large number of quaternary ammonium and HBDSs which can be used, and it is almost impossible to study all the variants. For this study choline chloride was used as HBAs and ethylene glycol, phenol and levulinic acid used as HBDs.



Figure 2.2. Some structures of typical HBA and HBD used for DESs synthesis (Zhang et al., 2012)

2.3. Properties of pure Deep Eutectic Solvents

In this section, thermodynamic properties of pure deep eutectic solvents will be discuss. Thermophysical properties of ILs and DESs are important starting point for analyzing their purity and observing their potential applications according to these characteristics. Properties like density, viscosity and thermal stability are essential for the complete characterization of the DESs.

2.3.1. Freezing point

When a halide salt is mixed in a specific molar ratio with a HBD, a large depression of the melting point, always compared with the pure components, is observed. Most of the reported DES have melting points below 423 K (Abbott, Boothby, Capper, Davies, & Rasheed, 2004), and some of then are liquid at 333 K or below, making the DES certainly attractive for various applications (e.g polyphenols extraction process at low temperature to avoid thermal decomposition).

	ChCl : HBD	T_m	
HBD	(molar ratio)	(K)	Reference
Urea	1:2	285	(Abbott et al., 2003)
Ethylene glycol	1:2	207	(Shahbaz, Mjalli, Hashim, Al-Nashef, et al., 2010)
Glycerol	1:2	233	(Abbott et al., 2011)
Imidazole	3:7	329	(Hou et al., 2008)
Malonic acid	1:1	283	(Abbott et al., 2004)
Levulinic acid	1:2	Liquid at RT	(Maugeri & de María, 2011)
Caffeic acid	1:0.5	340 ± 3	(Maugeri & de María, 2011)
Gallic acid	1:0.5	350 ± 3	(Maugeri & de María, 2011)
Resorcinol	1:4	360	(Gutiérrez et al., 2011)

Table 2.2. Freezing point (T_f) of some reported DESs. RT stands for room temperature. Adapted from (Zhang et al., 2012)

Table 2.2 lists melting temperatures of various DESs described in the literature. Some points to highlight is that liquids DESs at room temperature can be obtained from carboxilic acids (*e.g* levulinic acid) or sugar polyols (*e.g* xilitol). Also, some relationship between the molar ratio of the HBA:HBD or the nature of the ammonium salt and the freezing point can be observed (Abbott et al., 2004; E. L. Smith et al., 2014).

2.3.2. Thermal decomposition and surface tension

Thermal decomposition could arguably be one of the most important properties to measure during the initial screening of a DES, especially for the operating temperatures of the processes pertinent to this work. The decomposition temperature is the temperature at which the solvent begins to decompose or break down into smaller molecules. This temperature is identified by the mass loss of the sample.

Literature is not abundant in the study of DES decomposition. There are data on some of the traditional compounds and their decomposition curves (Florindo, Oliveira, Rebelo, Fernandes, & Marrucho, 2014; Ullah et al., 2015; Zhang et al., 2012; Altamash et al., 2017; Abbas & Binder, 2010). Furthermore, it is known that the thermal stability of DES improves compared to pure HBD and worsens compared to HBA. Also, some studies propose that some DES loses mass during the time when it is exposed to a moderate temperature lower than its decomposition temperature by simple volatilization (Delgado-Mellado et al., 2018).

Surface tension is one of the important properties that affects the reactivity of DESs and it is one of the crucial liquid characterization that is required in many industries. Surface tension is defined as the work necessary to increase the interfacial area in a certain area differential (Levine, 2009). In general, it increases as there are more intermolecular interactions, because this generates an increase in the work necessary to move the liquid. Although the measurement of the surface tension of solvents is important, only few data on surface tension of DESs is available.

The surface tension of some DES has been measured by some authors, noting that the increase in surface tension by increasing the molar ratio of HBA in the mixture, due to the increase in intermolecular interactions (Mjalli, Murshid, Al-Zakwani, & Hayyan, 2017; Mjalli, Vakili-Nezhaad, Shahbaz, & AlNashef, 2014; AlOmar et al., 2016; Hayyan et al., 2012). In addition, the importance of the surface tension as physical property is it use for the calculation of other properties such as conductivity or atomic radius through

the hole theory (Abbott, Capper, & Gray, 2006). There are also research on the use of surface tension as the basis for the calculation of critical properties of solvents using the Guggenheim and others equations (Marcus, 2018).

2.3.3. Density

Density is one of the most important properties to characterize a solvent. The DESs has a value above the density of water comparable with ILs density, which vary between $1100 \text{ kg} \cdot \text{m}^{-3}$ and $2400 \text{ kg} \cdot \text{m}^{-3}$ (Wasserscheid & Welton, 2008). Table 2.3 lists literature values of common studied DESs at 298.15 K. The relationship between the molar ratio and the density in Figure 4.5 can be observed, in general, the density decreases when the percentage of salt increases in the DES.



Figure 2.3. Density molar ratio dependence of DESs (Abbott et al., 2011)

This can also be observed in the values of the Table 2.3 for glycerol based DESs, this could be explained in terms of free volume and hole theory (Shahbaz, Mjalli, Hashim, & AlNashef, 2011; Abbott et al., 2011). It has also been reported that density decreases with temperature and the percentage of water in the sample (Shahbaz et al., 2011; Yadav &

Pandey, 2014; Yadav, Trivedi, Rai, & Pandey, 2014). This can be explained mainly by the increase in the internal energy of the particles which generates a larger vacancy space.

	ChCl : HBD	Density	
HBD	(molar ratio)	$(\rho, g \cdot \mathrm{cm}^{-3})$	Reference
Urea	1:2	1.25	(Yadav & Pandey, 2014)
Ethylene glycol	1:2	1.12	(Shahbaz, Baroutian, Mjalli, Hashim, & AlNashef, 2012)
Ethylene glycol	1:3	1.12	(Abbott, Harris, & Ryder, 2007)
Glycerol	1:1	1.16	(Abbott, Barron, et al., 2007)
Glycerol	1:2	1.18	(Abbott et al., 2011)
Glycerol	1:3	1.20	(Yadav et al., 2014)
Malonic acid	1:2	1.25	(D'Agostino, Harris, Abbott, Gladden, & Mantle, 2011)
Levulinic acid	1:2	1.14	(Sas, Fidalgo, Domínguez, Macedo, & Gonzlez, 2016)

Table 2.3. Density in $g \cdot cm^{-3}$ of common DESs at 298.15 K. Adapted from (Zhang et al., 2012)

Type IV DESs are the ones with the highest density, a phenomenon that can be explained by the greater number of vacancies in the molecular structure. According to hole theory the DESs are composed of empty holes or vacancies. This explains why these have higher density than their pure compound. As an example, DES formed by urea and zinc chloride has a density of 1.63 kg·m⁻³ and urea as a pure compound has a density of 1.32 kg·m⁻³ (Abbott, Barron, et al., 2007).

2.3.4. Viscosity

Like most of ILs, viscosity is an important issue for DESs industrial applications that needs to be addressed. Most of DESs exhibit a relatively high viscosity at room temperature (> 100 cP), except for the ChCl-ethylene glycol eutectic mixture (Zhang et al., 2012; Abbott et al., 2006). Similar to density behaviour, viscosity is related with the probability of finding holes for the solvents or ions to move into, the viscosity its also dependent on

the size of the ions (Abbott et al., 2004, 2006). Table 2.4 lists the viscosity data of common DES at different temperatures.

	ChCl : HBD	Viscosity	
HBD	(molar ratio)	(η, cP)	Reference
Urea	1:2	750 (298.15 K)	(D'Agostino et al., 2011)
Ethylene glycol	1:2	37 (298.15 K)	(Abbott et al., 2011)
Ethylene glycol	1:3	19 (293.15 K)	(D'Agostino et al., 2011)
Glycerol	1:2	376 (293.15 K)	(D'Agostino et al., 2011)
Glycerol	1:3	450 (293.15 K)	(Abbott et al., 2011)
Glycerol	1:4	503 (293.15 K)	(Yadav et al., 2014)
Malonic acid	1:2	1124 (298.15 K)	(D'Agostino et al., 2011)
Levulinic acid	1:2	255 (298.15 K)	(Sas et al., 2016)

Table 2.4. Viscosity in cP of common DESs at different temperatures. Adapted from (Zhang et al., 2012)

The reason of these high values can be related to the strong hydrogen bond network formed in the DESs structure, that inevitably reduces the mobility of the molecular compounds (Fukaya, Iizuka, Sekikawa, & Ohno, 2007; Abbott et al., 2006; Ruß & König, 2012). Other forces such as electrostatic or van der Walls interactions may lead to high viscosities (Bonhote, Dias, Papageorgiou, Kalyanasundaram, & Grätzel, 1996). The viscosity follows an Arrehenius behaviour as it decreases with increasing temperatures (Abbott et al., 2011; D'Agostino et al., 2011). It is reported that viscosity is closely dependent on the nature of the HBD. For instance, diols (e.g ethyle glycol) based DES have significantly lower viscosities than sugar based (e.g xilitol, sorbitol) or carboxylic acid (e.g malonic acid, levulinic acid). This could be related due the presence of a more robust 3D intermolecular hydrogen bond network (Zhang et al., 2012). Another important factor is that by increasing the amount of choline chlorine in the mixture the viscosity decreases. This can be explained due to the great cohesion energy that glycerol has, which generates a partial rupture of hydrogen bonds network when adding ChCl (Abbott et al., 2011).

2.4. Properties of binary systems of DESs + organic compound

Typical measurements performed for binary organic compound + DESs systems are VLE, LLE, γ_{13}^{∞} , H^E and V^E. VLE provides essential information to determine if simple distillation is possible in binary systems. LLE gives information about the presence of partial miscibility of a mixture at determined temperature. From these data selectivities can be determined but those measurements are very time consuming. H^E and V^E provide important information about the temperature and pressure dependency of the activity coefficients, intermolecular interaction and endothermic or exothermic behavior of the system. A more detailed description of the properties used in the present work are described in the following subsections.

2.4.1. Excess volume

The excess molar volume is described as follows (Walas, 2013; Letcher, 1975)

$$V_m^E = V_{mixture} - \sum x_i V_i^o \tag{2.1}$$

where x_i is the mole fraction of a component *i*, $V_{mixture}$ is the molar volume of the mixture and V_i is the volume of a component *i*. The simplified equation for a binary mixture,

$$V_m^E = V_{mixture} - (x_1 V_1^o + x_2 V_2^o)$$
(2.2)

The change in volume on the mixture can be attributed to a number of processes: (a) the breakdown of 1-1 and 2-2 intermolecular interaction which have a positive effect on the volume, (b) the formation of 1-2 intermolecular interaction which results in a decrease of the volume of the mixture, (c) packing effect caused by the difference in the size and shape of the component species and which may have positive or negative effect on the particular species involved and (d) formation of new chemical species (Redhi, 2003).

Changes on volume of binary mixing of liquids, V_m^E , at constant pressure and temperature is interesting as an indicator of non-idealities present in real mixtures (Renon & Prausnitz, 1968). In this work the excess molar volume will be measured by the indirect method. The details for the instrument used in this work are given in Chapter 3.3.3, a theoretical explanation of the technique is given here.

The development of highly accurate vibrating tube densitometers has made it possible to determine, V_m^E with acceptable accuracy from the mixture density using the following equation:

$$V_m^E = \frac{x_1 M_1 + x_2 M_2}{\rho_m} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2}$$
(2.3)

where x_1 and x_2 are mole fractions, M_1 and M_2 are molar masses of the compounds, ho_m is the density of the mixture and ho_i represent the density to the component 1 or 2 respectively (Wilhelm & Letcher, 2014; Y. Li, Ye, Zeng, & Qi, 2010). There are many works in the literature on excess molar volumes of ILs with different solvents (Arce, Rodil, & Soto, 2006; Domańska, Pobudkowska, & Wiśniewska, 2006; Nebig & Gmehling, 2011; Liebert, Nebig, & Gmehling, 2008; Singh & Kumar, 2008; González, González, Calvar, & Domínguez, 2007; Gómez, González, Calvar, Tojo, & Domínguez, 2006), but only a few that talk about the interaction of the DES with solvents (Yadav & Pandey, 2014; Yadav et al., 2014; Sas et al., 2016; Leron, Soriano, & Li, 2012; Harifi-Mood & Buchner, 2017; Yadav, Kar, Verma, Naqvi, & Pandey, 2015), and are mainly focused on aqueous mixtures as a way to reduce the viscosity of the mixture. Their results show that DES + solvent binary systems have a negative behavior for excess volumes. In the work of Sas et al. (2016) it is also shown that the excess molar volume is less negative when the solvents have a longer organic chain. A negative behavior generally shows a contraction in volume upon mixing. This interactions in the mixture are affected by the composition and the temperature. In binary liquid mixtures the value of V^E usually shows a negative

behaviour with the increasing temperatures. This could be related to a stronger interspecies interaction (hydrogen bond network) than intra-species interaction (Yadav et al., 2015).

2.4.2. Excess viscosity

Same as excess volume, the excess viscosity o viscosity deviation is described as follows (Ghosh, Prasad, Dutt, Rani, et al., 2007)

$$\eta^E = \eta_m - \sum x_i \eta_i \tag{2.4}$$

where x_i is the mole fraction of a component i, η^E is the viscosity deviation of the mixture and η_i is the viscosity of a component i. The simplify equation for a binary mixture is,

$$\eta^E = \eta_m - (x_1\eta_1 + x_2\eta_2) \tag{2.5}$$

The deviations viscosity may be explained by the following factors. The difference in size and shape of the system molecules and the loss of dipolar association reduce the viscosity and specific interactions between non similar molecules such as hydrogen bond formation may cause increase of viscosity in mixtures rather than in pure component (Mehra & Pancholi, 2006). The former effect produces negatives values in viscosity deviation, and latter effect produces positives values in viscosity deviations. (Yang, Xu, & Ma, 2005). Positive values of η^E are indicative of strong interactions whereas negative values indicate weaker interactions (Yang, Xu, & Ma, 2004).

In DESs + solvents binary mixtures the excess viscosity tend to be negative at temperatures near 293 K, and have some positives values at higher temperatures. Specific interactions between species of the system, e.g., formation of hydrogen bonds result in different effects in the excess viscosity. Both size and shape of DES are very different from the size and shape of the solvents, this causes certainly the loss of Coulombic attractive interaction (Yadav et al., 2014).

2.4.3. Excess enthalpy

The excess molar enthalpy data are one of the most measured excess thermodynamic property since it is relatively easy to obtain and the data can be used to calculate other excess thermodynamic properties like molar Gibbs free energy, vapor-liquid equilibrium values and can be usefull to understand the intermolecular forces (Wei, Han, & Wang, 2014). Heat of mixing is a very essential property in separation processes and also it determines the variation of activity coefficient with temperature. Activity coefficient is a critical parameter considered in the design of chemical processes which involving phase separation. The excess molar enthalpy is described by the Gibbs Helmholtz equation (Atkins, 1978)

$$H_m^E = -RT^2 \left[\frac{\partial G_m^E}{\partial T}\right]_{P,x} = -RT^2 \sum_i^n x_i \left[\frac{\partial ln\gamma_1}{\partial T}\right]_{P,x}$$
(2.6)

The excess molar enthalpy value can be determined directly from de calorimeter, then molar Gibbs free energy models can be calculated. Excess enthalpy data for binary mixtures of ILs are quite scarce. Up until 2015 there were only 65 articles with a total of 375 data sets for binary systems in the literature (Podgorsek, Jacquemin, Pádua, & Costa Gomes, 2016). These systems show the most diverse behaviors, that is why it is necessary to investigate this property for the mixtures of DES with organic compounds. However, in the literature there is no data on excess enthalpies yet, which makes it a very interesting area to explore.

2.4.4. The Redlich - Kister equation

The excess properties can be fitted to the empirical Redlich - Kister equation, which is shown in its general form for a binary mixture as follows:

$$M^{E} = x_{1}x_{2}\sum_{p=0}^{3} \alpha_{p} \left(x_{1} - x_{2}\right)^{p}$$
(2.7)

where M^E is the excess property, x_1 and x_2 the molar fraction from the mixture compounds and α_p are adjustable parameters to fit the equation to the data. Having a mathematical expression for the excess properties could facilitate the mathematical calculation of derived properties.

2.5. Viscosity prediction

Predictive models are necessary in the industry because the measurement of experimental data can increase costs and time used in processes, even more, in solvents such as DES that can combine multiple compounds of the most varied types. Furthermore, the DES have a relatively high viscosity, which complicates the measurements.

In general and as presented in this work, the experimental viscosity data is adjusted by correlations. However, these correlations lack predictive character. For ionic liquids, group contribution models (Gardas & Coutinho, 2008), neural network algorithms, quantitative structure-property relationship (Bini, Malvaldi, Pitner, & Chiappe, 2008), equation of state (EoS) models (Polishuk, 2013) and the hard—sphere scheme have been studied (Hosseini, Alavianmehr, & Moghadasi, 2016; Gaciño, Comuñas, Fernández, Mylona, & Assael, 2014). However, for DESs only the free volume models and the friction theory have been studied (Haghbakhsh, Parvaneh, Raeissi, & Shariati, 2018; Haghbakhsh, Raeissi, Parvaneh, & Shariati, 2018). This study will seek to apply the extended hardsphere model to pure DESs and binary mixtures with alcohols.

3. MATERIAL AND METHODS

3.1. Chemicals

All the compounds used in the study are shown in Table 3.1 with their respective purities and source. Three DESs were prepared using choline chloride as hydrogen bond acceptor, while the hydrogen bond donors were levulinic acid (DES1), ethylene glycol (DES2) and phenol (DES3). All the DES were prepared in a molar ratio of HBA:HBD of approximately 1:2.

Table 3.1. Chemical specifications

Chemical	M_w (g·mol ⁻¹)	CAS	Supplier	Purity
Choline chloride	139.62	67-48-1	Acros organics	> 0.990
Levulinic acid	116.12	123-76-2	Acros organics	> 0.980
Ethylene glycol	62.06	107-21-1	Acros organics	> 0.998
Phenol	94.11	106-95-2	Sigma aldrich	> 0.990
1-butanol	74.12	71-36-3	Sigma aldrich	> 0.998

3.2. Preparation of DES and 1-butanol + DES mixtures

DES were prepared gravimetrically using an analytic balance (Practum 224-1s Sartorius, Germany, uncertainty 0.1 mg). Initially, the HBA and HBD were mixed into a round bottom flask under nitrogen atmosphere and then heated at 353.15 K until a homogeneous liquid was formed. Choline chloride, which is very hygroscopic, was previously dried in a Schlenk line under high vacuum (10^{-4} mbar) for three days to avoid water gain due to environmental humidity. The amount of water present in each DES was measured using a Karl Fisher Coulometer (831KF Metrohm, Switzerland). DES composition and water content are shown in Table 3.2.

