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Synthesis and Properties of Hydrophilic and Hydrophobic Deep Eutectic Solvents by Different Methods

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Abstract: Deep eutectic solvents have emerged as a greener alternative and have attracted so much interest in the last two decades. This paper present alternative synthesis method to classical heating-stirring. The ultrasound method is one of the most promising syntheses DESs in terms of yield and energy. So, ultrasound synthesis method was studied to obtain hydrophobic (Aliquat 336: L-Menthol 3:7; Lidocaine: decanoic acid 1:2) and hydrophilic DESs based on Choline chloride and urea, ethylene glycol and oxalic acid. The physical characterization of DESs by comparison of FTIR spectra no show difference between DESs obtained by heating-stirring and ultrasound synthesis methods. The RMN spectra of the DESs obtained by heating-stirring revealed the DESs formation. Density and viscosity properties of DESs were evaluated. The density values are similar for both synthesis methods. However, lower viscosity values are obtained to the hydrophilic DESs prepared by ultrasound methods.

Keywords: deep eutectic solvents; synthesis; ultrasound method; heating-stirring method

1. Introduction

In recent years, scientific research and industry are making great efforts in the search for new, less polluting solvents to minimise environmental impact with the aim to achieve the principles of green chemistry.

Ionic liquids are considered an environmentally friendly alternative to traditional organic solvents; however, their poor biodegradability, biocompatibility and bio-sustainability and the high use of organic solvents for their synthesis minimise their large-scale use, as well as their cost. Deep eutectic solvents (DESs) have emerged as a greener alternative to ionic liquids since 2003 [1]. DESs share general characteristics with ionic liquids, such as thermal stability, low volatility, low vapour pressure and tunable polarity, but have advantages over ionic liquids, such as lower cost, biodegradability, lower toxicity and simpler production processes [2]. This is the reason DESs have attracted so much interest in the last two decades increasing their application in nanotechnology [3], food industry [4], medicine [5], or extraction [6,7].

DESs are obtained from the mixture of a hydrogen-bond donor (HBD) and a hydrogen-bond acceptor (HBA) [7]. The hydrogen bonding interactions allow for a very marked decrease in the freezing point. The synthesis methods of DESs are simple. They not require multiple steps or separation methods or purification step as no solvents are needed [8]. The most commonly used methods are high-temperature (> 50 °C) heating or grinding of the reagents.

The high-temperature heating method consists of mixing the reagents and heating at temperatures between 50-100 °C, under stirring until a homogeneous liquid is formed [9,10]. It is

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necessary to identify the appropriate synthesis temperature, which is selected according to the boiling point and stability of the reagents. One of the most commonly used families of DESs is derived from the combination of acids carboxylic and choline chloride (ChCl). However, conventional heating, in the above range of temperature, can lead to degradation of DESs due to esterification reactions, in general, between the alcohol moiety of ChCl and the carboxylic acids [11,12].

The grinding method was carried out by Florindo et *al.* [11] for the preparation of DESs based on ChCl and carboxylic acids. The grinding method consists of mixing the components and then, grinding them in a mortar with a pestle at room temperature under nitrogen atmosphere or in a glovebox until a homogeneous liquid is obtained. This method is applicable to all solid components unsuitable for direct heating to prevent the formation of by-products. However, the quality of the generated DESs could be compromised because of the difficult to mix them completely.

Ultrasound or microwaves can be used to accelerate the synthesis process [13,14] Stoichiometric amounts of HBD and HBA are mixed in a glass vial, sealed, and placed in an ultrasound bath. The time and temperature required for DESs formation is based on the properties of pure constituents.

The twin screw extrusion technique serves as an alternative approach for DES preparation, addressing the constraints posed by conventional heating and stirring methods [10,15]. This method employs a setup comprising two screws rotating in opposing directions within a stainless-steel barrel, featuring multiple transport and kneading segments. Within the transport segment, materials are propelled forward, while in the kneading segment, high shear and compression forces act upon the material as it progresses. Following the preheating of the dual screw sections, HBA and HBD are integrated in suitable proportions.

Other synthesis methods are based on freeze-drying, which involves the dissolution of the DES components separately in bi-distilled water to be subsequently mixed, frozen and freeze-dried until a clear viscous liquid is formed [16,17]. It is particularly suitable for the preparation of DESs with unstable thermal compounds but water soluble [14].

The vacuum evaporation method uses relatively lower temperatures compared to the traditional method of synthesising DESs by heating and stirring. This synthesis method, first used for the preparation of Natural DESs (NADES) by Dai et *al.* [18,19] consists of dissolving the DES components in water and then subjecting them to evaporation at 323 K, after which the DES is stored in a silica gel desiccator.

The microwave irradiation method often emerges as the more cost-effective and swifter option for synthesizing DESs [14]. In a groundbreaking study, Gomez et *al.* [20] unveiled a novel microwave-assisted technique, dramatically decreasing synthesis time from 60 minutes to a mere 20 seconds, while also achieving a remarkable 650-fold reduction in energy consumption. This method's efficacy relies heavily on the careful calibration of heating duration, power levels, and component selection. By prioritizing both time efficiency and energy conservation, Gomez et al.[20] pioneered a more environmentally friendly approach to preparing NADESs through microwave assistance.