Abbreviation	Salt	HBD	Molar ratio	Water content
			(Salt : HBD)	(%)
DES1	Choline chloride	Levulinic acid	1:2	0.065
DES2	Choline chloride	Ethylene glycol	1:2	0.041
DES3	Choline chloride	Phenol	1:2	0.056

Table 3.2. Water content and molar ratio of prepared DESs

In order to test if the low-pressure environment used for drying the DES in the Schlenk line would change their composition, 0.5 mL of choline chloride + phenol (\sim 1:2 molar ratio) mixture was placed into a 25 mL round-bottom flask. Three ¹H NMR samples of the DES were taken. The remainder of the sample was connected to a Schlenk line in a vacuum environment for one hour. Afterwards, three samples of the post-vacuum DES were taken for ¹H NMR measurement. The molar ratio of choline chloride to phenol changed from 1:2.026 to 1:1.971, suggesting that phenol preferentially evaporated. Therefore, DES were not placed under vacuum to remove water before any application, since that could affect their final composition. Mixtures of 1-butanol + DES were also prepared gravimetrically in glass vials with septum caps under nitrogen atmosphere. All the samples were kept in a desiccator while stand by.

3.3. Equipment and instrumentation

3.3.1. Nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FT-IR)

NMR and FT-IR measurements were used to characterize the DES precursors, DES and 1-butanol + DES mixtures. ¹H NMR and a 2D NMR ¹H-¹H correlation spectroscopy (COSY) measurements were carried out using an Bruker Advance 400 MHz spectrometer (Massachusetts, United States). Samples were dissolved in deuterium oxide (D_2O) and

tetramethylsilane was used as an internal reference. FT-IR measurements were carried out in a Shimadzu IRTracer-100 (Kyoto, Japan) between 400 and 4,000 cm⁻¹. The solid samples were prepared in KBr pellets, while the liquid samples were supported on transparent KBr films.

3.3.2. Thermogravimetric analysis (TGA) and surface tension

TGA was measured for DES precursors and DES and surface tension was measured only for DES. TGA were carried out on a Mettler Toledo TGA 851e thermal gravimetric analyzer (Ohio, United States) using STARe Mettler-Toledo 8.1 software for data collection. The sample pans were standard 40 μ L aluminum crucibles. Measurements were carried out between 300 and 800 K at 20 K/min under nitrogen atmosphere at 60 mL/min flow. The surface tension was measured using the plate method out in a Dataphysics DCAT9 tensiometer (Filderstadt, Germany). Measurements were performed four times at a temperature of 298.15 K and atmospheric pressure. Surface tension results were the average of the four measurements and the uncertainty obtained was ± 0.03 m·Nm⁻¹. The experimental method was tested using deionized distilled water.

The plate method is based on the measurement of the maximum force necessary to detach the plate from the surface of the liquid. The measuring device is a vertically hanged platinum plate with exactly known geometry. The surface of the plate is roughened to improve its wettability. The lower edge of the plate is brought into contact with the liquid surface. The liquid jumps the plate and pulls it a small portion into it. This "Wilhelmy"-force results from the wetting. It is measured by moving up the plate to the level of the liquid surface. Then, the surface tension is calculated as follows:

$$\gamma = \frac{P_w}{L_w \cdot \cos \theta} \tag{3.1}$$

where θ is the contact angle between the tangent at the wetting line and the plate surface, L_w is the wetted length and P_w is the measured Wilhelmy force.

3.3.3. Density

Density was measured in an Anton Paar 4500 DMA Densimeter (Graz, Austria). It uses the Anton Paar's vibrating U-tube technology to provide density measuraments with an accuracy of 0.005 kg·m⁻³. The internal temperature is measured with an accuracy of 0.01 K using an integrated Pt 100 thermometers.

The vibrating U-tube technology determines the density of a sample by

$$\rho = \left(\frac{c}{4\pi^2 V}\right) \cdot P^2 - \frac{M}{V} \tag{3.2}$$

where ρ is density, c is the spring constant, V is volume of the U-tube, P is oscillation period, and M is mass. The oscillation period, P, is known from the continuous oscillation at a frequency, f, dependent on the density of the sample. This equation can be reduced to

$$\rho = A \cdot P^2 - B \tag{3.3}$$

where A and B are apparatus constants determined through adjustments. The constants are determined using two known standards, air and water. The apparatus was calibrated with double distilled deionized, and degassed water, and dry air at atmospheric pressure.

3.3.4. Viscosity

A modular microviscometer Lovis 2000 ME provided by Anton Paar is used in conjunction with the DMA 4500 to perform dynamic viscosity measurements. The measurements of viscosity with Lovis 2000 ME is based on the falling ball principle. The microviscometer is equipped with three calibrated glass capillaries of different diameter, in addition to steel balls. The time taken by the steel ball to fall from one side of the capillary to the other of the sample filled capillary at a certain angle is measured. The time and the density were used to calculate the dynamic viscosity by

$$\eta = k_1 \cdot (\rho_b - \rho_s) \cdot t_1 \tag{3.4}$$

where η is the dynamic viscosity, k_1 a calibration constant, ρ_b the steel ball density, ρ_s the density of the measured sample in the DMA 4500 and t_1 the ball rolling time. The calibration of the capillaries was done by the manufacturer using fluids with standard viscosity and measured in our laboratory using the same standards and different solvents as methanol, water and glycerol. Viscosity measurements was given with a repeatability of 0.1%, the measurement accuracy varies between 0.17% and 0.50% depending on the size of the capillary and the temperature. Figure 3.1 shows he modular assembly of the DMA 4500 and Lovis 2000 ME.



Figure 3.1. Anton Paar DMA4500 and modular Lovis 2000 ME

3.3.5. Excess enthalpy

 H^E was measured in a Setaram C80 calorimeter for binary mixtures of 1-butanol + DES mixtures at 313.15 K and atmosphere pressure. The cell used in the experiments is composed by a cylindrical reversal mixing cell with two compartments. The bottom compartment holds the volatile sample, in this case 1-butanol, which is closed with a movable cap. Approximately 20 g of mercury are added over the cap to avoid the releasing of vapors from the solvent due to the temperature increasing during the experiment. The DES is added over the mercury and then, the cell is closed. All this process is done under nitrogen atmosphere. There is a very small solubility of the DES in the mercury which does not affect the experiment, according to the procedure described by Ficke et

al (Ficke, Rodrguez, & Brennecke, 2008). The cell is placed in the calorimeter along with a reference which is an identical empty mixing cell. Temperature is stabilized for 3 hours and then the reversal mechanism of the calorimeter is activated turning the cell in 180. This allows the movable cap to act as a stirring system for the sample and the two liquids mix at constant temperature, so the calorimeter detects any release or absorption of heat due to the mixing. After mixing, the temperature is kept constant approximately one hoyr until the system returns to ambient conditions. The error of the experimental measurements of H^E is 2

3.4. Viscosity prediction with the hard-sphere model

In the hard-sphere model all the thermodynamic and transport properties are expressed as function of the reduce volume $V^* = V_m/V_0$, where V_m is the molar volume and V_0 is the molar volume for closely packed hard spheres (Assael, Dymond, Papadaki, & Patterson, 1992). The hard-sphere scheme also work in terms of reduced transport coefficients and in Assael approach the reduced viscosity (η^*) was described as follows:

$$\eta * = \left(\frac{16}{5}\right) (2N_A)^{\frac{1}{3}} \left(\frac{\pi}{MRT}\right)^{\frac{1}{2}} V_m^{\frac{2}{3}} \eta \tag{3.5}$$

where M is the molar mass and R the universal gas constant. The reduced viscosity of a smooth hard sphere can be determined as a function of V^* by molecular simulation. This approach estimates the V^* value from the Enskog approximation for the viscosity of smooth hard spheres with a correction derived from molecular dynamics calculations (Ciotta, Trusler, & Vesovic, 2014). To model systems with the hard-sphere scheme it should be noted that the thermophysical properties of fluids are dominated by repulsive interactions and can be mapped approximately on to those of the hard-sphere model if the reducing volume V_0 is treated as a temperature-dependent parameter. Thus, having established the universal function V^{*} from simulation and theory, the viscosity of a simple molecular fluid could be correlated along an isotherm by selecting an optimal value of V_0
for that molecule at a given temperature. The universal curve is defined as a polynomial expansion of V^{*} and the parameters (a_i) have been calculated by various authors seeking to expand the scheme to different compounds and higher viscosities (Assael et al., 1992; Ciotta et al., 2014). In this work, the Ciotta's parameters were used. The universal curve was described as follows.

$$\log_{10}(\eta^*) = \sum_{i=1}^{7} a_i \left(\frac{1}{V^*}\right)^i$$
(3.6)

The scheme could be also applied in non spherical molecules, the rough- hard-spheres. In this case expression for viscosity is modified by a simple multiplicative parameter, usually taken to be temperature independent. Thus, a more general expression for the reduced viscosity is:

$$\eta * = \left(\frac{16}{5}\right) (2N_A)^{\frac{1}{3}} \left(\frac{\pi}{MRT}\right)^{\frac{1}{2}} V_m^{\frac{2}{3}} \left(\frac{\eta}{R_\eta}\right)$$
(3.7)

where R_{η} is called the roughness factor and it is used to correlate the experimental viscosity which is function of the temperature and the density. For this, it is necessary to determine the constant R_{η} and the parameters of V_0 (T) to fit the experimental reduced viscosity η^* , onto the universal curve smooth hard spheres. In this work, 230 reported data of density and viscosity of pure DESs were used to prove the validity of the application of the scheme for DES. The summary of the data used its reported in the Table 3.3

НВА	HBD	Molar Ratio (HBA:HBD)	M. Weight (g mol ⁻¹)	Abbreviation	Temp. Range (K)	Pressure (MPa)	N. data	ref
Choline Chloride	Levulinic acid	1:2	123.95	DES1	293.15-353.15	0.1	24	(Sas et al., 2016)
Choline Chloride	Ethylene glycol	1:2	87.92	DES2	308.15-363.15	0.1	10	(Harifi-Mood & Buchner, 2017)
Choline Chloride	Phenol	1:2	109.28	DES3	293.20-318.20	0.1	6	(Guo, Hou, Ren, Tian, & Wu, 2013)
Choline Chloride	Glycerol	1:2	107.93	DES4	283.15-263.15	0.1	9	(Yadav et al., 2014)
Choline Chloride	Phenol	1:3	105.49	DES5	293.20-318.20	0.1	6	(Guo et al., 2013)
Choline Chloride	Phenol	1:4	103.21	DES6	293.20-318.20	0.1	6	(Guo et al., 2013)
Choline Chloride	Phenol	1:5	101.70	DES7	293.20-318.20	0.1	6	(Guo et al., 2013)
Choline Chloride	Phenol	1:6	100.61	DES8	293.20-318.20	0.1	6	(Guo et al., 2013)
Choline Chloride	Levulinic acid	1:1	127.87	DES9	293.15-333.15	0.1	5	(G. Li, Jiang, Liu, & Deng, 2016)
Choline Chloride	Urea	1:2	86.58	DES10	293.15-363.15	0.1	15	(Yadav & Pandey, 2014; Haghbakhsh, Parvaneh, et al., 2018)
Choline Chloride	Malonic acid	1:1	121.84	DES11	293.15-353.15	0.1	13	(Florindo et al., 2014)
Choline Chloride	Glycolic acid	1:1	107.84	DES12	293.15-353.15	0.1	13	(Florindo et al., 2014)
Choline Chloride	Oxalic acid	1:1	114.83	DES13	293.15-353.15	0.1	13	(Florindo et al., 2014)
Acetylcholine chloride	Levulinic acid	1:1	148.89	DES14	293.15-333.15	0.1	5	(Florindo et al., 2014)
Tetrabutylammonium chloride	Propionic acid	1:2	140.03	DES15	288.15-338.15	0.1	11	(SU, YIN, LIU, & LI, 2015)
Tetrabutylammonium chloride	Ethylene glycol	1:2	132.02	DES16	288.15-338.15	0.1	11	(SU et al., 2015)
Tetrabutylammonium chloride	Phenylacetic acid	1:2	181.41	DES17	288.15-338.15	0.1	11	(SU et al., 2015)
Methyl triphenyl phosphonium bromide	Glycerol	1:3	158.37	DES18	293.15-363.15	0.1	15	(AlOmar et al., 2016)
Benzyl triphenyl phosphonium chloride	Glycerol	1:16	109.55	DES19	293.15-363.15	0.1	15	(AlOmar et al., 2016)
Allyl triphenyl phosphonium bromide	Glycerol	1:14	111.50	DES20	293.15-363.15	0.1	15	(AlOmar et al., 2016)
N,N-diethyl ethanol ammonium chloride	Glycerol	1:2	112.61	DES21	293.15-363.15	0.1	15	(AlOmar et al., 2016)

Table 3.3. Viscosity and density database of deep pure eutectic solvents

4. RESULTS AND DISCUSSION

4.1. NMR and FTIR analysis of DES

¹H-NMR structures for choline chloride, levulinic acid, DES1, ethylene glycol, DES2, phenol and DES3 are shown in Figure A1, Figure A2, Figure 4.1 and Figures A3-A7, respectively. Figures A1-A7 are presented in Annex A. In Figure 4.1, the ¹H NMR spectrum of DES1 composed of choline chloride and levulinic acid is shown and it is observed that all the main signals of the constituent compounds are present in the spectrum in agreement with the same DES spectra reported previously in literature (Sas et al., 2016).



Figure 4.1. NMR 1 H for DES1 in D₂O

This spectrum can be contrasted against Figures A1 and A2 of the pure choline chloride and levulinic acid and no shift in the ¹H signals is detected when compounds are mixed to form the DES1. 1 H- 1 H COSY analysis is shown for DES1 in Figure A.10, observing in black squares the interactions between the continuous protons. Here, three well-formed squares are present, each of them associated with a specific interaction. The square (A) shows the interaction N⁺-(CH₂-CH₂), the square (B) shows the structure of the positive center of choline chloride N⁺-(CH₂-N-CH₃) and finally the square (C) shows the interaction of the carbonyl group of levulinic acid. Thus, the 1 H- 1 H COSY analysis shows the complete structures of both levunilic acid and choline chloride in DES1, showing no reaction and concluding that the interaction between both compounds is only of an electrostatic nature. For this specific case, this observation is especially important because no



Figure 4.2. ¹H-¹H COSY analysis for DES1

esterification reaction is detected. Indeed, the ¹H-NMR and ¹H-¹H COSY measurements

for all the DES were performed at least after two weeks after they were synthesized, showing that DES1 is stable during all the measurements. Similar analysis was performed for DES2 and DES3.

Figure 4.3 shows that the FT-IR spectrum also agrees with the expected structures and shows characteristic signals for DES and precursors. The spectrum confirms the interaction that occurs between pure compounds when DES is formed.



Figure 4.3. FT-IR analysis for DES and precursors

The main effect is the shift of the -OH stretching bond that can be seen between 3500 - 2800 cm^{-1} , this is due to the interaction of the carbonyl group of the carboxylic acid with the positive center of the amine in the choline chloride, confirming the formation of

hydrogen bonds in the three DES. It can also be noted that this interaction is stronger for DES1, which presumes a greater interaction of the bands and therefore greater stability of the DES. In addition, the three DES present a new peak around 950 cm⁻¹ with respect to their HBD. This new peak is indicating the presence of the reported ammonium salt, a finding that coincides with previous literature (Aissaoui, 2015; Zullaikah, Rachmaniah, Utomo, Niawanti, & Ju, 2018). The FT-IR confirms that the mixture is formed due to interactions and not due to a reaction.

4.2. Thermal stability and surface tension

Figure 4.4 represent the shows TGA curves with a heating rate of 20 K·min⁻¹ for the three studied DESs and their precursors. Table 4.1 summarizes the values of the onset decomposition temperature (T_{onset}) obtained from the dynamic TGA curves with heating rates of 20 K·min⁻¹. The onset decomposition temperature is an important property because it determines the maximum temperature at which DESs can maintain their liquid state without decomposition and thus their range of use as solvents (Florindo et al., 2014). This values are higher than those reported by Delgado-Mellado et al. where is shown that a higher heating rate results in higher values of Tonset. Therefore, our results agree with this observation because their measurements were done at 5-10 Kmin-1.

Thermostability analysis for DES1 is shown in Figure 4.4 (A) showing intermediate decomposition curves between the pure choline chloride and the levulinic acid. which have boiling point of 518.7 K, the DES shows two degradation steps, the first one between (380-525) K related to the vaporization of the carboxylic acid constituent of levulinic acid, and the second one between (525-575) K that can be attributed with the decomposition of choline chloride. As can be seen in Figure 4.4 (B), DES2, composed of choline chloride and ethylene glycol, shows a higher stability than pure ethylene glycol, which have vaporized at 470 K. Three clear stages of DES decomposition are presented. The first is a decomposition below the boiling point of ethylene glycol due to its high volatility, this occurs between 420 K and 560 k, the second occurring between 530 K and 560 K is due to



Figure 4.4. Dynamic TGA curves with a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$. Continuous line (—) shows the results for the HBA, (---) for HBD and (…) for DESs. In (A) DES1, (B) DES2 and (C) DES3

the complete vaporization of ethylene glycol. Finally, the third stage above 560 K is due to the decomposition of choline chloride.

System	T _{onset} / K		
	DES	ChCl	HBD
DES 1	517.87	599.37	522.34
DES 2	538.01	599.37	455.29
DES 3	513.38	599.37	444.51

Table 4.1. Tonset for DESs constituents and DES

As can be seen in Figure 4.4 (C), DES3 composed by choline chloride and phenol, was less stable because of the low stability of phenol. The loss of mass of the DES occurs again in three stages, the first given by the loss of the -OH constituent group of the phenol between 370 K and 455 K, the second when the temperature exceeds 455 K due to the complete vaporization of the phenol and finally, above 530 K the stage where the remaining choline chloride decomposes.

Table 4.2 shows the results for the surface tension measurements at 298.15 K. The highest surface tension value was 45.66 mN·m⁻¹ for DES2, while the lowest surface tension value was 35.46 mN·m⁻¹ for DES3. The first effect observed is that the surface tension decreases from the pure HBD for all DES. For the levulinic acid sufarce tension goes down from 42.53 mN·m⁻¹ to 39.35 mN·m⁻¹ in DES1 (Lomba, Giner, Bandrés, Lafuente, & Pino, 2011), and for ethylene glycol from 48.9 mN·m⁻¹ (Azizian & Hemmati, 2003) to 45.66 mN·m⁻¹ in DES2. There is a 7% of difference in the values reported by Mjalli et al, which must be mainly due to the difference in the experimental method and water content.