Santana et *al*. [21] compared three different methods of synthesis of NADESs based on malic acid, citric acid, and water, as well as xylitol, malic acid or citric acid and water, in each case using a molar ratio of 1:1:10. The synthesis methods were heating and stirring, ultrasonic assisted and microwave assisted synthesis. The NADESs obtained have similar physicochemical properties. The synthesis conditions for traditional synthesis methods were 2 h at 323 K under magnetic stirring at 220 rpm. The ultrasound assisted synthesis was carried out in an ultrasonic bath for 45 min and the microwave synthesis was operated to 45 min at 353K in a pressure of 10 bar. Time reduction is possible using ultrasound and microwave assisted synthesis. Considering the synthesis time and volume of solvent synthesized and the equipment power, the electric energy consumption for the DES synthesis was 0.014 kWh/ml for heating and stirring, 0.106 kWh/ml for microwave-assisted and 0.006 kWh/ml for ultrasound assisted. So, ultrasound and microwave synthesis methods were faster and more efficient, in terms of energy ultrasound using 130% less of energy than conventional heating method. Dlugosz et *al.* [22] compared microwave and ultrasound as alternative synthesis methods for obtain choline chloride:urea (ChCl:U), choline chloride:ethylene glycol (ChCl:EG), ammonium formate:ethylene glycol and ammonium formate:glucose DESs to a conventional heating method. An

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increase in the yield is observed from 25 g/h for systems using conventional heating to as much 800 g/h for systems obtained by non-conventional methods. The heating efficiencies of the microwave and ultrasound methods are 74.5% and 53.3%, respectively, versus the heating, which is of the 5.0%.

Among methods for obtaining DESs described in the literature, the ultrasound method is one of the most promising in terms of yield and energy. So, this research work aims to obtain hydrophobic and hydrophilic DESs using the ultrasound method. The DESs obtained will be compared with those obtained by a conventional heating-stirring method. The obtained DESs will be characterised by Fourier-transform infrared (FTIR). The density and viscosity of the mixtures obtained by both two methods will be compared. The DESs synthesised by the heating-stirring method have been characterised by nuclear magnetic resonance (NMR) spectroscopy to confirm the stoichiometry of the mixtures.

2. Results and Discussion

The most common method of synthesis of DESs is heating and stirring the combination of the components until a clear liquid mixture is obtained. The purpose of this article is to analyse and discuss two methods of DESs preparation. The hydrophilic and hydrophobic DESs were synthesised from the different methods according to the conditions given in Table 1, until homogeneous transparent liquids (without precipitation) at room temperature were formed. Some authors indicate that in the case of microwave or ultrasound energy, it is necessary to provide a semiliquid or liquid reaction in order to conduct the energy of the ultrasonic waves [22–24]. However, in this work, DESs are synthesized by both methods regardless of the physical state of their individual components. The synthesis times and temperatures for obtaining DESs are lower for the ultrasound method than for the traditional one. The decrease in the reaction time is really significant in the systems based in liquid-solid components (ChCl:EG) compared with systems were raw materials are both solids (ChCl:U).

The formation of DESs is associated with the creation of hydrogen bonds between the precursors, hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), together with intermolecular interactions involving Van der Waals and electrostatic forces. FTIR is an important tool to analyse the supramolecular structure of the obtained DESs and to elucidate the effects of modifications in processing conditions in terms of the formation of functional groups and changes in composition [25]. The FTIR spectra obtained for the DESs from different synthesis methods are shown in Figures 1–5. Comparison of the spectra showed no difference in the DES regardless of the synthesis method. FTIR spectra of DESs are a combination of the spectra of their starting compounds except for a few frequency shifts associated with the formation of hydrogen bonds. No degradation of the samples has been observed.

Table 1. Synthesis conditions for each DES prepared by heating-stirring and ultrasound methods.

DES	Heating-stirring		Ultrasound	
	Time (h)	Temperature (ºC)	Time (h)	Temperature (ºC)
ChCl: U (1:2)	5	80	4	50
ChCl:EG (1:2)	24	80	1	50
ChCl:EG (1:3)	24	80	1	45
ChCl:EG (1:4)	24	80	1	45
ChCl:Ox (1:1)	4.5	60	3	58
Aliq:LMet (3:7)	0.5	60	0.5	46
Lid: Ac Dec (1:2)	1	60	1	44

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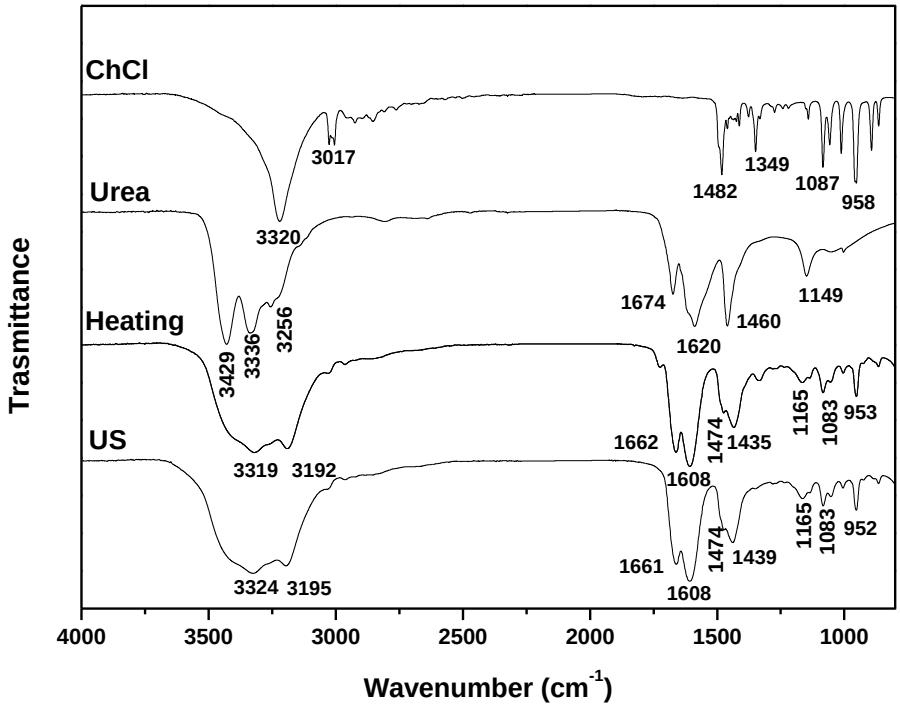
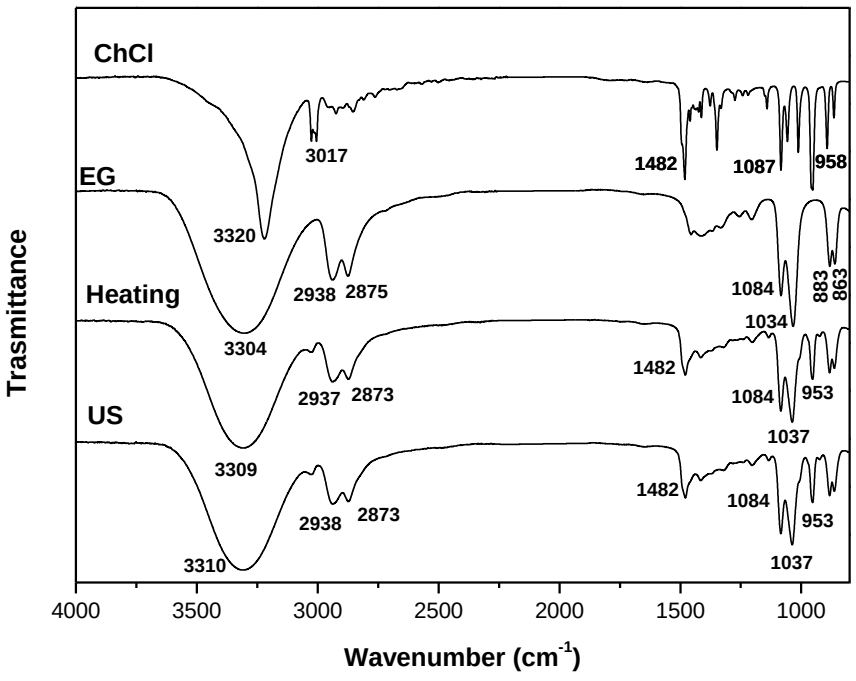


Figure 1. FTIR spectra of ChCl, Urea and ChCl-Urea (1:2) DESs obtained from the heating-stirring and ultrasound (US) methods.



(**a**)

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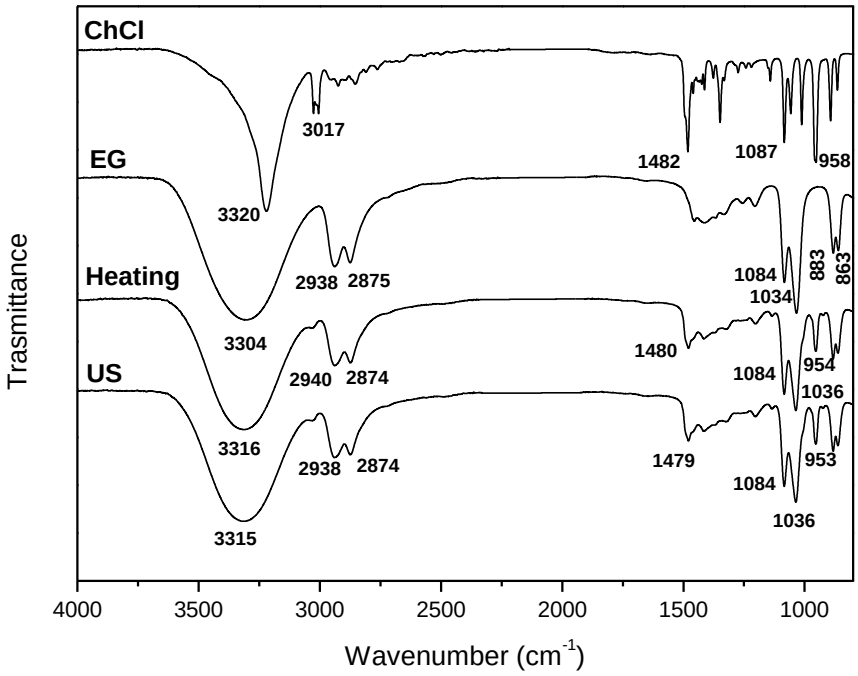