Table 4.2. Measured DES surface tension and literature comparison with pure HBD

System	$\gamma/mN\cdot \mathbf{m}^{-1}$	Lit. pure HBD	Reference
DES 1	39.35	42.53	(Lomba et al., 2011)
DES 2	45.66	48.90	(Azizian & Hemmati, 2003)
DES 3	35.46	Solid at RT	-

The surface tension its highly dependent on the strength of the molecular interaction so, although it was not measured, a descending behavior is expected with temperature. As can be noted, when choline chloride is added, the surface tension of DES decreases because there is a strong interaction between choline chloride with the respective HBD, this generates a reduction in the forces of cohesion with the surface of the pure HBD, decreasing to the surface tension.

4.3. Pure DESs density

The measurements were carried out for density and viscosity for three pure DES and their binary mixtures with 1-butanol between the temperature of 293.15 K and 333.15 K at atomospheric pressure. The results for pure compound and its comparison with values of the literature can be seen in Figure 4.5. It can be seen that the density decreases linearly with temperature, which is why a linear adjustment is made.

$$\rho(T) = a + bT \tag{4.1}$$

Parameters a and b of equation 4.1 and the correlation coefficient are presented in Table 4.3.

a	b	\mathbb{R}^2
1.3376	-0.0007	1
1.2855	-0.0006	1
1.2735	-0.0006	1
	a 1.3376 1.2855 1.2735	a b 1.3376 -0.0007 1.2855 -0.0006 1.2735 -0.0006

Table 4.3. Linear equation parameters for pure DESs density



Figure 4.5. Density (ρ) of pure DES1 (**•**), DES2 (**•**) and DES3 (**▲**) as function of temperature. Comparison with data reported from (\Box), (\circ) and (\triangle) (Sas et al., 2016; Harifi-Mood & Buchner, 2017; Guo et al., 2013). Dash shows fit according equation 4.1, parameters reported in Table 4.3

4.4. Pure DESs viscosity

For the viscosity, three adjustable parameter correlations were used, which were the Vogel-Fulcher-Tamman (VFT), Arrhenius and Litovitz equations (Andrade, 1934; Vogel, 1921; Litovitz, 1952). The Arrhenius equation is the one that follows:

$$\eta(T) = A \exp\left(\frac{-B}{RT}\right) \tag{4.2}$$

where A and B are adjustable parameters. The behavior of the Arrhenius equation seeks to explain in a simple way the behavior of the viscosity as a function of the temperature, which is an exponential decrease. However, the equation does not behave in a good way when the molecules to be described have small charge points, such as DES. For this it is necessary other equations such as VFT:

$$\eta(T) = A \cdot \exp\left(\frac{B}{T - T_0}\right) \tag{4.3}$$

where A, B and T_0 are adjustable parameters. The other equation that can describe this behavior its the Litovitz equation:

$$\eta(T) = A \cdot \exp\left(\frac{B}{RT^3}\right) \tag{4.4}$$

where A and B are the adjustable parameters. Figure 4.6 shows the viscosity of the pure



Figure 4.6. Viscosity (η) of pure DES1 (**•**), DES2 (**•**) and DES3 (**•**) as function of temperature. Fitted using different curves: Arrhenius (.....), Voguel-Fulcher-Tamman (---) and Litoviz (—). Parameters reported in Table 4.4

compounds and their exponential dependence on temperature. The equations are shown with continuous lines. It can be seen how VFT and Litovitz have a better performance in adjusting the viscosity curves for DES than Arrehnius, this is due as mentioned above to the ability of the latter two to adjust substances that have symmetric cations such as ionic liquids or DES. The adjustment parameters of the models for the pure substances of the DES studied can be found in Table 4.4.

DES1							
Model	А	В	T_0	AAD (%)			
Arrhenius	7.8E-06	-4.3E+04	-	6.27			
VFT	5.3E-05	4.0E+03	36.91	5.88			
Litovitz	3.4E-01	1.5E+09	-	0.87			
		DES2					
Model	А	В	T_0	AAD (%)			
Arrhenius	1.4E-06	-4.3E+04	-	24.52			
VFT	1.1E-04	4.3E+03	-34.73	2.06			
Litovitz	7.8E-01	9.1E+08	-	0.29			
		DES3					
Model	А	В	T ₀	AAD (%)			
Arrhenius	3.0E-06	-4.3E+04	-	9.15			
VFT	4.1E-05	4.0E+03	22.78	4.77			
Litovitz	3.8E-01	1.2E+09	-	2.20			

Table 4.4. Fitting parameters for pure DESs viscosity for differents models

4.5. DESs binary mixture properties

It is important to understand the molecular interactions that occur when mixing both compounds, for this purpose the excess properties were used. The experimental data available in Appendix C, shows the behavior of the density and viscosity, respect to the molar concentration and temperature.

4.5.1. Excess volume

It is expected that the density of the mixture will decrease monotonously when adding 1-butanol. It should be noted that this decrease is non-linear. The excess volume is calculated from equation 2.3. It is noteworthy that the DESs were treated as a pseduo-compound and not as a mixture, and therefore its molar weight was calculated as the weighting of the individual molecular weights by the molar fraction of each of the species. The Figure



Figure 4.7. Variation of excess molar volume (VE) with the mole fraction of 1-butanol, for the binary mixture of (A) DES1 + 1-butanol, (B) DES2 + 1-butanol, (C) DES3 + 1-butanol at different temperatures. (I) 293.15 K, (\bullet) 303.15 K, (\bullet) 313.15 K, (\bullet) 323.15 K and (\bullet) 333.15 K. Dash curve (---) shows fit according Redlich-Kister equation with parameters reported in Appendix C

4.7 shows the excess volume of the binary mixture of DESs + 1-butanol. This property,

show a clear negative behavior throughout the range of temperature and composition. It also shows a clear asymmetrical behavior, which is mainly due to the difference of shapes and sizes of the constituent compounds of the mixture. The minimum value of the volume of excess is obtained for a molar fraction of 1-butanol between 0.35 and 0.6 depending on the DES. The negative value of the excess volume shows a negative deviation from the ideality, that is, a contraction of the components when mixing. This contraction is affected by the concentration of 1-butanol, as well as by the temperature in all the range of the measurements. It is observed that the volume of excess becomes increasingly negative with the increase in temperature. This is the opposite of what happens with aqueous mixtures of DES (Yadav & Pandey, 2014; Kim & Park, 2018), where the volume of excess becomes less negative with the increase in temperature. This effect is probably due to the difference between the shapes and sizes of the compounds and the availability to form hydrogen bonds.

The excess volume is strongly influenced by intermolecular forces and interactions occurring between the alcohol and the DES, it is believed that the creation of a stable network of hydrogen bonds by mixing causes contraction of the substance. This chemical effect governs the mixture over physical, geometric or structural effects. Figure 4.8 shows the V^E for the three studied systems for each temperature as function of the molar fraction of 1-butanol. It can be seen that the DES3 shows a greater contraction in its volume than the other two components measured. This is probably due to the fact that the molecule that contributes the hydrogen bonds is a solid compound before the mixture (phenol) and that its structure only contributes with one position to form the hydrogen bonds.

4.5.2. Excess viscosity

At fixed temperature, the viscosities of mixtures decreased as the amount of 1-butanol increased. This can be explained by the presence of hydrogen bonding in pure DESs and between DESs with 1-butanol. The decrement of the strength of hydrogen bonding between the HBA and the HBD because the interaction between DES and 1-butanol leads



Figure 4.8. Variation of excess molar volume (VE) with the mole fraction of 1-Butanol (a), for the binary mixture of (\blacksquare) (DES1 + 1-Butanol), (\bullet) (DES2 + 1-Butanol) and (\blacktriangle) (DES3 + 1-Butanol) at the temperature of 293.15 K. Dash curve (---) show fit according Redlich-Kister equation with parameters reported in Appendix C

to a decrease in mixture viscosity. In addition, as the temperature increases the mixture viscosity decrease at fixed mixture concentration. This means that the mixture viscosity also represent temperature-dependent behavior.

The excess viscosity was calculated from equation 2.5 and shown in Figure 4.9. DESs were treated as a pseduo-compound. The excess viscosity curves are asymmetric, and the minimum are found in the DES-rich region, especially in DES1, which obtains the largest deviation from ideality with a low addition of a 1-butanol. In other words, 1-butanol effectively reduces the viscosity of DESs. In addition, it is observed that the excess viscosity shows an inverse behavior to the volume of excess, this becomes less negative when the temperature increases. It is believed that this interaction is mediated mainly

by the interstitial accommodation of the components of the mixture and the creation of networks of hydrogen bonds as mentioned above.



Figure 4.9. Variation of excess viscosity (η^E) with the mole fraction of 1-butanol, for the binary mixture of (A) DES1 + 1-butanol, (B) DES2 + 1-butanol, (C) DES3 + 1-butanol at different temperatures. (**•**) 293.15 K, (**•**) 303.15 K, (**•**) 313.15 K, (**•**) 323.15 K and (**•**) 333.15 K. Dash curve shows fit according Redlich-Kister equation with parameters reported in Appendix C

4.5.3. Excess enthalpy

Experimental excess molar enthalpies (H^E) as well as fitting curves from Redlich-Kister equation are presented in Figure 4.10. Negative enthalpies were found for the three DES + 1-butanol systems. Moderate negatives values were found for DESs systems with the minimum around (1100 - 800 J·mol⁻¹). Therefore, taking into account that negative excess enthalpy involves a net creation of interactions like hydrogen bonds upon mixing as previously proposed, it can be stated that for DESs the forces between the ions or molecules that form the dissimilar species, (DES-1-butanol interactions), are stronger than between those of similar species as DES with DES and HBD with HBD.



Figure 4.10. Variation of excess enthalpy (H^E) with the mole fraction of 1-butanol, for the binary mixture of (**•**) DES1 + 1-butanol, (**•**) DES2 + 1-butanol and (**•**) DES3 + 1-butanol at 313.15 K. Dash curve shows fit according Redlich-Kister equation with parameters reported in Appendix C

For all systems studied, the signs of excess volumes and viscosity coincide with those of the excess enthalpies. This is due to the fact that, like the excess volume, the excess enthalpy can be explained due to the creation of new networks of hydrogen bonds due to the mixing and interstitial accommodation of the 1-butanol molecules in the structure of the DES. As discussed previously, this network of hydrogen bonds is created immediately after mixing due to the interactions between carbonyl groups and the different electrically charged centers that have the DES, which explains that all enthalpies of excess are negative, like the excess volume.

4.6. Viscosity prediction using hard-sphere scheme

As noted, viscosity had been correlated for a large number of DESs for which data were available at atmospheric pressure. Parameters of V₀ (equation 3.6 by fitting viscosity data for each DESs data set and R_{η} was obtained by fitting viscosity experimental data using the value of V₀ obtained previously. Optimized values of d_i, as well as the parameter R_{η} for the data at 0.1 MPa are listed in Table 4.5, together with data references and values of Average Absolute Deviations (AADs) between calculated and experimental data. In all, 230 viscosity data points for 21 DESs data points were correlated. The overall AAD for the viscosity data was 1.212 %, the BIAS was 0.018 % and the maximum deviation (MD) was 2.613 %.

Values of V_0 and R_η for DESs with a common anion were found to follow regular trends with the molecular weight (M_w) of the DES for atmospheric pressure systems. The predictive capability of the scheme was demonstrated in all the cases of DESs using calculated values of V_0 and R_η and the experimental density at one specific temperature. This is shown in the Figure 4.11 where for almost all the systems the scheme retains an error of less than 5%. This work can be compared with Gaciño *et al.* (2014) where the hard-sphere scheme was used to predict ionic liquids viscosity and thermal conductivity , in general it is observed that the orders of magnitude of the parameters V_0 and R_η are aligned with this work for DES. In addition, similar values were obtained for the AAD and points below the 5% of error, that is, the use of the scheme for viscosity prediction from experimental DESs density data could be validated.



Figure 4.11. Pure DESs viscosity prediction error using the hard-sphere scheme.

The method was also used for mixtures of DESs + solvent. Excess viscosities of such mixtures are generally small. Therefore, simple linear mixing rules can be used to calculate the viscosity of the mixture. Not surprisingly, the viscosities of mixtures specially with water cannot be predicted using equation 3.6, because the addition of water usually leads to a dramatic decrease in the viscosity. Therefore, the following mixing rule for mixtures of DES:

$$\log(\eta_{\rm mix}) = x_1 \log(\eta_1) + x_2 \log(\eta_2) + 2x_1 x_2 k_{12} \left(\frac{M_1 M_2}{M_{\rm mix}}\right)^{1/2}$$
(4.5)

where M_{mix} , M_1 , and M_2 are molecular weights of the mixture, component 1, and component 2, respectively, and k_{12} is a interaction parameter which was found to be temperature dependent, in a polynomial form with a parameter a_i . Values for a_i for mixtures

Abbreviaton	\mathbf{d}_0	d ₁	d_2	d_3	Viscosity				
	Ť	-	-	÷	•	Dev>5%	AAD (%)	BIAS (%)	MD (%)
DES1	2.36E-04	-1.23E-06	3.70E-09	-3.65E-12	4.93	0	0.607	-0.094	1.004
DES2	1.03E-04	-2.74E-07	7.92E-10	-7.04E-13	2.03	0	0.167	0.011	0.286
DES3	3.37E-04	-2,39E-06	7.76E-09	-8.35E-12	1.00	0	1,433	-0.003	3.285
DES4	4.13E-05	4.90E-07	-1.78E-09	2.14E-12	2.16	0	0.590	0.007	1.261
DES5	-3.12E-03	3.13E-05	-1.02E-07	1.10E-10	1.01	0	1.897	-0.029	3.890
DES6	1.32E-03	-1.21E-05	3.93E-08	-4.26E-11	1.03	0	2.034	-0.027	4.280
DES7	1.73E-03	-1.60E-05	5.21E-08	-5.63E-11	1.05	0	2.031	-0.022	3.351
DES8	1.11E-03	-1.00E-05	3.28E-08	-3.56E-11	1.06	0	1.288	-0.006	1.864
DES9	5.15E-12	9.75E-07	-3.06E-09	3.29E-12	1.60	0	1.934	-0.012	3.411
DES10	1.04E-04	-2.17E-07	3.36E-10	2.53E-16	2.15	1	2.434	-0.117	5.505
DES11	1.20E-04	-2.41E-07	7.20E-10	-6.98E-13	5.94	1	2.261	-0.067	5.263
DES12	8.38E-05	4.10E-08	-2.10E-10	3.30E-13	0.99	1	1.931	0.223	5.079
DES13	6.88E-05	2.33E-07	-8.89E-10	1.11E-12	0.98	0	2.564	0.230	4.689
DES14	3.51E-04	-2.07E-06	6.17E-09	-5.98E-12	1.99	0	1.885	-0.012	3.563
DES15	1.92E-04	-4.98E-07	1.36E-09	-1.10E-12	5.09	0	0.221	0.011	0.451
DES16	1.52E-04	-2.55E-07	6.50E-10	-4.40E-13	6.17	0	0.167	0.007	0.389
DES17	5.49E-04	-3.54E-06	1.08E-08	-1.08E-11	7.56	1	1.653	-0.068	6.674
DES18	1.26E-04	-6.82E-08	1.71E-10	-1.32E-13	2.00	0	0.300	0.300	0.550
DES19	8.99E-05	-4.85E-08	1.26E-10	-9.62E-14	7.65	0	0.010	0.010	0.021
DES20	8.91E-05	-4.66E-08	1.19E-10	-8.37E-14	4.04	0	0.029	0.018	0.050
DES21	9.58E-05	-4.90E-08	1.28E-10	-7.65E-14	5.14	0	0.009	0.009	0.016
						4/230	1,212	0,018	2,613

Table 4.5. V_0 parameters and prediction statistical results in hard-sphere viscosity prediction scheme

were obtained by fitting mixtures viscosity data as described for pure DESs, and calculated viscosities of mixtures are shown in Table 4.6. Although the errors of the model are greater than for the pure DES, the model shows good results. In the future the work should be focus on finding a more adequate mixing rule than the linear to avoid the dependence on the interaction parameter and thus not add adjustable parameters to the model. Table 4.6 also lists AADs between calculated and experimental viscosities, as well as the number of data points for each system. AADs were found to be 4.82 %, for all systems. Especially the system with water shows a bad behavior as expected due to the inability of the model to detect large changes in the viscosity of the mixture, having an AAD of 8.45 %, this is shown in the Figure 4.12.



Figure 4.12. Pure DESs viscosity prediction error using the hard-sphere scheme.

Table 4.6. Fitting parameters for DESs binary mixtures viscosity for different models. Data obtained from (Sas et al., 2016; Yadav & Pandey, 2014; Harifi-Mood & Buchner, 2017)

Abbreviaton	a ₀	a_1	a_2	Viscosity				
				Ν	Dev>5%	AAD (%)	BIAS (%)	MD (%)
DES1 + Ethanol	-39.68	0.23	-3.38E-04	39	0	1.53	-0.26	3,67
DES1 + 1-Propanol	202.38	-1.34	2.20E-03	39	15	6.06	-0.74	32.75
DES1 + 1-Butanol	-22.36	0.12	-1.60E-04	39	15	4.51	-0.88	12.22
DES1 + 1-Pentanol	-51.87	0.31	-4.66E-04	39	16	6.28	-0.52	21.84
DES10 + Water	-384.71	2.36	-3.62E-03	88	54	8.45	2.21	41,11
DES2 + DMSO	-33.43	0.24	-4.07E-04	110	11	2.08	0.09	7.51
					111/354	4,82	-0,02	19,85

5. CONCLUSIONS AND PERSPECTIVES

In this study, thermophysical properties such as, decomposition temperature, surface tension, density and viscosity were measured for three pure DESs from T = (293.15 to 333.15) K at atmospheric pressure. Different experimental methods such as NMR and FTIR were used to describe the interaction between the functional groups constituting the mixture, proving that no reaction occurs in the mixture but strong intermolecular interactions. In addition, the decomposition temperature was analyzed by TGA to check the thermostability of the DES, t was demonstrated that the DES have better thermal stability than their HBD and that their decomposition temperatures are above 400 K, which could classify them as good candidates for separation processes at moderate temperatures. However, it was also observed that the analyzed DES were decomposed in stages and not as a single compound, which would not be beneficial in an industrial process. The density and viscosity data were adjusted using different equations and the parameters are shown in this work. It is shown that the density and viscosity decrease as the temperature increases.

To study the dependence of the concentration, the physicochemical properties of the binary mixture of the three DESs studied with 1-butanol in a temperature range from T = (293.15 to 333.15) K at atmospheric pressure were measured. From the experimental data, the excess molar volume and excess viscosity were determined, and the results were fitted with the RedlichKister equation. The molar excess volume, excess viscosity and excess enthalpy are negative in the entire range of compositions and temperature. This behavior, which is far from ideality, is mainly caused by the strong hydrogen bond type interactions that were generated between the DES and 1-butanol. A complete new network of hydrogen bonds was created, that achieved a contraction of the excess properties. The viscosity deviation presents a deviation close from ideality as the temperature increases while the excess molar volume presents a more negative deviation with as the temperature increases.

The knowledge about physicochemical properties of the DES will serve to use both empirical and predictive models in the calculation of the properties necessary to carry out the industrial scaling of a separation process. In order to get futher knowledge about how intermolecular interactions behave, it would be interesting to study the excess properties for DES constituted from a single chemical family of HBD (ie carboxylic acids) with a varied amount of alcohols (methanol, ethanol, propanol , butanol), in order to understand how the length of the chain, or the amount of hydroxyl groups affects the thermophysical properties. At the same time, carry out an isothermal analysis of thermogavimetry, since this way it could be known if the DES volatilizes under its decomposition temperature, for example, to extraction conditions for a separation. Finally, measure the density and viscosity of DESs with different families of HBDs and molar concentrations to generate relationships of the adjustable parameters of the hard-sphere model, and with this improve the predictive capacity of the model.

REFERENCES

- Abbas, Q., & Binder, L. (2010). Synthesis and characterization of choline chloride based binary mixtures. *ECS transactions*, *33*(7), 49–59.
- Abbott, A. P., Barron, J. C., Ryder, K. S., & Wilson, D. (2007). Eutectic-based ionic liquids with metal-containing anions and cations. *Chemistry-A European Journal*, 13(22), 6495–6501.
- Abbott, A. P., Boothby, D., Capper, G., Davies, D. L., & Rasheed, R. K. (2004). Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids. *Journal of the American Chemical Society*, 126(29), 9142–9147.
- Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K., & Tambyrajah, V. (2003). Novel solvent properties of choline chloride/urea mixtures. *Chemical Communications*(1), 70–71.
- Abbott, A. P., Capper, G., & Gray, S. (2006). Design of improved deep eutectic solvents using hole theory. *Chemphyschem: a European journal of chemical physics and physical chemistry*, 7(4), 803–806.
- Abbott, A. P., Harris, R. C., & Ryder, K. S. (2007). Application of hole theory to define ionic liquids by their transport properties. *The Journal of Physical Chemistry B*, 111(18), 4910–4913.
- Abbott, A. P., Harris, R. C., Ryder, K. S., D'Agostino, C., Gladden, L. F., & Mantle, M. D. (2011). Glycerol eutectics as sustainable solvent systems. *Green Chemistry*, 13(1), 82–90.
- Aissaoui, T. (2015). Novel contribution to the chemical structure of choline chloride based deep eutectic solvents. *Pharm Anal Acta*, *6*, 11.
- AlOmar, M. K., Hayyan, M., Alsaadi, M. A., Akib, S., Hayyan, A., & Hashim, M. A. (2016). Glycerol-based deep eutectic solvents: physical properties. *Journal of Molecular Liquids*, 215, 98–103.

- Altamash, T., Atilhan, M., Aliyan, A., Ullah, R., Nasser, M., & Aparicio, S. (2017). Rheological, thermodynamic, and gas solubility properties of phenylacetic acid-based deep eutectic solvents. *Chemical Engineering & Technology*, 40(4), 778–790.
- Andrade, E. d. C. (1934). Lviii. a theory of the viscosity of liquids.part ii. *The London*, *Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 17(113), 698–732.
- Arce, A., Rodil, E., & Soto, A. (2006). Physical and excess properties for binary mixtures of 1-methyl-3-octylimidazolium tetrafluoroborate,[omim][bf 4], ionic liquid with different alcohols. *Journal of solution chemistry*, 35(1), 63–78.
- Aschenbrenner, O., Supasitmongkol, S., Taylor, M., & Styring, P. (2009). Measurement of vapour pressures of ionic liquids and other low vapour pressure solvents. *Green Chemistry*, 11(8), 1217–1221.
- Assael, M., Dymond, J., Papadaki, M., & Patterson, P. (1992). Correlation and prediction of dense fluid transport coefficients. i. n-alkanes. *International journal of thermophysics*, 13(2), 269–281.
- Atkins, P. (1978). Molecules in motion: ion transport and molecular diffusion. *Physical chemistry*, 819–848.
- Atkins, P., & De Paula, J. (2006). Atkins physical chemistry. New York, 77.
- Azizian, S., & Hemmati, M. (2003). Surface tension of binary mixtures of ethanol+ ethylene glycol from 20 to 50 c. *Journal of Chemical & Engineering Data*, 48(3), 662–663.
- Bini, R., Malvaldi, M., Pitner, W. R., & Chiappe, C. (2008). Qspr correlation for conductivities and viscosities of low-temperature melting ionic liquids. *Journal of Physical Organic Chemistry*, 21(7-8), 622–629.
- Blusztajn, J. K. (1998). Choline, a vital amine. Science, 281(5378), 794–795.
- Bonhote, P., Dias, A.-P., Papageorgiou, N., Kalyanasundaram, K., & Grätzel, M. (1996). Hydrophobic, highly conductive ambient-temperature molten salts. *Inorganic chemistry*, 35(5), 1168–1178.
- Ciotta, F., Trusler, J. M., & Vesovic, V. (2014). Extended hard-sphere model for the

viscosity of dense fluids. Fluid Phase Equilibria, 363, 239-247.

- Crosthwaite, J. M., Muldoon, M. J., Dixon, J. K., Anderson, J. L., & Brennecke, J. F. (2005). Phase transition and decomposition temperatures, heat capacities and viscosities of pyridinium ionic liquids. *The Journal of Chemical Thermodynamics*, 37(6), 559–568.
- D'Agostino, C., Harris, R. C., Abbott, A. P., Gladden, L. F., & Mantle, M. D. (2011).
 Molecular motion and ion diffusion in choline chloride based deep eutectic solvents studied by 1 h pulsed field gradient nmr spectroscopy. *Physical Chemistry Chemical Physics*, *13*(48), 21383–21391.
- Delgado-Mellado, N., Larriba, M., Navarro, P., Rigual, V., Ayuso, M., García, J., & Rodríguez, F. (2018). Thermal stability of choline chloride deep eutectic solvents by tga/ftir-atr analysis. *Journal of Molecular Liquids*, 260, 37–43.
- De Los Rios, A. P., & Fernandez, F. J. H. (2014). *Ionic liquids in separation technology*. Elsevier.
- Domańska, U., Pobudkowska, A., & Wiśniewska, A. (2006). Solubility and excess molar properties of 1, 3-dimethylimidazolium methylsulfate, or 1-butyl-3-methylimidazolium octylsulfate ionic liquids with n-alkanes and alcohols: Analysis in terms of the pfp and fbt models. *Journal of solution chemistry*, 35(3), 311–334.
- Ficke, L. E., Rodrguez, H., & Brennecke, J. F. (2008). Heat capacities and excess enthalpies of 1-ethyl-3-methylimidazolium-based ionic liquids and water. *Journal of Chemical & Engineering Data*, 53(9), 2112–2119.
- Florindo, C., Oliveira, F., Rebelo, L., Fernandes, A. M., & Marrucho, I. (2014). Insights into the synthesis and properties of deep eutectic solvents based on cholinium chloride and carboxylic acids. ACS Sustainable Chemistry & Engineering, 2(10), 2416–2425.
- Francisco, M., van den Bruinhorst, A., & Kroon, M. C. (2012). New natural and renewable low transition temperature mixtures (lttms): screening as solvents for lignocellulosic biomass processing. *Green Chemistry*, 14(8), 2153–2157.

- Francisco, M., van den Bruinhorst, A., & Kroon, M. C. (2013). Low-transitiontemperature mixtures (lttms): A new generation of designer solvents. *Angewandte Chemie international edition*, 52(11), 3074–3085.
- Fredlake, C. P., Crosthwaite, J. M., Hert, D. G., Aki, S. N., & Brennecke, J. F. (2004). Thermophysical properties of imidazolium-based ionic liquids. *Journal of Chemical & Engineering Data*, 49(4), 954–964.
- Fukaya, Y., Iizuka, Y., Sekikawa, K., & Ohno, H. (2007). Bio ionic liquids: room temperature ionic liquids composed wholly of biomaterials. *Green Chemistry*, 9(11), 1155–1157.
- Gaciño, F. M., Comuñas, M. J., Fernández, J., Mylona, S. K., & Assael, M. J. (2014). Correlation and prediction of dense fluid transport coefficients. ix. ionic liquids. *International Journal of Thermophysics*, 35(5), 812–829.
- Gardas, R. L., & Coutinho, J. A. (2008). A group contribution method for viscosity estimation of ionic liquids. *Fluid Phase Equilibria*, 266(1-2), 195–201.
- Ghosh, T., Prasad, D., Dutt, N., Rani, K., et al. (2007). Viscosity of liquids: Theory, estimation, experiment, and data. Springer: New York.
- Gómez, E., González, B., Calvar, N., Tojo, E., & Domínguez, Á. (2006). Physical properties of pure 1-ethyl-3-methylimidazolium ethylsulfate and its binary mixtures with ethanol and water at several temperatures. *Journal of Chemical & Engineering Data*, 51(6), 2096–2102.
- González, E. J., González, B., Calvar, N., & Domínguez, Á. (2007). Physical properties of binary mixtures of the ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate with several alcohols at t=(298.15, 313.15, and 328.15) k and atmospheric pressure. *Journal of Chemical & Engineering Data*, 52(5), 1641–1648.
- Guo, W., Hou, Y., Ren, S., Tian, S., & Wu, W. (2013). Formation of deep eutectic solvents by phenols and choline chloride and their physical properties. *Journal of Chemical & Engineering Data*, 58(4), 866–872.
- Gutiérrez, M. C., Carriazo, D., Ania, C. O., Parra, J. B., Ferrer, M. L., & del Monte, F.(2011). Deep eutectic solvents as both precursors and structure directing agents in

the synthesis of nitrogen doped hierarchical carbons highly suitable for co 2 capture. *Energy & Environmental Science*, 4(9), 3535–3544.

- Haghbakhsh, R., Parvaneh, K., Raeissi, S., & Shariati, A. (2018). A general viscosity model for deep eutectic solvents: the free volume theory coupled with association equations of state. *Fluid Phase Equilibria*, 470, 193–202.
- Haghbakhsh, R., Raeissi, S., Parvaneh, K., & Shariati, A. (2018). The friction theory for modeling the viscosities of deep eutectic solvents using the cpa and pc-saft equations of state. *Journal of Molecular Liquids*, 249, 554–561.
- Harifi-Mood, A. R., & Buchner, R. (2017). Density, viscosity, and conductivity of choline chloride+ ethylene glycol as a deep eutectic solvent and its binary mixtures with dimethyl sulfoxide. *Journal of Molecular Liquids*, 225, 689–695.
- Hayyan, A., Mjalli, F. S., AlNashef, I. M., Al-Wahaibi, T., Al-Wahaibi, Y. M., & Hashim,
 M. A. (2012). Fruit sugar-based deep eutectic solvents and their physical properties. *Thermochimica acta*, 541, 70–75.
- Homan, T., Shahbaz, K., & Farid, M. M. (2017). Improving the production of propyl and butyl ester-based biodiesel by purification using deep eutectic solvents. *Separation* and Purification Technology, 174, 570–576.
- Hosseini, S. M., Alavianmehr, M. M., & Moghadasi, J. (2016). Transport properties of pure and mixture of ionic liquids from new rough hard-sphere-based model. *Fluid Phase Equilibria*, 429, 266–274.
- Hou, Y., Gu, Y., Zhang, S., Yang, F., Ding, H., & Shan, Y. (2008). Novel binary eutectic mixtures based on imidazole. *Journal of Molecular Liquids*, 143(2-3), 154–159.
- Kareem, M. A., Mjalli, F. S., Hashim, M. A., Hadj-Kali, M. K., Bagh, F. S. G., & Alnashef, I. M. (2012). Phase equilibria of toluene/heptane with tetrabutylphosphonium bromide based deep eutectic solvents for the potential use in the separation of aromatics from naphtha. *Fluid Phase Equilibria*, 333, 47–54.
- Kareem, M. A., Mjalli, F. S., Hashim, M. A., Hadj-Kali, M. K., Bagh, F. S. G., & Alnashef, I. M. (2013). Phase equilibria of toluene/heptane with deep eutectic solvents based on ethyltriphenylphosphonium iodide for the potential use in the separation of

aromatics from naphtha. The Journal of Chemical Thermodynamics, 65, 138-149.

- Kim, K.-S., & Park, B. H. (2018). Volumetric properties of solutions of choline chloride+ glycerol deep eutectic solvent with water, methanol, ethanol, or iso-propanol. *Journal of Molecular Liquids*, 254, 272–279.
- Leron, R. B., Soriano, A. N., & Li, M.-H. (2012). Densities and refractive indices of the deep eutectic solvents (choline chloride+ ethylene glycol or glycerol) and their aqueous mixtures at the temperature ranging from 298.15 to 333.15 k. *Journal of the Taiwan Institute of Chemical Engineers*, 43(4), 551–557.
- Letcher, T. (1975). The excess volumes of some mixtures of saturated and unsaturated c6 hydrocarbons. *ChemInform*, 6(22).
- Levine, I. (2009). Physical chemistry. McGrawHill Book Company, 3.
- Li, G., Jiang, Y., Liu, X., & Deng, D. (2016). New levulinic acid-based deep eutectic solvents: Synthesis and physicochemical property determination. *Journal of Molecular Liquids*, 222, 201–207.
- Li, Y., Ye, H., Zeng, P., & Qi, F. (2010). Volumetric properties of binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate with aniline. *Journal of solution chemistry*, 39(2), 219–230.
- Liebert, V., Nebig, S., & Gmehling, J. (2008). Experimental and predicted phase equilibria and excess properties for systems with ionic liquids. *Fluid Phase Equilibria*, 268(1-2), 14–20.
- Litovitz, T. A. (1952). Temperature dependence of the viscosity of associated liquids. *The Journal of Chemical Physics*, 20(7), 1088–1089.
- Lomba, L., Giner, B., Bandrés, I., Lafuente, C., & Pino, M. R. (2011). Physicochemical properties of green solvents derived from biomass. *Green chemistry*, 13(8), 2062– 2070.
- Marcus, Y. (2018). Estimation of the critical temperatures of some more deep eutectic solvents from their surface tensions. *Advances in Materials Science and Engineering*, 2018.

Maugeri, Z., & de María, P. D. (2011). Rsc adv., 2012, 2, 421-425 rsc;(b) ap abbott, rc

harris, ks ryder, c. d'agostino, lf gladden and md mantle. Green Chem, 13, 82-90.

- Mehra, R., & Pancholi, M. (2006). Temperature-dependent studies of thermo-acoustic parameters in hexane+ 1-dodecanol and application of various theories of sound speed. In *Indian journal of physics and proceedings of the indian association for the cultivation of science* (Vol. 80, pp. 253–263).
- Merza, F., Fawzy, A., AlNashef, I., Al-Zuhair, S., & Taher, H. (2018). Effectiveness of using deep eutectic solvents as an alternative to conventional solvents in enzymatic biodiesel production from waste oils. *Energy Reports*, 4, 77–83.
- Mjalli, F. S., Murshid, G., Al-Zakwani, S., & Hayyan, A. (2017). Monoethanolaminebased deep eutectic solvents, their synthesis and characterization. *Fluid Phase Equilibria*, 448, 30–40.
- Mjalli, F. S., Vakili-Nezhaad, G., Shahbaz, K., & AlNashef, I. M. (2014). Application of the eötvos and guggenheim empirical rules for predicting the density and surface tension of ionic liquids analogues. *Thermochimica Acta*, *575*, 40–44.
- Mulyono, S., Hizaddin, H. F., Alnashef, I. M., Hashim, M. A., Fakeeha, A. H., & Hadj-Kali, M. K. (2014). Separation of btex aromatics from n-octane using a (tetrabutylammonium bromide+ sulfolane) deep eutectic solvent–experiments and cosmo-rs prediction. *Rsc Advances*, 4(34), 17597–17606.
- Nebig, S., & Gmehling, J. (2011). Prediction of phase equilibria and excess properties for systems with ionic liquids using modified unifac: Typical results and present status of the modified unifac matrix for ionic liquids. *Fluid Phase Equilibria*, 302(1-2), 220–225.
- Pham, T. P. T., Cho, C.-W., & Yun, Y.-S. (2010). Environmental fate and toxicity of ionic liquids: a review. *Water research*, 44(2), 352–372.
- Podgorsek, A., Jacquemin, J., Pádua, A., & Costa Gomes, M. (2016). Mixing enthalpy for binary mixtures containing ionic liquids. *Chemical reviews*, 116(10), 6075–6106.
- Polishuk, I. (2013). Implementation of perturbed-chain statistical associating fluid theory (pc-saft), generalized (g) saft+ cubic, and cubic-plus-association (cpa) for modeling thermophysical properties of selected 1-alkyl-3-methylimidazolium ionic liquids in

a wide pressure range. The Journal of Physical Chemistry A, 117(10), 2223–2232.

- Redhi, G. G. (2003). *Thermodynamics of liquid mixtures containing carboxylic acids* (Unpublished doctoral dissertation). University of Natal, Durban.
- Renon, H., & Prausnitz, J. M. (1968). Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE journal*, 14(1), 135–144.
- Rodríguez, H. (2015). Ionic liquids for better separation processes. Springer.
- Ruß, C., & König, B. (2012). Low melting mixtures in organic synthesis–an alternative to ionic liquids? *Green Chemistry*, 14(11), 2969–2982.
- Sander, A., Rogošić, M., Slivar, A., & Žuteg, B. (2016). Separation of hydrocarbons by means of liquid-liquid extraction with deep eutectic solvents. *Solvent Extraction and Ion Exchange*, 34(1), 86–98.
- Sas, O. G., Fidalgo, R., Domínguez, I., Macedo, E. A., & Gonzlez, B. (2016). Physical properties of the pure deep eutectic solvent,[chcl]:[lev](1: 2) des, and its binary mixtures with alcohols. *Journal of Chemical & Engineering Data*, 61(12), 4191– 4202.
- Shahbaz, K., Baroutian, S., Mjalli, F., Hashim, M., & AlNashef, I. (2012). Densities of ammonium and phosphonium based deep eutectic solvents: Prediction using artificial intelligence and group contribution techniques. *Thermochimica Acta*, 527, 59–66.
- Shahbaz, K., Mjalli, F., Hashim, M., & AlNashef, I. (2011). Prediction of deep eutectic solvents densities at different temperatures. *Thermochimica Acta*, 515(1-2), 67–72.
- Shahbaz, K., Mjalli, F. S., Hashim, M., Al-Nashef, I. M., et al. (2010). Using deep eutectic solvents for the removal of glycerol from palm oil-based biodiesel. *Journal* of Applied Sciences, 10(24), 3349–3354.
- Singh, T., & Kumar, A. (2008). Physical and excess properties of a room temperature ionic liquid (1-methyl-3-octylimidazolium tetrafluoroborate) with n-alkoxyethanols (c 1 e m, m= 1 to 3) at t=(298.15 to 318.15) k. *The Journal of Chemical Thermodynamics*, 40(3), 417–423.