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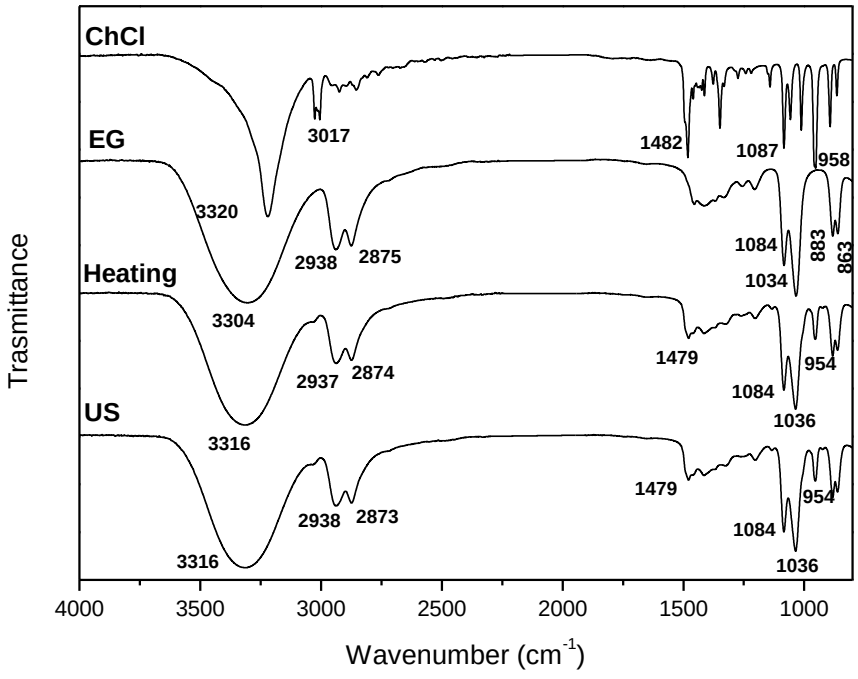

(**c**)

Figure 2. FTIR spectra of DESs a) ChCl:EG (1:2), b) ChCl:EG (1:3) and c) ChCl:EG (1:4).

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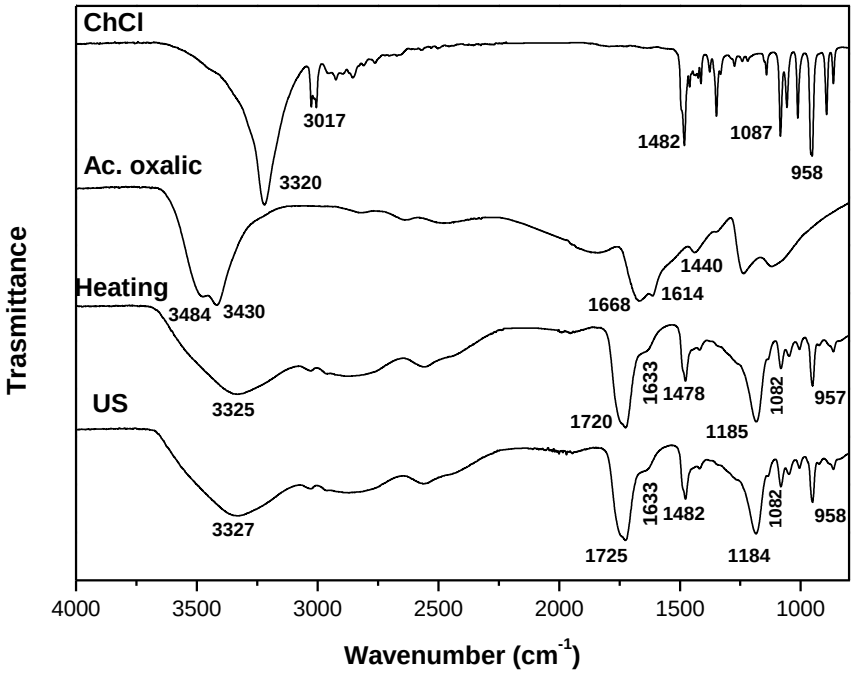

Figure 3. FTIR spectra of ChCl, Oxalic Ac. and ChCl: Ox DESs (1:1) obtained from the heating-stirring and ultrasound method.

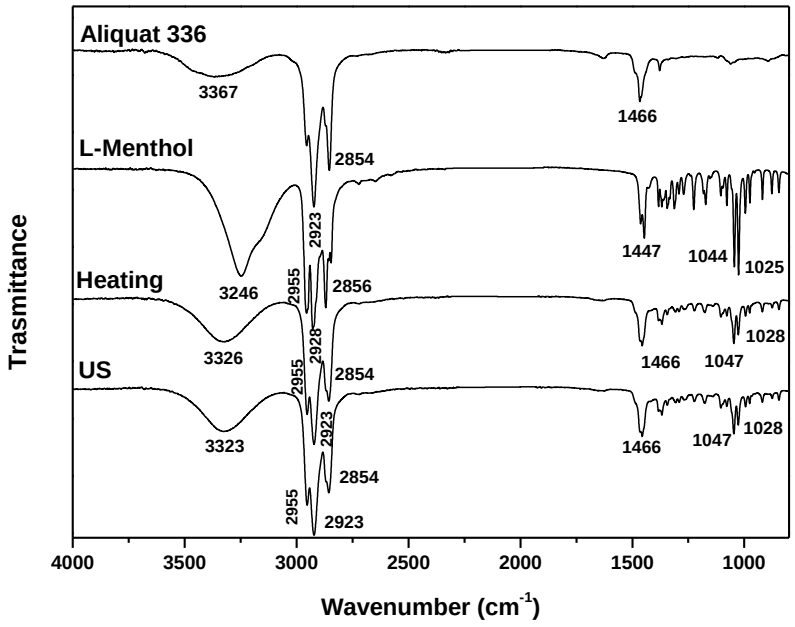

Figure 4. FTIR spectra of L-menthol, Aliquat 336 and Aliq:LMet (3:7) DESs obtained from heating-stirring and ultrasound methods.

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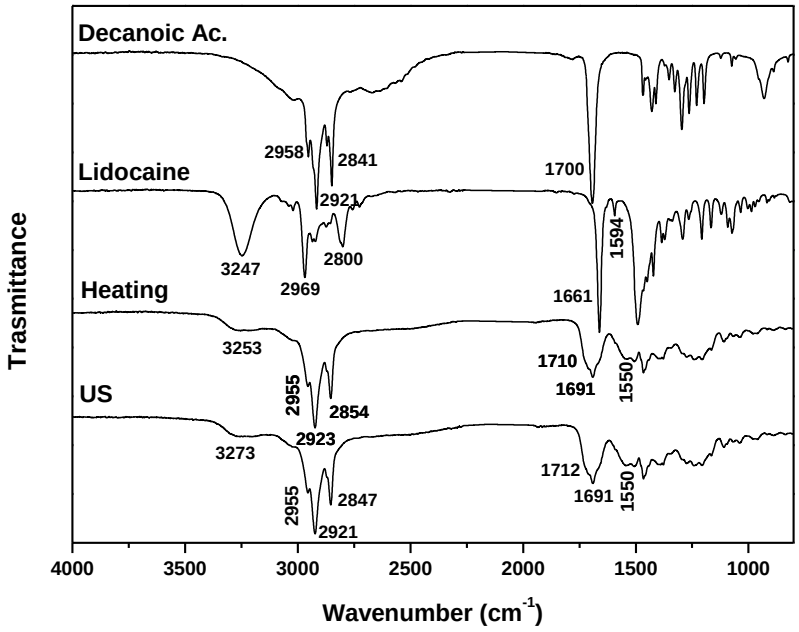

Figure 5. FTIR spectra of Decanoic ac, lidocaine and Ac Dec:Liq (1:2) DESs obtained from the heating-stirring and ultrasound methods.

Figure 1 shows the spectra of the ChCl:U DESs synthesised by both methods, both spectra are similar. The urea absorption bands at 3429 cm^{-1}, 3336 cm^{-1} and 3256 cm^{-1} are assigned to νas NH_2, νs NH_2 and δs NH_2. After the formation of the DESs, broader bands are observed at shorter wavelengths, between 3319 cm^{-1} and 3192 cm^{-1}. This may be due to the result of the formation of hydrogen bonds between urea and ChCl. The formation of strong hydrogen bonds is also observed by the shift of the signals at 1674 cm^{-1} and 1620 cm^{-1} associated with δs NH_2 and δas NH_2 at values of 1662 cm^{-1} and 1608 cm^{-1}.[26]. Also, a shift to lower wavenumbers of the 1460 cm-1 signal assigned to ϱs NH_2 to values around 1435 cm^{-1} is observed. The band at 3320 cm^{-1} of ChCl assigned to the ν_{sm} of OH disappears in the DESs [25]. The signals at 1474 cm^{-1} and 958 cm^{-1} are assigned to the N-C bond and the νCCO of ChCl, respectively, indicating that the ChCl structure has not been destroyed in the formation of the DES [26,27].