Smith, E. L., Abbott, A. P., & Ryder, K. S. (2014). Deep eutectic solvents (dess) and their

applications. Chemical reviews, 114(21), 11060-11082.

- Smith, W. F., & Hashemi, J. (2011). Foundations of materials science and engineering. McGraw-Hill.
- SU, H.-Z., YIN, J.-M., LIU, Q.-S., & LI, C.-P. (2015). Properties of four deep eutectic solvents: Density, electrical conductivity, dynamic viscosity and refractive index. *Acta Physico-Chimica Sinica*, 31(8), 1468–1473.
- Sun, L., Wick, C. D., Siepmann, J. I., & Schure, M. R. (2005). Temperature dependence of hydrogen bonding: An investigation of the retention of primary and secondary alcohols in gas- liquid chromatography. *The Journal of Physical Chemistry B*, 109(31), 15118–15125.
- Tang, B., Zhang, H., & Row, K. H. (2015). Application of deep eutectic solvents in the extraction and separation of target compounds from various samples. *Journal of separation science*, 38(6), 1053–1064.
- Ullah, R., Atilhan, M., Anaya, B., Khraisheh, M., García, G., ElKhattat, A., ... Aparicio, S. (2015). A detailed study of cholinium chloride and levulinic acid deep eutectic solvent system for co 2 capture via experimental and molecular simulation approaches. *Physical Chemistry Chemical Physics*, 17(32), 20941–20960.
- Verma, R., & Banerjee, T. (2018). Liquid–liquid extraction of lower alcohols using menthol-based hydrophobic deep eutectic solvent: Experiments and cosmo-sac predictions. *Industrial & Engineering Chemistry Research*, 57(9), 3371–3381.
- Vogel, H. (1921). The law of the relation between the viscosity of liquids and the temperature. *Phys. Z*, 22, 645–646.
- Walas, S. M. (2013). Phase equilibria in chemical engineering. Butterworth-Heinemann.
- Wasserscheid, P., & Welton, T. (2008). Ionic liquids in synthesis. John Wiley & Sons.
- Wei, D., Han, S., & Wang, B. (2014). Excess molar enthalpies for binary mixtures of cyclopentanone, cyclohexanone, or cycloheptanone with n-nonane at t= 298.15 k and atmospheric pressure. *The Journal of Chemical Thermodynamics*, 76, 87–92.
- Wilhelm, E., & Letcher, T. (2014). Volume properties: Liquids, solutions and vapours.Royal Society of Chemistry.

- Yadav, A., Kar, J. R., Verma, M., Naqvi, S., & Pandey, S. (2015). Densities of aqueous mixtures of (choline chloride+ ethylene glycol) and (choline chloride+ malonic acid) deep eutectic solvents in temperature range 283.15–363.15 k. *Thermochimica Acta*, 600, 95–101.
- Yadav, A., & Pandey, S. (2014). Densities and viscosities of (choline chloride+ urea) deep eutectic solvent and its aqueous mixtures in the temperature range 293.15 k to 363.15 k. *Journal of Chemical & Engineering Data*, 59(7), 2221–2229.
- Yadav, A., Trivedi, S., Rai, R., & Pandey, S. (2014). Densities and dynamic viscosities of (choline chloride+ glycerol) deep eutectic solvent and its aqueous mixtures in the temperature range (283.15–363.15) k. *Fluid Phase Equilibria*, 367, 135–142.
- Yang, C., Xu, W., & Ma, P. (2004). Thermodynamic properties of binary mixtures of p-xylene with cyclohexane, heptane, octane, and n-methyl-2-pyrrolidone at several temperatures. *Journal of Chemical & Engineering Data*, 49(6), 1794–1801.
- Yang, C., Xu, W., & Ma, P. (2005). Thermodynamic properties of binary mixtures of p-xylene with cyclohexane, heptane, octane, and n-methyl-2-pyrrolidone at several temperatures. *Journal of Chemical & Engineering Data*, 50(2), 732–732.
- Zhang, Q., Vigier, K. D. O., Royer, S., & Jérôme, F. (2012). Deep eutectic solvents: syntheses, properties and applications. *Chemical Society Reviews*, 41(21), 7108– 7146.
- Zhao, D., Liao, Y., & Zhang, Z. (2007). Toxicity of ionic liquids. *Clean–soil, air, water*, 35(1), 42–48.
- Zullaikah, S., Rachmaniah, O., Utomo, A. T., Niawanti, H., & Ju, Y. H. (2018). Green separation of bioactive natural products using liquefied mixture of solids. In *Green chemistry*. InTech.

APPENDIX



A. APPENDIX A: NMR AND FTIR SPECTRA

Figure A.1. NMR - 1 H for choline chloride in D₂O



Figure A.2. NMR - 1 H for levulinic acid in D₂O



Figure A.3. NMR - 1 H for ethylene glycol in D₂O



Figure A.4. NMR - 1 H for phenol in D₂O


Figure A.5. NMR - 1 H for DES1 in D₂O



Figure A.6. NMR - 1 H for DES2 in D₂O



Figure A.7. NMR - 1 H for DES3 in D₂O



Figure A.8. ¹H-¹H COSY analysis for DES1







Figure A.10. ¹H-¹H COSY analysis for DES3

B. APPENDIX B: EXPERIMENTAL DATA AND PARAMETERS

1-butanol + DES1 Temperature (K) 293.15 303.15 313.15 323.15 333.15 \mathbf{x}_1 0.0000 1.1419 1.1352 1.1285 1.1219 1.1153 0.1658 1.0976 1.0907 1.0838 1.0770 1.0703 0.3163 1.0533 1.0463 1.0393 1.0323 1.0254 0.4555 1.0095 1.0024 0.9953 0.9881 0.9810 0.9746 0.9673 0.9601 0.9528 0.9455 0.5597 0.9196 0.9122 0.9047 0.8972 0.8896 0.7163 0.8220 0.8799 0.8724 0.8648 0.8572 0.8494 0.8912 0.8536 0.8461 0.8384 0.8307 0.8227 1.0000 0.8095 0.8019 0.7941 0.7862 0.7781 1-butanol + DES2 Temperature (K) 293.15 303.15 313.15 323.15 333.15 \mathbf{X}_1 0.0000 1.1195 1.1139 1.1081 1.1025 1.0969 0.1328 1.0738 1.0679 1.0620 1.0561 1.0503 0.2454 1.0349 1.0288 1.0227 1.0167 1.0106 0.9946 0.9883 0.9819 0.9756 0.9693 0.3660 0.5226 0.9449 0.9383 0.9316 0.9249 0.9181 0.6290 $0.9128 \quad 0.9059 \quad 0.8990 \quad 0.8920 \quad 0.8850$ 0.8767 0.8696 0.8624 0.8551 0.8477 0.7538 0.8699 $0.8443 \quad 0.8370 \quad 0.8296 \quad 0.8220 \quad 0.8143$ $0.8095 \quad 0.8019 \quad 0.7941 \quad 0.7862 \quad 0.7781$ 1.0000 1-butanol + DES3 Temperature (K) 293.15 303.15 313.15 323.15 333.15 \mathbf{X}_1 0.0000 1.0994 1.0934 1.0874 1.0815 1.0756 1.0406 1.0342 1.0277 1.0214 1.0150 0.2347 0.9850 0.9783 0.9716 0.9649 0.9581 0.4483 0.9449 0.9380 0.9310 0.9241 0.9170 0.5861 0.6829 $0.9151 \quad 0.9080 \quad 0.9009 \quad 0.8937 \quad 0.8865$ 0.7724 $0.8867 \quad 0.8795 \quad 0.8722 \quad 0.8648 \quad 0.8573$ 0.8976 0.8454 0.8380 0.8305 0.8228 0.8150 0.8095 0.8019 0.7941 0.7862 0.7781 1.0000

Table B.1. Densities $(g \cdot cm^{-3})$ of 1-Butanol (1) + DESs (2) at different temperatures (K)

1-butanol + DES1			Tempera	ture (K)	
\mathbf{x}_1	293.15	303.15	313.15	323.15	333.15
0.0000	362.08	183.72	103.46	62.80	39.59
0.1658	135.20	77.76	46.39	32.38	22.81
0.3163	59.97	37.95	25.46	18.12	12.73
0.4555	30.25	20.42	14.07	9.99	7.50
0.5597	18.79	12.50	8.89	6.61	5.14
0.7163	8.52	6.28	4.77	3.77	3.13
0.8220	5.48	4.15	3.21	2.55	2.05
0.8912	4.23	3.24	2.53	2.02	1.63
1.0000	2.95	2.28	1.79	1.42	1.15
1-butanol + DES2	Temperature (K)				
x ₁	293.15	303.15	313.15	323.15	333.15
0.0000	58.81	38.90	27.04	19.74	14.69
0.1328	40.94	27.95	20.10	14.53	10.75
0.2454	30.18	21.12	15.10	10.91	8.28
0.3660	21.77	15.45	10.87	8.09	6.25
0.5226	13.18	9.37	6.96	5.38	4.26
0.6290	9.23	6.86	5.24	4.09	3.26
0.7538	6.34	4.80	3.72	2.94	2.36
0.8699	4.48	3.43	2.68	2.13	1.72
1.0000	2.95	2.28	1.79	1.42	1.15
1-butanol + DES3			Tempera	ture (K)	
x ₁	293.15	303.15	313.15	323.15	333.15
0.0000	129.98	74.00	44.33	30.23	21.50
0.2347	38.11	25.19	17.87	12.48	9.15
0.4483	18.81	12.70	9.12	6.88	5.40
0.5861	11.18	8.12	6.19	4.88	3.82
0.6829	7.99	5.96	4.57	3.59	2.88
0.7724	6.00	4.55	3.53	2.79	2.25
0.8976	4.09	3.14	2.46	1.96	1.58
1.0000	2.95	2.28	1.79	1.42	1.15

Table B.2. Densities (mPa·s) of 1-Butanol (1) + DESs (2) at different temperatures (K)

1-butanol + DES1				
T (K)	a_0	a_1	a_2	a_3
293.15	-1.99	0.40	-0.46	-0.48
303.15	-2.12	0.40	-0.43	-0.54
313.15	-2.28	0.38	-0.39	-0.55
323.15	-2.47	0.35	-0.41	-0.53
333.15	-2.72	0.30	-0.44	-0.54
1-butanol + DES2				
T (K)	a_0	a_1	a_2	a_3
293.15	-1.758	0.281	-0.804	0.517
303.15	-1.952	0.292	-0.819	0.458
313.15	-2.191	0.310	-0.877	0.449
323.15	-2.451	0.298	-0.942	0.427
333.15	-2.761	0.285	-1.017	0.348
1-butanol + DES3				
T (K)	a_0	a_1	a_2	a_3
293.15	-3.919	-0.541	1.971	-3.110
303.15	-4.097	-0.597	1.992	-3.185
313.15	-4.283	-0.656	2.023	-3.317
323.15	-4.512	-0.764	2.064	-3.381
333.15	-4.782	-0.882	2.075	-3.477

Table B.3. Excess volume parameters for Redlich-Kister equation, for binary mixtures of 1-butanol (1) + DESs (2) at the studied temperatures

1-butanol + DES1				
T (K)	a_0	a_1	a_2	a_3
293.15	-629.425	487.454	-407.383	235.506
303.15	-304.827	213.697	-161.091	94.304
313.15	-162.629	100.818	-85.362	69.220
323.15	-94.406	53.225	-25.481	13.954
333.15	-56.164	31.803	-3.344	-11.467
1-butanol + DES2				
T (K)	a_0	a_1	a_2	a_3
293.15	-66.275	18.635	-7.883	17.039
303.15	-41.236	8.894	-1.200	10.513
313.15	-27.872	8.753	3.250	-3.713
323.15	-19.508	7.351	-0.308	-1.744
333.15	-13.604	4.737	-1.799	1.406
1-butanol + DES3				
T (K)	a_0	a_1	a_2	a_3
293.15	-61.579	-5.122	45.540	-25.696
303.15	-39.633	0.752	28.988	-22.238
313.15	-26.409	1.717	21.742	-20.479
323.15	-18.266	3.132	7.599	-8.302
333.15	-12.725	2.302	1.851	-1.694

Table B.4. Excess viscosity parameters for Redlich-Kister equation, for binary mixtures of 1-butanol (1) + DESs (2) at the studied temperatures

System	a_0	a_1	a_2	a_3
DES1	-4238.679	-1162.851	-2066.070	-1036.566
DES2	-3557.729	-606.643	739.654	-1383.131
DES3	-3197.255	-924.606	894.785	-496.509

Table B.5. Excess enthalpy parameters for Redlich-Kister equation, for binary mixtures of 1-butanol (1) + DESs (2) at 313.15 K

APENDIX C. Physicochemical properties of choline chloridebased deep eutectic solvents and excess properties of their pseudobinary mixtures with 1-butanol

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KEYWORDS

Deep eutectic solvents, excess enthalpy, density, viscosity, 1-butanol

ABSTRACT

Ionic liquids and deep eutectic solvents have aroused interest as alternative solvents for separation processes due to their favorable properties. For instance, deep eutectic solvents are usually biodegradable, non-toxic, low-cost and also share some properties with ionic liquids, such as their tunability to be used in specific applications. Recently, deep eutectic solvents have been studied more extensively but their physicochemical characterization is still in the initial stages if the final objective is to select alternatives for industrial processes. Decomposition temperature, surface tension, density, and viscosity were measured for deep eutectic solvents based on choline chloride as the hydrogen bond acceptor and levulinic acid, ethylene glycol and phenol as hydrogen bond donors (in a 1:2 mole ratio). Density, viscosity and excess enthalpy were measured for pseudo-binary mixtures of the different deep eutectic solvents with 1-butanol. The excess properties were calculated to understand the behavior of the deep eutectic solvents in the mixture. The results suggest that deep eutectic solvents are formed due to strong intermolecular forces between their constituents, with no reaction observed. This generates a higher thermal stability of the deep eutectic solvents compared to their constituent hydrogen bond donor. Also, with the addition of 1-butanol to the deep eutectic solvents, the mixture has a lower volume compared with the ideal case due to the creation of new networks of hydrogen bonds and interstitial site accommodations. Hence, the excess molar volumes and excess enthalpies have a negative deviation from the ideal behavior. The viscosity deviation is related to the Arrhenius equation observing a negative deviation for the deep eutectic solvents containing levulinic acid and phenol, and a positive deviation for the one with ethylene glycol. Experimental data for the different properties allows a qualitative understanding of the magnitude of the interactions that occur when mixing deep eutectic solvents with 1-butanol.

INTRODUCTION

Separations are essential for recovering high-value products in process industries but they are energy intensive, often use toxic or harmful extraction solvents and present high capital and operation costs. Efforts are needed to select green and sustainable solvents that are not only safe for the environment but they should have favorable physicochemical properties and a low cost that could compete with the typical organic solvents. To perform this change, understanding the experimental thermophysical properties and phase behavior is indispensable, not only to improve the experimental thermodynamic knowledge but to develop new models or enhance the application of the current theory that is useful for predicting the performance through micro- and macroscopic simulations. In this context, ionic liquids have emerged as an alternative due to their low volatility, high thermal stability and cation/anion tunability, but they show high viscosities and a large life cycle tree,¹ which increases their cost because of the materials and steps required for their synthesis. The result could also be a toxic and a non-biodegradable ionic liquid. Thus, deep eutectic solvents (DES) have captured attention because they are easily synthesized by just mixing a hydrogen bond acceptor (HBA) with a hydrogen bond donor (HBD) which can be natural products as choline chloride, betaine and proline, used as HBA, and sugars, organic acids, polyols, etc. as HBD. Since these precursors have a natural origin, usually DES have lower toxicity and better biodegradability compared to ionic liquids.² DES were introduced by Abbott et al.³ who showed that mixing a HBA with a HBD resulted in a significant reduction of the melting temperature compared with the pure compounds due to the internal interactions that create a highly non symmetric structure that reduces the lattice energy.⁴ DES have captured attention as solvents for separations processes^{5,6} but they also present some drawbacks. For instance, they have a noticeable volatility⁷ and some combinations have a large viscosity,⁸ which makes them non-applicable to industrial processes. In general, DES have been proposed as an alternative in applications such as separation of natural compounds,^{9,10} catalysis,^{11,12} biodiesel,¹³ and carbon capture.^{14,15} In the literature, there is a significant amount of information on properties of pseudo-pure DES,^{8,16,17} but, despite all the potential applications of these solvents, the literature is still scarce in research on physicochemical properties of DES and their mixtures with organic compounds. There are some works on volumetric and transport properties, mainly focused on pseudo-binary mixtures with water,^{18–21} dimethyl sulfoxide²² and some alcohols.^{23–26} Data is even scarcer on enthalpies of mixing where, within our knowledge, only two publications on mixtures of water + DES can be found.^{27,28}

The first aim of this work is to measure density, viscosity and surface tension for three DES formed by choline chloride + levulinic acid, choline chloride + ethylene glycol and choline chloride + phenol with a molar ratio of 1:2 and compare the results with literature values. Densities and viscosities are measured at ambient pressure and a temperature range

of 293.15 K to 333.15 K. Surface tension is measured at ambient pressure and 298.15 K. In addition, all the DES are characterized by NMR and FT-IR spectroscopy to study potential interactions and to determine whether or not any reaction takes place between the components in the mixture. The second objective is to characterize mixtures of 1butanol + DES. For this purpose, densities and viscosities of the mixtures are measured at the same conditions of pressure and temperature as the pseudo-pure DES over the full range of compositions. Finally, excess enthalpies are obtained for the same mixtures at 313.15 K. The selection of an alcohol was made because they are used in many industrial applications as solvents and to analyze the effect of presence of these compounds in a mixture governed by strong hydrogen bonding. 1-butanol was chosen as the specific alcohol due to its importance, for example, in biodiesel.^{13,29} This alcohol has been studied because its energy content is similar in magnitude to conventional diesel, so it can be used as a potential substitute.³⁰ Therefore, 1-butanol could be involved in separation processes where a DES is used as an extractant and the physicochemical data for these kind of mixtures is required in order to understand their macroscopic behavior.