Figure 2 shows the DESs obtained for ChCl:EG in the different ratios, (1:2) (a), (1:3) (b) and (1:4) (c). Again, the FTIRs obtained for the DESs from the heating-stirring or ultrasound synthesis methods are similar. In all of them, the formation of the DESs associated with the shift of the νas OH signal is observed, which in EG appears at 3304 cm^{-1} and in the DESs formed appears between 3316-3309 cm^{-1}. This displacement is due to a loss of the crystalline structure associated with the formation of hydrogen bonds [28–31]. The signal assigned to the νsm of the OH of ChCl disappears in the DESs. In all the DESs synthesised regardless of the ChCl:EG ratio used, similar signals to those of the starting compounds are observed, the bands at 2938 cm^{-1} and 2875 cm^{-1} corresponding to the νas and νs of the C-H and the signals at 1084 and 1037 cm^{-1} corresponding to the νas and νs of the C-O. As well as those at 883 and 863 cm^{-1} assigned to ϱ CH_2 and ν C-C [32,33]. Again, the signals around 1482 cm^{-1} and 958 cm^{-1}, above assigned to the C-N bond and the νCCO of ChCl, respectively, indicate that the ChCl structure has not changed in the formation of the DESs. No changes are observed in the spectra with increasing EG ratio.

Figure 3 shows the FTIR spectrum obtained for ChCl:oxalic acid (ChCl:Ox 1:1). The spectrum of oxalic acid shows broad overlapping bands centred at 3450 cm^{-1} in the -OH stretching region typical of carboxylic acid forming dimer rings strongly linked through intermolecular H-bonds and H-bonds between the C=O and O-H groups. It presents a band between 1668 and 1614 cm^{-1} assigned to the C=O stretching frequency, its splitting is interpreted by the coupling of slightly different C=O groups [34]. Around 1440 cm^{-1} a signal assigned to C-O stretching appears. These last two signals can

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be used to recognise the presence of free oxalic acid in the synthesised DESs [25]. The DESs obtained by stirring heating as well as ultrasound methods show similar FTIR spectra. These correspond to a combination of the spectra of the starting compounds with the shift of certain signals. A broadening and shifting to lower wavenumbers of the signal assigned to the OH stretching is observed around 3325 cm^{-1}, the band assigned to the OH group of ChCl at 3320 cm^{-1} disappears. Signals at 1720 cm^{-1} indicate the presence of free carbonyl groups (COOH) and the signal at 1633 cm^{-1} the presence of dissolved Ox [25]. As in the previous DESs, the bands at 1482 cm^{-1} and 958 cm^{-1} are assigned to the C-N bond and the νCCO of ChCl, respectively, and the bands at 1184 and 1084 cm^{-1} correspond to the νas and νs of the C-O [25,27,35].

The FTIR spectra for the hydrophobic compounds are presented in Figures 4 and 5. The FTIR spectra of the DESs of Aliquat 336: L-menthol (Aliq:LMet 3:7) obtained by both methods are similar and present the signals of the starting compounds, see Figure 4. At 3362 cm^{-1} the bands assigned to the hydroxyl group are observed, between 2855 cm^{-1} and 2924 cm^{-1} appear the signals assigned to the νas and νs of the C-H, and at 1025 cm^{-1} and 1045 cm^{-1} attributed to the stretching vibration of the C-O group and the band at 1368 cm^{-1} corresponding to the isopropyl group of LMet. [36]. In the region 1460-1463 cm^{-1} the signals assigned to the quaternary amine $(CH3)_3N^+$ appear, and the region between 2922 cm^{-1} and 3028 cm^{-1} correspond to the asymmetric bands of the C-H [37,38]. The formation of DESs is confirmed by the broadening of the signal assigned to the OH group (3326 cm^{-1}) and its displacement to higher wavenumbers (3326 cm^{-1}), which indicates that the formation mechanism corresponds to the intermolecular interaction of the hydroxyl groups of LMet with the Cl^- of Aliq. It is also observed the displacement of the signals that appear at 1047 cm^{-1} and 1028 cm^{-1} assigned to the stretching vibration of the C-O group, due to a change in the state of aggregation associated with the formation of hydrogen bonds [31].

The FTIR obtained for the DESs Decanoic Ac: Lidocaine (Ac Dec:Lid 2:1) from the heating-stirring or ultrasound synthesis method are similar, see Figure 5. The DES signals assigned to the starting compounds are observed. The formation of DESs is associated with the presence of a signal centred at 1550 cm^{-1} which is not present in the starting compounds, this vibrational mode corresponds to the asymmetric stretching vibration of the carboxylate ion, i.e., the deprotonated Ac Dec. In addition, a signal is observed at 1690 cm^{-1}, which is related to the strong hydrogen bonding that occurs between the carboxyl group of Ac Dec and the tertiary amino group of Lid. [39].