EXPERIMENTAL SECTION

Chemicals

All the compounds used in the study are shown in Table 1 with their respective purities and source. Three DES were prepared using choline chloride as hydrogen bond acceptor, while the hydrogen bond donors were levulinic acid (DES1), ethylene glycol (DES2) and phenol (DES3). All the DES were prepared in a molar ratio of HBA:HBD of approximately 1:2.

Table 1. Specifications of chemicals used in this work

Chemical name	MW	CAS	Supplier	Туре	Purity
Choline chloride	139.62	67-48-1	Acros organics	-	> 0.990
Levulinic acid	116.12	123-76-2	Acros organics	-	> 0.980
Ethylene glycol	62.06	107-21-1	Acros organics	Anhydrous, AcroSeal®	> 0.998
Phenol	94.11	106-95-2	Sigma aldrich	≥99%, Aldrich	> 0.990
1-Butanol	74.12	71-36-3	Sigma aldrich	Anhydrous	> 0.998

Preparation of DES and 1-butanol + DES mixtures

DES were prepared gravimetrically using an analytic balance (Practum 224-1s Sartorius, Germany, uncertainty \pm 0.1 mg). Initially, the HBA and HBD were placed into a round bottom flask under nitrogen atmosphere and then heated at 353.15 K until a homogeneous liquid was formed. Choline chloride, which is very hygroscopic, was previously dried in a Schlenk line under high vacuum (10⁻⁴ mbar) for three days to avoid water gain due to ambient humidity. The amount of water present in each DES was measured using a Karl Fisher Coulometer (831KF Metrohm, Switzerland). DES compositions and their water contents are shown in Table 2.

Table 2. Water content and molar ratio of DES used in this work

Abbreviation	Salt	HBD	Molar ratio	Water content
			(Salt : HBD)	(wt. %)
DES1	Choline chloride	Levulinic acid	1:2.006	0.065
DES2	Choline chloride	Ethylene glycol	1:1.997	0.041

	DES3	Choline chloride	Phenol	1:2.026	0.056
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To test if the low-pressure environment used for drying the DES in the Schlenk line would change their composition, 0.5 mL of choline chloride + phenol (~1:2 molar ratio) mixture was placed into a 25 mL round-bottom flask. Three ¹H-NMR samples of the DES were taken. The remainder of the sample was connected to a Schlenk line in a vacuum environment for one hour. Afterwards, three samples of the post-vacuum DES were taken for ¹H-NMR measurements. The molar ratio of choline chloride to phenol changed from 1:2.026 to 1:1.971, suggesting that phenol preferentially evaporated. Therefore, DES were not placed under vacuum to remove additional water before any application, since that could affect their final composition. However, choline chloride was dried before use and the HBD were always manipulated under nitrogen atmosphere. Also, DES samples were kept in a septum cap vial in a desiccator in order to avoid water gain. Mixtures of 1-butanol + DES were also prepared gravimetrically using the same procedure as pseudo-pure DES.

Nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FT-IR)

NMR and FT-IR spectroscopy measurements were made to characterize the DES precursors, DES and 1-butanol + DES mixtures. ¹H NMR and a 2D NMR ¹H-¹H correlation spectroscopy (COSY) measurements were carried out using an Bruker Advance 400 MHz spectrometer (Massachusetts, United States). Samples were dissolved in deuterium oxide (D₂O) and tetramethylsilane was used as an internal reference. FT-IR measurements were carried out in a Shimadzu IRTracer-100 (Kyoto,

Japan) between 400 and 4,000 cm⁻¹. The solid samples were prepared in KBr pellets, while the liquid samples were supported on transparent KBr films.

Thermogravimetric analysis (TGA) and surface tension

TGA was measured for DES precursors and DES but surface tension was measured only for DES. TGA was performed with a Mettler Toledo 851e thermal gravimetric analyzer (Ohio, United States) using STARe Mettler-Toledo 8.1 software for data collection. The sample pans were standard 40 μ L aluminum crucibles. Measurements were carried out between 300 and 800 K at 20 K·min⁻¹ under a nitrogen atmosphere at 60 mL·min⁻¹ flow. The surface tension was measured using the plate method in a Dataphysics DCAT9 tensiometer (Filderstadt, Germany). Measurements were performed four times at a temperature of 298.15 K and atmospheric pressure. Surface tension results were the average of four measurements and the uncertainty obtained was \pm 0.03 m·Nm⁻¹. The experimental method was tested using deionized distilled water.

Density and dynamic viscosity measurements

Density (ρ) and dynamic viscosity (η) were measured for DES and 1-butanol + DES mixtures. Both properties were obtained simultaneously in an Anton Paar DMA4500M Densitometer (Graz, Austria) with a coupled modular Anton Paar Lovis 2000ME microviscometer. The densitometer uses a vibrating U-tube to provide density measurements with an accuracy of 0.00005 g·cm⁻³. The internal temperature has an accuracy of 0.01 K using an integrated Pt-100 thermometer. The densitometer was

calibrated with double distilled deionized and degassed water, and dry air at atmospheric pressure. The dynamic viscosity measurements are based on the falling ball principle. The microviscometer is equipped with three calibrated glass capillaries of different diameter (1.59, 1.8 and 2.5 mm) and steel balls. The dynamic viscosity is obtained by measuring the time taken by the steel ball to fall from one side to the end of the capillary filled with sample at a certain angle and temperature. The calibration of the capillaries was done using viscosity standards provided by the manufacturer and with methanol, water and glycerol. Viscosity measurements have a repeatability of 0.1% and the measurement accuracy varies between 0.17% and 0.50% depending on the size of the capillary and the temperature.

Excess Molar Enthalpy (H^E) measurements

 H^E was measured in a Setaram C80 calorimeter for binary mixtures of 1-butanol + DES mixtures at 313.15 K and atmosphere pressure. The cell used in the experiments is composed of a cylindrical reversal mixing cell with two compartments. The bottom compartment holds the volatile sample, in this case 1-butanol, which is closed with a movable cap. Approximately 20 g of mercury are added over the cap to avoid the release of vapors from the solvent due to the temperature increase during the experiment. The DES is added over the mercury and then, the cell is closed. All this process is done under a nitrogen atmosphere. There is a very small solubility of the DES in the mercury which does not affect the experiment, according to the procedure described by Ficke *et al.*³¹ The cell is placed in the calorimeter along with a reference which is an identical empty mixing

cell. Temperature is stabilized for about 3 hours and then the reversal mechanism of the calorimeter is activated turning the cell by 180° . This allows the movable cap to act as a stirring system for the sample and the two liquids mix at constant temperature, so the calorimeter can detect any release or absorption of heat due to the mixing. After the mixing, the temperature is kept constant for 1 hour more and then the system returns to ambient conditions. The error of the experimental measurements of H^E is $\pm 2\%$.

RESULTS AND DISCUSSION

NMR and FT-IR analysis of DES

¹H-NMR spectra for choline chloride, levulinic acid, DES1, ethylene glycol, DES2, phenol and DES3 are shown in Figure S1, Figure S2, Figure 1 and Figures S3-S6, respectively. Figures S1-S6 are presented in the Supporting Information. In Figure 1, the ¹H-NMR spectrum of DES1 composed of choline chloride and levulinic acid shows that all the main signals of the constituent compounds are present in agreement with the same DES spectra reported previously in literature.²⁶



This spectrum can be compared against Figures S1 and S2 of the pure choline chloride and levulinic acid and no shift in the ¹H signals is detected when compounds are mixed to form the DES1. ¹H-¹H COSY analysis for DES1 is shown in Figure 2, observing in black squares the correlation between the continuous protons. Here, two well-formed squares are present, each of them associated with a specific 2D proton correlation. The square (A) shows the 2D correlation of methylene protons of choline N⁺-CH₂-CH₂, and the square (B) shows the 2D correlation of methylene protons of levulinic acid -CO-CH₂-CH₂-CO-. Additionally, the correlation of the methyl groups of choline at 3.15 ppm and the correlation of the methyl group of levulinic acid at 3.20 ppm, are clearly observed. Thus, the ¹H-¹H COSY analysis corroborates the presence of both levulinic acid and choline chloride in DES1, without structural changes. For this specific case, this observation is especially important because no esterification reaction was detected.



Figure 2. 'H-'H COSY analysis for DEST,

Indeed, the ¹H-NMR and ¹H-¹H COSY measurements for all the DES were performed at least two weeks after they were synthesized. Similar analysis was performed for DES2 and DES3. In the ¹H-¹H NMR COSY spectra for DES2 and DES3 shown in Figure S7 and S8, respectively, the same 2D correlation of methylene protons of choline present in the DES1 is observed. Additionally, in DES2 ¹H-¹H NMR COSY spectrum, an intense signal of correlation of methylene protons of ethylene glycol is observed at 3.60 ppm; while in DES3 ¹H-¹H NMR COSY spectrum the correlation of aromatic protons is observed between 6.8 and 7.3 ppm. Figures S9 and S10 show the ¹H NMR and ¹H-¹H NMR COSY spectrum, respectively, for 1-butanol + DES1 mixtures, which comfirms that there is no transesterification reaction between the 1-butanol and levulinic acid. Figure 3 shows the FT-IR spectra of choline chloride, levulinic acid, ethylene glycol, phenol, DES1, DES2, and DES3. The spectra also agree with the expected structures and show characteristic signals, both for the precursors and for the respective DES. The spectrum confirms the interaction that occurs between pure compounds when the DES is formed. The main effect is the shift of the signal corresponding to stretching of -OH bonds that can be seen between 3500 - 2800 cm⁻¹, that is caused by the interaction of hydrogen bonds between the components of the DES (protons of hydroxyl groups with oxygens of either hydroxyl groups or carbonyl groups).



Figure 3. FT-IR analysis for DES and their precursors,

These interactions are most noticeable in the FT-IR spectrum of DES1, where in addition to the shift of the signal corresponding to the hydroxyl groups, it is possible also to detect a shift of the signals corresponding to the carbonyls groups in the spectra of levulinic acid and DES1, observed at 1745 and 1735 cm⁻¹, respectively. Moreover, the three DES present a peak around 950 cm⁻¹, indicating the presence of the ammonium salt, a finding that is consistent with previous literature.^{32,33} Thus, the FT-IR study confirms that the mixture is formed due to intermolecular interactions and there is no evidence that a chemical reaction between the components occurs.

TGA and surface tension of DES

Figure 4 represents the dynamic TGA curves with a heating rate of 20 K·min⁻¹ for the three DES and their precursors. Table 3 summarizes the values of the onset temperature (T_{onset}) obtained from the dynamic TGA curves with heating rates of 20 K·min⁻¹. Values for DES1 and DES2 are higher than those reported by Delgado-Mellado *et al.*⁷, consistent with a faster heating rate resulting in higher values of T_{onset} .

Table 3. Onset temperature and surface tension of DES

System	Tonset (K)	$\sigma(\text{m}\cdot\text{Nm}^{-1})$	$\sigma_{literature} (\mathrm{m}\cdot\mathrm{Nm}^{-1})$
DES1	517.87	39.35	-
DES2	538.01	45.66	48.91 ³⁶
DES3	513.38	35.46	-

Therefore, our results are in general agreement with the literature, given that their measurements were done at 5-10 K·min⁻¹. Pure choline chloride and HBD show only one

step of thermal degradation at well-defined temperatures, while DES1, DES2 and DES3 show decomposition at temperatures intermediate between choline chloride and the corresponding HBD, corroborating the interactions between the components. DES1 shows also one degradation step, while DES2 and DES3 show multiple degradation steps.



Figure 4. Dynamic TGA curves with a heating rate of 20 K \cdot min⁻¹. Continuous line (----) shows the results for choline chloride, dashed line (----) for each HBD and dotted line (----) for the DES where the Figures are (A) DES1, (B) DES2 and (C) DES3.

These results indicate that the interactions in DES1 are stronger than those for DES2 and DES3. Thus, the thermal degradation profile of DES1 indicates that it would be degraded in a way similar to a pure compound. By contrast, for DES2 and DES3, the steps of decomposition can be associated with degradation of the separate components of the DES. As can be seen in Figure 4 (B), DES2, composed of choline chloride and ethylene glycol, shows a higher stability than pure ethylene glycol (470 K boiling point). Three clear stages of DES weight loss are observed. The first two could correspond to volatilization of ethylene glycol with different degrees of association via hydrogen bonds with choline, and the latter to the thermal degradation of choline chloride itself. In Figure 4 (C), DES3, composed by choline chloride and phenol, was less stable because the boiling point of phenol (454.8 K) is lower than that of ethylene glycol. The loss of mass of the DES also occurs in three stages. Again, the first two could correspond to volatilization of phenol with different degrees of association with choline by hydrogen bonds and finally, above 530 K, there is a stage where the choline chloride decomposes.

Table 3 shows the results for the surface tension measurements at 298.15 K. The highest surface tension value was 45.66 m·Nm⁻¹ for DES2, while the lowest one was 35.46 m·Nm⁻¹ for DES3. The first effect observed is that the surface tension decreases from the pure HBD for all DES. For instance, the surface tension of levulinic acid³⁴ goes down from 42.53 m·Nm⁻¹ to 39.35 m·Nm⁻¹ in DES1, and for ethylene glycol³⁵ from 48.9 m·Nm⁻¹ to 45.66 m·Nm⁻¹ in DES2. There is a 7% of difference in the values reported by Shahbaz *et al.*,³⁶ which must be mainly due to the difference in the experimental method and water content. The surface tension is highly dependent on the strength of the molecular

interaction so, although it was not measured, a decrease in surface tension is expected with increasing temperature. As can be noted, when choline chloride is added, the surface tension of DES decrease, indicating a reduction in the cohesive forces of the pure HBD at the surface. According to this, choline chloride would act as a surfactant.

Density and dynamic viscosity of DES

Density and dynamic viscosity measurements were carried out for the three DES at temperatures between 293.15 K and 333.15 K at atmospheric pressure. Density results reported in this work are in agreement with data collected from the literature for DES1,^{16,26,37,38} DES2,^{9,21,22,37,39} and DES^{40,41} and the comparison is shown in Figure 5. For all the systems, the density decreases linearly with temperature, as expected, and depends on the type of HBD used. In general, density increases when more –OH groups are present in the HBD, and decreases with more aromatic groups and longer alkyl chains in the organic acids.⁸



Figure 5. Density (g·cm⁻³) of DES1 (**■**) DES2 (**■**) and DES3 (**■**) as a function of temperature. Black: DES1, red: DES2 and blue: DES3. Comparison with data reported from (Δ) Sas *et al.*²⁶, (\circ) Florindo *et al.*¹⁶, (\bigstar , \bigstar) Larriba *et al.*³⁷, (+) Ullah *et al.*³⁸, (\times) Harifi-Mood and Buchner²², (\diamond) Shahbaz *et al.*³⁹, (∇) Leron *et al.*²¹, (\triangleleft) Otzurk *et al.*⁹, (*) Li *et al*⁴⁰ and (\bigcirc) Guo *et al.*⁴¹ Dashed line (---) represents the fitting with a linear equation with parameters reported in Table 4.

A smaller density corresponds to an increase in the free volume of the DES.⁴² Thus, the densities obtained in this work, in terms of the HBD, are levulinic acid > ethylene glycol > phenol. This is consistent with the densities of the pure components compared at the same temperature, i.e. 1.10591 g·cm⁻³ for levulinic acid (obtained in this work and reported in Table S1 of the Supporting Information), 1.08468 g·cm⁻³ for ethylene glycol⁹ and 1.04116 g·cm⁻³ for phenol⁴³ at 333.15 K. Moreover, density increases by adding choline chloride but its effect is not strong, as reported previously for DES1,⁴⁴ DES2⁹ and DES3.⁴⁵ The effect of water content in the DES on density is also small. For instance, when using DES1, Ullah *et al.*⁴⁶ reports 1.69 wt.% of water, Larriba *et al.*³⁷ lower than 0.5 wt.% and this work lower than 0.1 wt.%, but all of them fall in the same a straight line with small differences. This can be attributed to the fact that the density of the DES is only a little greater than the density of pure water.

Table 4. Linear fitting coefficients for correlating DES densities

System	а	$10^4 \cdot b$	R^2	AAD (%)
DES1	1.33603	-6.659	0.997	0.052
DES2	1.28363	-5.600	0.996	0.046
DES3	1.26644	-5.717	0.989	0.045

Therefore, density data from this work, along with literature values, were fitted with a linear equation depicted in equation 1, where parameter a represents the intercept and b the slope. Fitting parameters for Equation 1 are presented in Table 4, obtaining an average absolute deviation (*AAD*) between 0.045 to 0.052 %, demonstrating strong agreement

between data from different authors. *AAD* is represented in Equation 2, where θ can be viscosity or density and *n* the number of data considered in the calculation.

$$\rho(T) = a + bT \tag{1}$$

$$AAD = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{\theta_{experimental} - \theta_{calculated}}{\theta_{calculated}} \right|$$
(2)

Viscosities measured in this work are compared with literature for DES1,^{16,26,37,38} DES2^{9,22,37} and DES3^{47,48} and all the collected data are shown graphically in Figure 6. In general, viscosity drops markedly with temperature; thus, this property is usually correlated in terms of the temperature (*T*) as an exponential decreasing function in the form of the Arrhenius expression shown in equation 3, where *A* and *B* are fitting parameters, and *R* the universal gas constant. The viscosity trend observed for the DES studied in this work in terms of the HBD is levulinic acid > phenol > ethylene glycol. A higher viscosity is related to stronger molecular interactions, i.e. hydrogen bonds and electrostatic interactions affecting the molecular movement.⁴⁹



Figure 6. Dynamic viscosity (mPa·s) of DES1 (**•**) DES2 (**•**) and DES3 (**•**) as a function of temperature. Black: DES1, red: DES2 and blue: DES3. Comparison with data reported from (Δ) Sas *et al.*²⁶, (\circ) Florindo *et al.*¹⁶, (\bigstar, \bigstar) Larriba *et al.*³⁷, (+) Ullah *et al.*³⁸, (\times) Harifi-Mood and Buchner²², (\triangleleft) Otzurk *et al.*⁹, (\bigcirc) Guo *et al.*⁴¹ and (-) Zhu *et al.*⁴⁷. Dashed line (---) represents the fitting with VFT equation with parameters reported in Table 5.

Hence, the largest difference between viscosities of the three DES are observed at the lower temperature, i.e. 293.15 K, where the molecules have a lower kinetic energy and intermolecular interactions are predominant. If the viscosities of pure HBD are compared at constant temperature, they are 14.824 mPa·s for levulinic acid,⁵⁰ 5.2480 mPa·s for ethylene glycol⁹ and 4.90 mPa·s for phenol⁵¹ at 313.15 K, giving a different tendency compared with the DES reported in this work. When choline chloride is added to the HBD

in a mole ratio 1:2, viscosities for DES1, DES2 and DES3 at 313.15 K are 103.46 mPa·s, 27.04 mPa·s and 44.43 mPa·s, respectively. Therefore, viscosities increase by adding choline chloride in a mole ratio 1:2 HBA:HBD, but a crossover in viscosity is observed for the case when the HBDs are ethylene glycol and phenol. This is because the presence of choline chloride produces a stronger increase in the viscosity of the DES formed with phenol compared with the one with ethylene glycol. This suggests that interaction between ethylene glycol-ethylene glycol molecules are stronger than the phenol-phenol molecules, but the choline chloride-ethylene glycol interaction is weaker than the choline chloride-phenol at a mole ratio 1:2 HBA:HBD. In all the cases, the levulinic acid and its DES have a higher viscosity compared with the other two HBDs and DES. The biggest concern when comparing viscosity measurements of DES from different authors are the large differences among data. According to García et al.,⁵² these differences can arise from the experimental method, the sample preparation procedure and/or the impurities present in the sample. Since experimental methods are often calibrated with known samples or standards, probably the main source of error could come from sample preparation and impurities. DES are highly hygroscopic, so the main impurity is the quick absorption of water,⁵³ producing a strong decrease in the viscosity of the DES.^{26,38} Unlike the density, the viscosity of the DES is much different than the viscosity of pure water. In order to avoid the presence of water in the final DES, choline chloride should be dried before its use as done in this work. HBDs must also be dried under vacuum if they are solids or low volatility liquids, under molecular sieves if they are more volatile or simply purchase anhydrous solvents. The HBA:HBD mixtures should be made in a dry atmosphere, avoiding its further vacuum drying because the possibility of volatilization of one of the components,⁷ affecting the mole ratio of the DES. Thus, viscosity data from this work are in agreement with the measurements from Sas *et al.*²⁶ for DES1, Harifi-Mood and Buchner²² for DES2 and Zhu *et al.*⁵⁴ for DES3. All of them report a water content below 0.1 wt.% and only Zhu *et al.*⁵⁴ has a different experimental technique. The other literature values are suspected to have a lower DES viscosity due to higher water contents in the samples rather than the choice of experimental technique.

Viscosity data was fitted to the Arrhenius correlation and its empirical modifications proposed by Litovitz (with fitting parameters A' and B') and Vogel-Fulcher-Tamman (VFT, with fitting parameters A'', B'' and T_0) shown in equations 4 and 5, respectively.

$$\eta_{Arrhenius}(T) = A \exp\left(\frac{-B}{RT}\right)$$
(3)

$$\eta_{Litovitz}(T) = A' \exp\left(\frac{B'}{RT^3}\right) \tag{4}$$

$$\eta_{VFT}(T) = A^{\prime\prime} \exp\left(\frac{B^{\prime\prime}}{T - T_0}\right)$$
(5)

Fitting parameters for all the DES from the three correlations are shown in Table 5, along with their respective *AAD*. VFT equation provides the best correlation for all the DES with an *AAD* of 0.459 %, 0.228 % and 0.885 % for DES1, DES2 and DES3, respectively. Therefore, viscosity data from this work are correlated with VFT equation in Figure 6.

Arrhenius							
System	A	В	AA	D (%)			
DES1	3.681·10 ⁻⁶	$-4.475 \cdot 10^4$	3	.000			
DES2	$5.705 \cdot 10^{-4}$	$-2.809 \cdot 10^4$	1	.455			
DES3	3.707.10-5	$-3.661 \cdot 10^4$	4.079				
Litovitz							
System	A'	B'	AAD (%)				
DES1	0.356	$1.449 \cdot 10^9$	0.589				
DES2	0.768	$9.092 \cdot 10^8$	0.308				
DES3	0.441	$1.187 \cdot 10^{9}$	1.772				
VFT							
System	A ''	<i>B</i> ''	T_{θ}	AAD (%)			
DES1	0.029	$1.238 \cdot 10^3$	162	0.459			
DES2	0.085	$9.759 \cdot 10^2$	144	0.228			
DES3	0.335	$5.492 \cdot 10^2$	201	0.885			

Table 5. Viscosity fitting coefficients from Arrhenius, Litovitz and VFT equations (3),(4) and (5), respectively.

Excess volume, viscosity deviation and excess enthalpy of 1-butanol + *DES*

Density and dynamic viscosity measurements of mixtures composed by 1-butanol + DES were obtained at ambient pressure at temperatures between 293.15 K – 333.15 K in the full range of compositions. 1-butanol is completely miscible with the different DES used in this work at all the measurement conditions. Density and viscosity data for these mixtures are shown in Tables 6 and 7, respectively. Since 1-butanol has a lower density and viscosity than all the DES, when increasing the 1-butanol composition in the mixture with DES, the density and viscosity of the mixture decreases. Also, at constant 1-butanol composition in the mixture, these properties decrease by increasing the temperature, as

expected. In order to explain the non-ideality, structural arrangement and molecular interactions of the mixtures between the 1-butanol and the different DES it is more convenient to show the data from Tables 6 and 7 in the form of the excess molar volume and the deviation of the mixture viscosity from an expected mixture model.

Table 6. Densities $(g \cdot cm^{-3})$ of 1-butanol (1) + DES (2) at different temperatures (K)

1-butanol + DES1							
<u>-</u>		Density $(g \cdot cm^{-3})$					
x_l	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K		
0.0000	1.1419	1.1352	1.1285	1.1219	1.1153		
0.1658	1.0976	1.0907	1.0838	1.0770	1.0703		
0.3163	1.0533	1.0463	1.0393	1.0323	1.0254		
0.4555	1.0095	1.0024	0.9953	0.9881	0.9810		
0.5597	0.9746	0.9673	0.9601	0.9528	0.9455		
0.7163	0.9196	0.9122	0.9047	0.8972	0.8896		
0.8220	0.8799	0.8724	0.8648	0.8572	0.8494		
0.8912	0.8536	0.8461	0.8384	0.8307	0.8227		
1.0000	0.8095	0.8019	0.7941	0.7862	0.7781		
	1-butanol + DES2						
		De	ensity (g·cm ⁻	3)			
x_{l}	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K		
0.0000	1.1195	1.1139	1.1081	1.1025	1.0969		
0.1328	1.0738	1.0679	1.0620	1.0561	1.0503		
0.2454	1.0349	1.0288	1.0227	1.0167	1.0106		
0.3660	0.9946	0.9883	0.9819	0.9756	0.9693		
0.5226	0.9449	0.9383	0.9316	0.9249	0.9181		
0.6290	0.9128	0.9059	0.8990	0.8920	0.8850		
0.7538	0.8767	0.8696	0.8624	0.8551	0.8477		
0.8699	0.8443	0.8370	0.8296	0.8220	0.8143		
1.0000	0.8095	0.8019	0.7941	0.7862	0.7781		
		1-butano	1 + DES3				
		De	ensity (g·cm ⁻	3)			
x_l	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K		
0.0000	1.0994	1.0934	1.0874	1.0815	1.0756		

0.2347	1.0406	1.0342	1.0277	1.0214	1.0150
0.4483	0.9850	0.9783	0.9716	0.9649	0.9581
0.5861	0.9449	0.9380	0.9310	0.9241	0.9170
0.6829	0.9151	0.9080	0.9009	0.8937	0.8865
0.7724	0.8867	0.8795	0.8722	0.8648	0.8573
0.8976	0.8454	0.8380	0.8305	0.8228	0.8150
1.0000	0.8095	0.8019	0.7941	0.7862	0.7781

Standard uncertainties u are $u(x_1) = 0.001$, u(T) = 0.01 K, u(P) = 1 kPa. Relative standard uncertainties u_r are $u_r(\rho) = 0.00005$ g·cm⁻³

Table 7. Viscosities	(mPa∙s) of	`1-butanol ((1) + DES ((2) at	t different temp	peratures (K)
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1-butanol + DES1						
	Viscosity (mPa·s)					
x_1	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K	
0.0000	362.08	183.72	103.46	62.80	39.59	
0.1658	135.20	77.76	46.39	32.38	22.81	
0.3163	59.97	37.95	25.46	18.12	12.73	
0.4555	30.25	20.42	14.07	9.99	7.50	
0.5597	18.79	12.50	8.89	6.61	5.14	
0.7163	8.52	6.28	4.77	3.77	3.13	
0.8220	5.48	4.15	3.21	2.55	2.05	
0.8912	4.23	3.24	2.53	2.02	1.63	
1.0000	2.95	2.28	1.79	1.42	1.15	
1-butanol + DES2						
_	Viscosity (mPa·s)					
<i>x</i> 1	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K	
0.0000	58.81	38.90	27.04	19.74	14.69	
0.1328	40.94	27.95	20.10	14.53	10.75	
0.2454	30.18	21.12	15.10	10.91	8.28	
0.3660	21.77	15.45	10.87	8.09	6.25	
0.5226	13.18	9.37	6.96	5.38	4.26	
0.6290	9.23	6.86	5.24	4.09	3.26	
0.7538	6.34	4.80	3.72	2.94	2.36	
0.8699	4.48	3.43	2.68	2.13	1.72	
1.0000	2.95	2.28	1.79	1.42	1.15	
1-butanol + DES3						

-	Viscosity (mPa·s)					
x_1	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K	
0.0000	129.98	74.00	44.33	30.23	21.50	
0.2347	38.11	25.19	17.87	12.48	9.15	
0.4483	18.81	12.70	9.12	6.88	5.40	
0.5861	11.18	8.12	6.19	4.88	3.82	
0.6829	7.99	5.96	4.57	3.59	2.88	
0.7724	6.00	4.55	3.53	2.79	2.25	
0.8976	4.09	3.14	2.46	1.96	1.58	
1.0000	2.95	2.28	1.79	1.42	1.15	

Standard uncertainties *u* are $u(x_1) = 0.001$, u(T) = 0.01 K, u(P) = 1 kPa. Relative standard uncertainties u_r are $u_r(\eta) = 0.0017$ mPa·s

The excess volume (V^E) is calculated using equation 6, where x_i , ρ_i and M_i are the composition, density and molecular weight of the compound *i*, respectively and ρ is the density of the mixture. The deviation of the mixture viscosity from an expected mixture model is analyzed from equations 7 and 8, where η_i is the viscosity of the compound *i* and η the viscosity of the mixture. Equation 7 represents the viscosity deviation in terms of a linear relationship used often in literature. On the other hand, equation 8 is a viscosity deviation related to the Arrhenius equation for mixtures.⁵⁵ It is noteworthy that the DES is treated as a pseudo-pure component and not as a mixture, so its molecular weight was calculated using the individual molecular weights times the molar fraction of each species.

$$V^{E} = \frac{x_{1}M_{1} + x_{2}M_{2}}{\rho} - \left(\frac{x_{1}M_{1}}{\rho_{1}}\right) - \left(\frac{x_{2}M_{2}}{\rho_{2}}\right)$$
(6)

$$\eta^{deviation,linear} = \eta - x_1 \eta_1 - x_2 \eta_2 \tag{7}$$

$$ln(\eta^{deviation,Arrhenius}) = ln(\eta) - x_1 \ln(\eta_1) - x_2 ln(\eta_2)$$
(8)

 V^E of the binary mixtures of 1-butanol + DES show a clear negative behavior throughout the range of temperature and composition for all the DES, as seen in Figure 7; that is, the volume of the mixture is lower than in the ideal mixture. V^E values are in quantitative agreement with the experimental data for 1-butanol + DES1 reported by Sas *et al.*²⁶ No data for comparison were found for the other DES.



Figure 7. Excess molar volume (cm³·mol⁻¹) in terms of the mole fraction of 1-butanol for the binary mixtures (A) 1-butanol + DES1, (B) 1-butanol + DES2 and (C) 1-butanol + DES3 at different temperatures: (**•**) 293.15 K, (**•**) 303.15 K, (**•**) 313.15 K, (**V**) 323.15 K and (**•**) 333.15 K. Dashed curve (---) represents the Redlich-Kister polynomial fitting with parameters reported in Table 8.
It is also observed that the V^E becomes increasingly negative at higher temperatures for all the systems measured in this work. This is opposite the behavior observed for aqueous mixtures of DES,^{18,20,21,25} where the V^E is less negative at higher temperatures. Haghbakhsh and Raeissi²⁴ suggest that intermolecular interactions between alcoholalcohol and DES-DES decrease more strongly with increasing temperature than alcohol-DES interactions, resulting in a smaller volume of the mixture at higher temperatures due to stronger interactions and better interstitial accommodation of the mixed molecules.

In the case of water, the intermolecular interactions are stronger at low temperatures because the hydrogen bond strength increases. This could produce stronger intermolecular interactions of the water-DES mixture, yielding a smaller V^E at lower temperatures. This is basically because the hydrogen bonding in water is stronger than in alcohols. Further studies are needed for a better understanding of this behavior.

Figure 8 shows the V^E for the three DES systems at 293.15 K as a function of the mole fraction of 1-butanol. DES3 shows a greater contraction in its volume when mixed with 1-butanol than the other two DES measured. This is probably because the intermolecular interaction of the phenol with 1-butanol is stronger due to the presence of OH-OH and OH- π interactions⁵⁶ and the higher free volume of the phenol, which is the compound with the lowest density of the three HBDs used, allowing for greater interstitial accommodation of 1-butanol.



Figure 8. Excess molar volume (cm³·mol⁻¹) in terms of the mole fraction of 1-butanol, for the binary mixtures (\blacksquare) 1-butanol + DES1, (\bullet) 1-butanol + DES2 and (\blacktriangle) 1-butanol + DES3 at 293.15 K. Dashed curve (---) represents the Redlich-Kister polynomial fitting with parameters reported in Table 8.

Figure 9 shows experimental data of the viscosities of mixtures composed by 1-butanol + DES as a function of the composition of 1-butanol. Viscosity decreases with temperature and by adding 1-butanol as expected, since pure 1-butanol has a much lower viscosity compared with all the DES. This difference is intensified at lower temperatures. Figure

S11 in the Supporting Information shows the comparison of the experimental mixture viscosities as a function of the composition of 1-butanol, shown in Table 7, with the viscosities predicted with the linear equation ($\eta^{deviation,linear} = 0$ from equation 7) and the Arrhenius equation ($\eta^{deviation,Arrhenius} = 0$ from Equation 8) at 293.15 K.



Figure 9. Dynamic viscosity (mPa·s) of 1-butanol + DES1 (A), 1-butanol + DES2 (B) and 1-butanol + DES3 (C) as a function of 1-butanol molar composition. Temperatures
(■) 293.15 K, (●) 303.15 K, (▲) 313.15 K, (▼) 323.15 K and (♦) 333.15 K.

In general, experimental values quickly decrease by adding butanol and it is observed that Arrhenius equation has a better prediction of the experimental data compared with the linear relationship. In literature, equation 7 is used repeatedly to analyze the viscosity deviations but given the exponential nature of the mixture viscosity in terms of the composition of 1-butanol, the Arrhenius type is appropriate to represent the data and to study their deviations. Thus, using equation 8, DES1 and DES3 have a negative deviation and DES2 a positive deviation from Arrhenius equation. Also, for DES1, AAD of viscosity prediction decreases linearly with temperature from 21.8 % at 293.15 K to 3.6 % at 333.15 K. A similar behavior is observed for DES3, with an AAD decreasing from 18.2 % at 293.15 K to 4.4 % at 333.15 K. However, DES2 has an increasing AAD from 5.3 % at 293.15 K to 7.6 % at 333.15 K. Then, Arrhenius equation for mixtures better predicts the viscosity of mixtures 1-butanol + DES2 where the smaller deviations are obtained.

Experimental excess molar enthalpies (H^E) were measured at 313.15 K for the mixtures of 1-butanol + DES and the results are shown in Figure 10.



Figure 10. Excess molar enthalpy $(J \cdot mol^{-1})$ in terms of the mole fraction of 1-butanol for the binary mixtures (**a**) 1-butanol + DES1, (**•**) 1-butanol + DES2 and (**\land**) 1-butanol + DES3 at 313.15 K. Dashed curve (---) represents the Redlich-Kister polynomial fitting with parameters reported in Table 10.

Negative H^E values were found for the three systems with the minimum ranging around 800 - 1100 J·mol⁻¹, following the trend DES1 > DES2 > DES3 in absolute values of H^E . Negative H^E , or exothermic behavior, involves a net creation of interactions like hydrogen bonds upon mixing and the forces between the molecules that form the dissimilar species; i.e. 1-butanol-DES interactions are stronger than those between the same species, i.e. DES - DES and 1-butanol - 1-butanol interactions, indicating that energy is liberated upon mixing.

Overall, the V^E and H^E of all the DES+ 1-butanol systems are negative, suggesting a strong interaction between the 1-butanol and the DES. The Arrhenius equation was used to model the mixture viscosities, obtaining better results for the mixture 1-butanol + DES2. The DES with levulinic acid shows the most negative H^E , but with a higher V^E compared with the other DES at constant temperature due to its lower free volume to accommodate molecules of 1-butanol.

The excess molar volume and excess enthalpy, were fitted to the Redlich - Kister correlation shown in equation 9, where M^E can be V^E or H^E , and α_i are the adjustable parameters of the polynomial of k + 1 terms.

$$M^{E} = x_{1}x_{2}\sum_{i=0}^{k} \alpha_{i}(x_{1} - x_{2})^{i}$$
(9)

Tables 8 and 9 show the parameters for the Redlich – Kister equation for each 1-butanol + DES systems for V^E and H^E , respectively, and all the experimental values presented in Figures 7, 8 and 10 are correlated with those parameters. In general, all the systems show a good fit to the experimental data which is observed in the low *AAD* in Tables 8 and 9. **Table 8.** Redlich-Kister polynomial fitting coefficients for excess volume

1-butanol + DES1								
$T(\mathbf{K})$	a_0	a_1	a_2	<i>a</i> ₃	AAD (%)			
293.15	-1.987	0.398	-0.465	-0.484	4.276			
303.15	-2.118	0.397	-0.431	-0.538	4.129			
313.15	-2.278	0.382	-0.394	-0.548	3.832			
323.15	-2.475	0.349	-0.413	-0.534	3.667			
333.15	-2.721	0.297	-0.439	-0.543	3.352			
1-butanol + DES2								
$T(\mathbf{K})$	a_0	a_1	a_2	<i>a</i> ₃	AAD (%)			
293.15	-1.758	0.281	-0.804	0.517	0.545			
303.15	-1.952	0.292	-0.819	0.458	0.320			
313.15	-2.191	0.310	-0.877	0.449	0.294			
323.15	-2.451	0.298	-0.942	0.427	0.236			
333.15	-2.761	0.285	-1.017	0.348	0.266			
1-butanol + DES3								
$T(\mathbf{K})$	a_0	a_1	a_2	<i>a</i> 3	AAD (%)			
293.15	-3.919	-0.541	1.971	-3.110	0.222			
303.15	-4.097	-0.597	1.992	-3.185	0.183			
313.15	-4.283	-0.656	2.023	-3.317	0.160			
323.15	-4.512	-0.764	2.064	-3.381	0.192			
333.15	-4.782	-0.882	2.075	-3.477	0.207			

System	a_0	a_1	a_2	<i>a</i> ₃	AAD (%)
DES1	-4238.679	-1162.851	-2066.070	-1036.566	7.449·10 ⁻⁵
DES2	-3557.729	-606.643	739.654	-1383.131	7.324·10 ⁻⁵
DES3	-3197.255	-924.606	894.785	-496.509	4.193·10 ⁻⁵

Table 9. Redlich-Kister polynomial fitting coefficients for excess enthalpy

CONCLUSION

In this study, decomposition temperature, surface tension, density and viscosity were measured for three pure choline chloride-based DES from 293.15 to 333.15 K at atmospheric pressure. The HBD studied in this work were levulinic acid, ethylene glycol and phenol, all of them in a mole ratio 1:2 of HBA:HBD. NMR and FT-IR were used to describe the interaction between the functional groups constituting the HBA:HBD mixture and to determine that no reactions are observed in the synthesized DES. In addition, the decomposition temperature was analyzed by TGA to check the thermostability of the DES. It is shown that the density and viscosity decrease as the temperature increases and our data is consistent with values obtained from literature. Larger deviations are observed for viscosities, due to differences in water content in the DES and preparation of samples. In summary, the highest thermal stability is observed for the DES formed by choline chloride + levulinic acid, which has stronger HBD:HBA intermolecular interactions, producing the highest viscosity and density of the three DES studied.