The following figures (Figures 6 and 7) show the NMR spectra of DESs prepared by the heating-stirring method. The spectra were acquired for all DESs but for ChCl:Ox (1:1), the semisolid aspect of which and the presence of bubbles made not possible to fill the capillary tube and register its spectrum. The acquired spectra revealed the presence of the DES components in the respective molar ratios they are combined for DES formation. Moreover, DESs composed by mixtures of carboxylic acids and ChCl were found to evolve into the respective ester derivatives by esterification reaction between the alcohol moiety of ChCl and the carboxylic acid. Rodriguez Rodriguez et al. [12] described significant esterification of Ox upon initial DES preparation at 60 ^oC, around 11 mol % of ChCl. Besides the esterification reaction, some of this family of DESs containing acids could show an additional type of thermal decomposition. It is well-known that oxalic acid decomposes into formic acid and carbon dioxide when heated and this reaction also could also take place when Ox forms part of the DESs.

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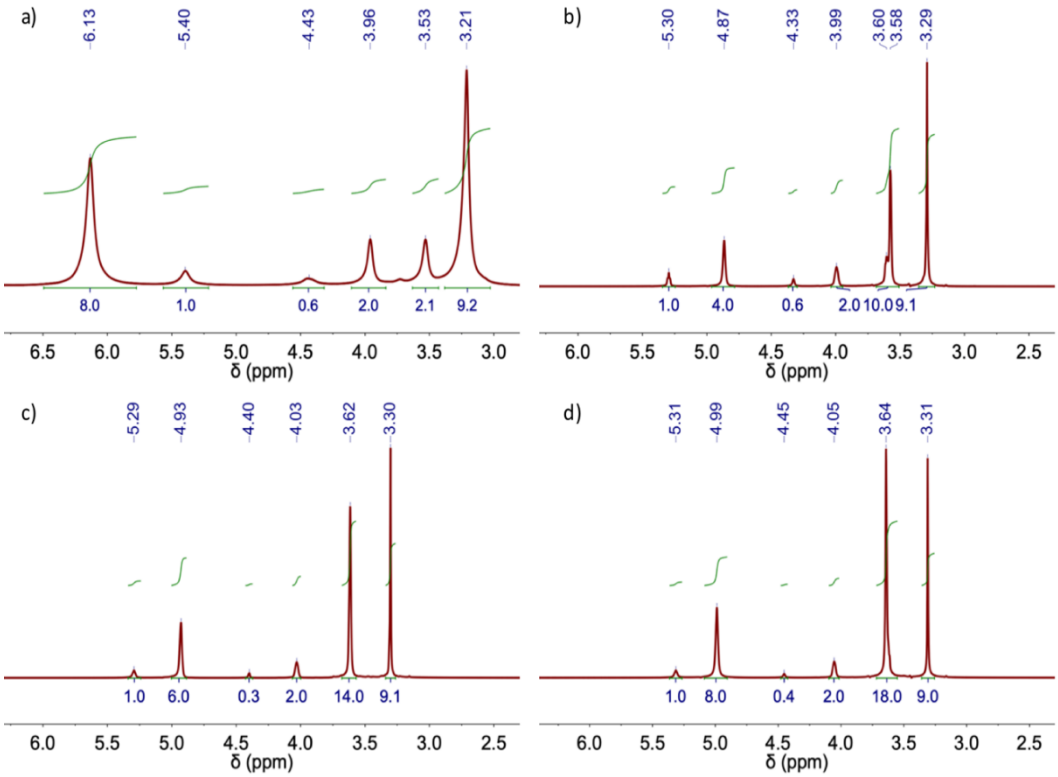

Figure 6. NMR spectrum of DES obtained from the heating-stirring method. (a) ChCl-Urea (1:2), (b) ChCl:EG (1:2), (c) ChCl:EG (1:3) and (d) ChCl:EG (1:4).