Mixtures formed by 1-butanol + DES were characterized by measurements of density and viscosity at temperatures ranging from 293.15 K to 333.15 K at ambient pressure. Excess

molar volumes and viscosity deviations at different compositions of 1-butanol in the DES are reported. Excess enthalpy was directly measured for the same mixtures at 313.15 K. Excess volumes and enthalpies, are negative over the entire range of compositions and temperature, suggesting strong intermolecular interactions among unlike molecules. Finally, the viscosity deviations are analyzed with an Arrhenius type equation for mixtures, observing negative deviations with DES1 and DES3 and a positive deviation with DES2. This equation has the best prediction of the system with DES2.

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ACKNOWLEDGMENT

We acknowledge the financial support from CONICYT through the project Fondecyt de Iniciación 2016 N° 11160882

REFERENCES

- Clarke, C. J.; Tu, W.-C.; Levers, O.; Bröhl, A.; Hallett, J. P. Green and Sustainable Solvents in Chemical Processes. *Chem. Rev.* 2018, *118* (2), 747–800.
- Kudłak, B.; Owczarek, K.; Namieśnik, J. Selected Issues Related to the Toxicity of Ionic Liquids and Deep Eutectic Solvents—a Review. *Environ. Sci. Pollut. Res.* 2015, *22* (16), 11975–11992.
- (3) Abbott, A. P.; Capper, G.; Davies, D. L.; Munro, H. L.; Rasheed, R. K.;
 Tambyrajah, V. Preparation of Novel, Moisture-Stable, Lewis-Acidic Ionic
 Liquids Containing Quaternary Ammonium Salts with Functional Side Chains. *Chem. Commun.* 2001, 0 (19), 2010–2011.
- (4) Abbott, A. P.; Boothby, D.; Capper, G.; Davies, D. L.; Rasheed, R. K. Deep Eutectic Solvents Formed between Choline Chloride and Carboxylic Acids: Versatile Alternatives to Ionic Liquids. *J. Am. Chem. Soc.* 2004, *126* (29), 9142– 9147.
- (5) Zhang, Q.; De Oliveira Vigier, K.; Royer, S.; Jérôme, F. Deep Eutectic Solvents:

Syntheses, Properties and Applications. Chem. Soc. Rev. 2012, 41 (21), 7108.

- (6) Cunha, S. C.; Fernandes, J. O. Extraction Techniques with Deep Eutectic Solvents. *TrAC Trends Anal. Chem.* 2018, 105, 225–239.
- Delgado-Mellado, N.; Larriba, M.; Navarro, P.; Rigual, V.; Ayuso, M.; García, J.;
 Rodríguez, F. Thermal Stability of Choline Chloride Deep Eutectic Solvents by
 TGA/FTIR-ATR Analysis. J. Mol. Liq. 2018, 260, 37–43.
- (8) García, G.; Aparicio, S.; Ullah, R.; Atilhan, M. Deep Eutectic Solvents:
 Physicochemical Properties and Gas Separation Applications. *Energy & Fuels* 2015, 29 (4), 2616–2644.
- Ozturk, B.; Parkinson, C.; Gonzalez-Miquel, M. Extraction of Polyphenolic Antioxidants from Orange Peel Waste Using Deep Eutectic Solvents. *Sep. Purif. Technol.* 2018, 206, 1–13.
- (10) Ivanović, M.; Alañón, M. E.; Arráez-Román, D.; Segura-Carretero, A. Enhanced and Green Extraction of Bioactive Compounds from Lippia Citriodora by Tailor-Made Natural Deep Eutectic Solvents. *Food Res. Int.* 2018, *111*, 67–76.
- (11) Gage, S. H.; Ruddy, D. A.; Pylypenko, S.; Richards, R. M. Deep Eutectic Solvent Approach towards Nickel/Nickel Nitride Nanocomposites. *Catal. Today* 2018, 306, 9–15.
- Tran, P. H.; Thi Hang, A.-H. Deep Eutectic Solvent-Catalyzed Arylation of Benzoxazoles with Aromatic Aldehydes. *RSC Adv.* 2018, 8 (20), 11127–11133.
- (13) Merza, F.; Fawzy, A.; AlNashef, I.; Al-Zuhair, S.; Taher, H. Effectiveness of Using Deep Eutectic Solvents as an Alternative to Conventional Solvents in

Enzymatic Biodiesel Production from Waste Oils. *Energy Reports* **2018**, *4*, 77–83.

- (14) Zulkurnai, N. Z.; Md. Ali, U. F.; Ibrahim, N.; Abdul Manan, N. S. Carbon Dioxide Capture by Deep Eutectic Solvent Impregnated Sea Mango Activated Carbon. *E3S Web Conf.* 2018, *34*, 02030.
- (15) Sarmad, S.; Mikkola, J.-P.; Ji, X. Carbon Dioxide Capture with Ionic Liquids and Deep Eutectic Solvents: A New Generation of Sorbents. *ChemSusChem* 2017, *10*(2), 324–352.
- (16) Florindo, C.; Oliveira, F. S.; Rebelo, L. P. N.; Fernandes, A. M.; Marrucho, I. M. Insights into the Synthesis and Properties of Deep Eutectic Solvents Based on Cholinium Chloride and Carboxylic Acids. *ACS Sustain. Chem. Eng.* 2014, *2* (10), 2416–2425.
- (17) Francisco, M.; van den Bruinhorst, A.; Kroon, M. C. Low-Transition-Temperature Mixtures (LTTMs): A New Generation of Designer Solvents.
 Angew. Chemie Int. Ed. 2013, *52* (11), 3074–3085.
- (18) Yadav, A.; Trivedi, S.; Rai, R.; Pandey, S. Densities and Dynamic Viscosities of
 (Choline Chloride + Glycerol) Deep Eutectic Solvent and Its Aqueous Mixtures in
 the Temperature Range (283.15–363.15) K. *Fluid Phase Equilib.* 2014, 367, 135–
 142.
- (19) Yadav, A.; Pandey, S. Densities and Viscosities of (Choline Chloride + Urea)
 Deep Eutectic Solvent and Its Aqueous Mixtures in the Temperature Range
 293.15 K to 363.15 K. J. Chem. Eng. Data 2014, 59 (7), 2221–2229.

- (20) Yadav, A.; Kar, J. R.; Verma, M.; Naqvi, S.; Pandey, S. Densities of Aqueous Mixtures of (Choline Chloride + Ethylene Glycol) and (Choline Chloride + Malonic Acid) Deep Eutectic Solvents in Temperature Range 283.15– 363.15 K. *Thermochim. Acta* 2015, 600, 95–101.
- (21) Leron, R. B.; Soriano, A. N.; Li, M.-H. Densities and Refractive Indices of the Deep Eutectic Solvents (Choline Chloride + Ethylene Glycol or Glycerol) and Their Aqueous Mixtures at the Temperature Ranging from 298.15 to 333.15 K. J. *Taiwan Inst. Chem. Eng.* 2012, *43* (4), 551–557.
- (22) Harifi-Mood, A. R.; Buchner, R. Density, Viscosity, and Conductivity of Choline Chloride + Ethylene Glycol as a Deep Eutectic Solvent and Its Binary Mixtures with Dimethyl Sulfoxide. J. Mol. Liq. 2017, 225, 689–695.
- (23) Haghbakhsh, R.; Raeissi, S. Densities and Volumetric Properties of (Choline Chloride + Urea) Deep Eutectic Solvent and Methanol Mixtures in the Temperature Range of 293.15–323.15 K. J. Chem. Thermodyn. 2018, 124, 10–20.
- (24) Haghbakhsh, R.; Raeissi, S. Investigation of Solutions of Ethyl Alcohol and the Deep Eutectic Solvent of Reline for Their Volumetric Properties. *Fluid Phase Equilib.* 2018, 472, 39–47.
- (25) Kim, K.-S.; Park, B. H. Volumetric Properties of Solutions of Choline
 Chloride + glycerol Deep Eutectic Solvent with Water, Methanol, Ethanol, or Iso Propanol. J. Mol. Liq. 2018, 254, 272–279.
- (26) Sas, O. G.; Fidalgo, R.; Domínguez, I.; Macedo, E. A.; González, B. PhysicalProperties of the Pure Deep Eutectic Solvent, [ChCl]:[Lev] (1:2) DES, and Its

Binary Mixtures with Alcohols. J. Chem. Eng. Data 2016, 61 (12), 4191–4202.

- Ma, C.; Guo, Y.; Li, D.; Zong, J.; Ji, X.; Liu, C. Molar Enthalpy of Mixing and Refractive Indices of Choline Chloride-Based Deep Eutectic Solvents with Water. *J. Chem. Thermodyn.* 2017, *105*, 30–36.
- Ma, C.; Guo, Y.; Li, D.; Zong, J.; Ji, X.; Liu, C.; Lu, X. Molar Enthalpy of Mixing for Choline Chloride/Urea Deep Eutectic Solvent + Water System. J. Chem. Eng. Data 2016, 61 (12), 4172–4177.
- Homan, T.; Shahbaz, K.; Farid, M. M. Improving the Production of Propyl and Butyl Ester-Based Biodiesel by Purification Using Deep Eutectic Solvents. *Sep. Purif. Technol.* 2017, *174*, 570–576.
- (30) Rubio-Pérez, G.; Muñoz-Rujas, N.; Srhiyer, A.; Montero, E. A.; Aguilar, F. Isobaric Vapor-Liquid Equilibrium, Density and Speed of Sound of Binary Mixtures 2,2,4-Trimethylpentane + 1-Butanol or Dibutyl Ether (DBE) at 101.3 KPa. *Fluid Phase Equilib.* 2018, 475, 10–17.
- (31) Ficke, L. E.; Rodríguez, H.; Brennecke, J. F. Heat Capacities and Excess
 Enthalpies of 1-Ethyl-3-Methylimidazolium-Based Ionic Liquids and Water. J.
 Chem. Eng. Data 2008, 53 (9), 2112–2119.
- (32) Aissaoui, T. Pharmaceutica Analytica Acta Novel Contribution to the Chemical Structure of Choline Chloride Based Deep Eutectic Solvents. *Aissaoui, Pharm Anal Acta* 2015, 6 (11), 11–14.
- (33) Zullaikah, S.; Rachmaniah, O.; Utomo, A. T.; Niawanti, H.; Ju, Y. H. Green Separation of Bioactive Natural Products Using Liquefied Mixture of Solids.

Green Chem. 2018.

- (34) Lomba, L.; Giner, B.; Bandrés, I.; Lafuente, C.; Pino, M. R. Physicochemical Properties of Green Solvents Derived from Biomass. *Green Chem.* 2011, *13* (8), 2062–2070.
- (35) Azizian, S.; Hemmati, M. Surface Tension of Binary Mixtures of Ethanol +
 Ethylene Glycol from 20 to 50°C. J. Chem. Eng. Data 2003, 48 (3), 662–663.
- (36) Shahbaz, K.; Mjalli, F. S.; Hashim, M. A.; AlNashef, I. M. Prediction of the Surface Tension of Deep Eutectic Solvents. *Fluid Phase Equilib.* 2012, *319*, 48– 54.
- (37) Larriba, M.; Ayuso, M.; Navarro, P.; Delgado-Mellado, N.; Gonzalez-Miquel, M.;
 García, J.; Rodríguez, F. Choline Chloride-Based Deep Eutectic Solvents in the
 Dearomatization of Gasolines. *ACS Sustain. Chem. Eng.* 2018, 6 (1), 1039–1047.
- (38) Ullah, R.; Atilhan, M.; Anaya, B.; Khraisheh, M.; García, G.; ElKhattat, A.;
 Tariq, M.; Aparicio, S. A Detailed Study of Cholinium Chloride and Levulinic Acid Deep Eutectic Solvent System for CO2 Capture via Experimental and Molecular Simulation Approaches. *Phys. Chem. Chem. Phys.* 2015, *17* (32), 20941–20960.
- (39) Shahbaz, K.; Mjalli, F. S.; Hashim, M. A.; AlNashef, I. M. Prediction of Deep Eutectic Solvents Densities at Different Temperatures. *Thermochim. Acta* 2011, 515 (1–2), 67–72.
- (40) Li, G.; Deng, D.; Chen, Y.; Shan, H.; Ai, N. Solubilities and ThermodynamicProperties of CO2 in Choline-Chloride Based Deep Eutectic Solvents. *J. Chem.*

Thermodyn. 2014, 75, 58–62.

- (41) Guo, W.; Hou, Y.; Ren, S.; Tian, S.; Wu, W. Formation of Deep Eutectic Solvents by Phenols and Choline Chloride and Their Physical Properties. *J. Chem. Eng. Data* 2013, *58* (4), 866–872.
- (42) Abbott, A. P.; Harris, R. C.; Ryder, K. S.; D'Agostino, C.; Gladden, L. F.;
 Mantle, M. D. Glycerol Eutectics as Sustainable Solvent Systems. *Green Chem.*2011, 13 (1), 82–90.
- (43) Cunha, D. L.; Coutinho, J. A. P.; Daridon, J. L.; Reis, R. A.; Paredes, M. L. L.
 Experimental Densities and Speeds of Sound of Substituted Phenols and Their
 Modeling with the Prigogine–Flory–Patterson Model. *J. Chem. Eng. Data* 2013, 58 (11), 2925–2931.
- (44) Lu, M.; Han, G.; Jiang, Y.; Zhang, X.; Deng, D.; Ai, N. Solubilities of Carbon Dioxide in the Eutectic Mixture of Levulinic Acid (or Furfuryl Alcohol) and Choline Chloride. J. Chem. Thermodyn. 2015, 88, 72–77.
- (45) Li, G.; Deng, D.; Chen, Y.; Shan, H.; Ai, N. Solubilities and Thermodynamic Properties of CO2 in Choline-Chloride Based Deep Eutectic Solvents. *J. Chem. Thermodyn.* 2014, 75, 58–62.
- (46) Ullah, R.; Atilhan, M.; Anaya, B.; Khraisheh, M.; García, G.; ElKhattat, A.; Tariq, M.; Aparicio, S. A Detailed Study of Cholinium Chloride and Levulinic Acid Deep Eutectic Solvent System for CO2 Capture via Experimental and Molecular Simulation Approaches. *Phys. Chem. Chem. Phys.* 2015, *17* (32), 20941–20960.

- (47) Zhu, J.; Yu, K.; Zhu, Y.; Zhu, R.; Ye, F.; Song, N.; Xu, Y. Physicochemical Properties of Deep Eutectic Solvents Formed by Choline Chloride and Phenolic Compounds at T = (293.15 to 333.15) K: The Influence of Electronic Effect of Substitution Group. *J. Mol. Liq.* 2017, *232*, 182–187.
- (48) Guo, W.; Hou, Y.; Ren, S.; Tian, S.; Wu, W. Formation of Deep Eutectic Solvents by Phenols and Choline Chloride and Their Physical Properties. *J. Chem. Eng. Data* 2013, *58* (4), 866–872.
- (49) Zhao, B.-Y.; Xu, P.; Yang, F.-X.; Wu, H.; Zong, M.-H.; Lou, W.-Y.
 Biocompatible Deep Eutectic Solvents Based on Choline Chloride:
 Characterization and Application to the Extraction of Rutin from Sophora
 Japonica. ACS Sustain. Chem. Eng. 2015, 3 (11), 2746–2755.
- (50) Wohlfarth, C. Viscosity of Levulinic Acid BT Viscosity of Pure Organic
 Liquids and Binary Liquid Mixtures; Wohlfarth, C., Lechner, M. D., Eds.;
 Springer Berlin Heidelberg: Berlin, Heidelberg, 2017; p 161.
- (51) Byers, C. H.; Williams, D. F. Viscosities of Pure Polyaromatic Hydrocarbons. J.
 Chem. Eng. Data 1987, 32 (3), 344–348.
- (52) García, G.; Aparicio, S.; Ullah, R.; Atilhan, M. Deep Eutectic Solvents:
 Physicochemical Properties and Gas Separation Applications. *Energy & Fuels*2015, 29 (4), 2616–2644.
- (53) Maugeri, Z.; Domínguez de María, P. Novel Choline-Chloride-Based Deep-Eutectic-Solvents with Renewable Hydrogen Bond Donors: Levulinic Acid and Sugar-Based Polyols. *RSC Adv.* 2012, 2 (2), 421–425.

- (54) Zhu, J.; Yu, K.; Zhu, Y.; Zhu, R.; Ye, F.; Song, N.; Xu, Y. Physicochemical Properties of Deep Eutectic Solvents Formed by Choline Chloride and Phenolic Compounds at T = (293.15 to 333.15) K: The Influence of Electronic Effect of Substitution Group. *J. Mol. Liq.* 2017, *232*, 182–187.
- (55) Arrhenius Svante. Über Die Innere Reibung Verdünnter Wässeriger Lösungen. Zeitschrift für Physikalische Chemie. 1887, p 285.
- (56) Šerbanović, S. P.; Kijevčanin, M. L.; Radović, I. R.; Djordjević, B. D. Effect of Temperature on the Excess Molar Volumes of Some Alcohol+aromatic Mixtures and Modelling by Cubic EOS Mixing Rules. *Fluid Phase Equilib.* 2006, 239 (1), 69–82.