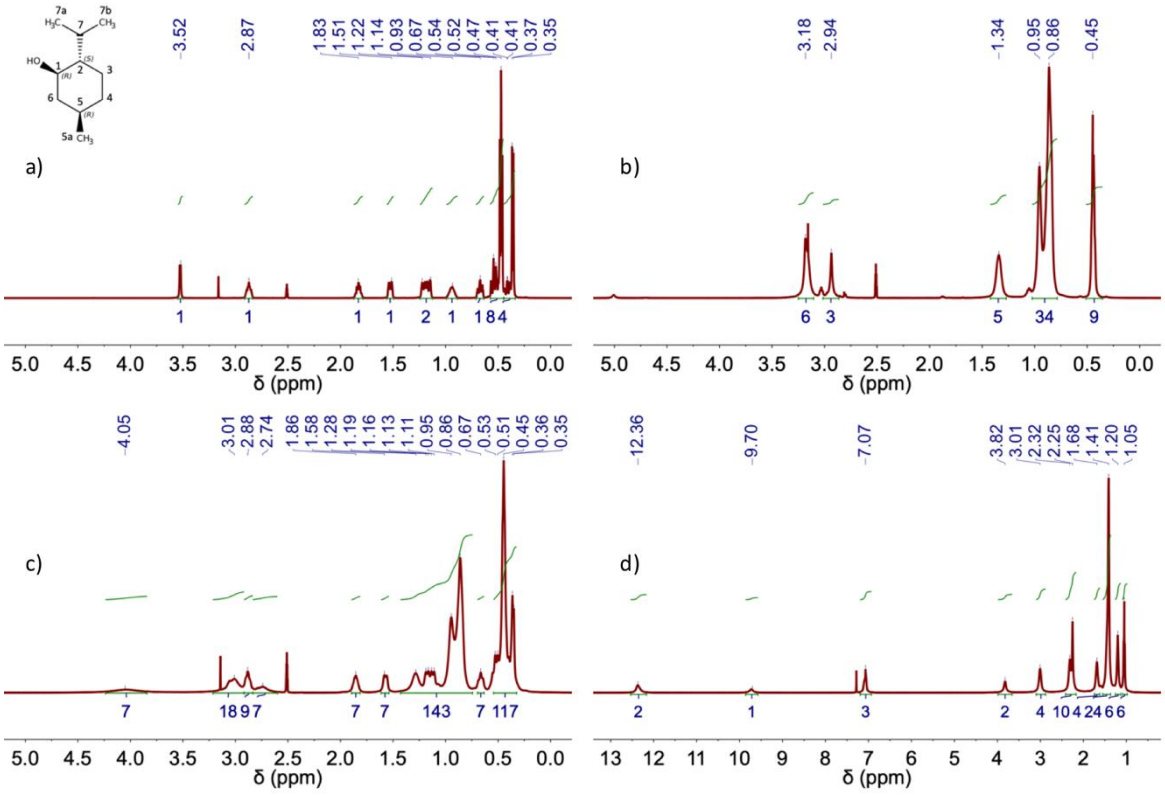

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Figure 7. NMR spectra of (a) L-Menthol, (b) Aliquat 336 TG, (c) Aliq:LMet (3:7) and (d) Ac Dec:Liq (1:2) DES obtained from the heating-stirring method.

Tables 2–5 show the assignment of the peaks corresponding to each NMR spectrum. A signal for water protons is observed in the spectra of the hydrophilic DESs (Tables 2 and 3).

Table 2. ^{1}H NMR chemical shifts of hydrophilic DESs of (ChCl) and (EG). In this case, the spectra were recorded at 298 K using $CDCl_3$ as the external reference.

	δ (ppm)						
DES	**EG**		**ChCl**				**H_2O**
	OH	**O-CH_2**	**OH**	**O-CH_2**	**$^{+}$N-CH_2**	**$^{+}$N-$(CH_3)_3$**	**HO**
ChCl:EG (1:2)	4.87 (4H)	3.60-3.58 (**8H**+2H)	5.30 (1H)	3.99 (2H)	3.60-3.58 (**2H**+8H)	3.29 (9H)	4.33 (0.6H)
ChCl:EG (1:3)	4.93 (6H)	3.63 (**12H**+2H)	5.29 (1H)	4.03 (2H)	3.62 (**2H**+12H)	3.30 (9H)	4.40 (0.3H)
ChCl:EG (1:4)	4.99 (8H)	3.64 (**16H**+2H)	5.31 (1H)	4.05 (2H)	3.64 (**2H**+16H)	3.31 (9H)	4.45 (0.4H)

Table 3. ^{1}H NMR chemical shifts of hydrophilic DES of (ChCl) and (U). The spectrum was recorded at 298 K using $CDCl_3$ as the external reference.

	δ (ppm)					
DES	**U**	**ChCl**				**H_2O**
	C-**NH_2**	**OH**	O-**CH_2**	**$^{+}$N-CH_2**	**$^{+}$N-$(CH_3)_3$**	**HO**
ChCl: U (1:2)	6.13 (8H)	5.40 (1H)	3.96 (2H)	3.53 (2H)	3.21 (9H)	4.43 (0.6H)

Table 4. ^{1}H NMR chemical shifts of hydrophobic DES of Lid:Ac Dec (1:2), The spectrum was recorded at 298 K using $CDCl_3$ as the external reference.

δ (ppm)										
Decanoic acid					**Lidocaine**					
HOOC	HOOC-CH_2	OC-CH_2-CH_2-$(CH_2)_6$	$(CH_2)_6$	CH_3	**NH**	Ar-**H**	Ar-CH_3	OC-CH_2-N	CH_2CH_3	CH_2CH_3
12.36 (2H)	2.32 (**4H**+6H)	1.68 (4H)	1.41 (24H)	1.05 (6H)	9.70 (1H)	7.07 (3H)	2.25 (**6H**+4H)	3.82 (2H)	3.01 (4H)	1.20 (6H)

Table 5 include the chemical shifts of the hydrophobic DES Aliq:LMet (3:7) and its individual components. The formation of H-bond complexes in this DES was confirmed by the upfield chemical shift of the signals ascribed to Aliq and LMet in the ^{1}H NMR spectrum of the DES as compared to that of the individual components (see for example: $^{+}$N-CH_3 shifts from 2.94 ppm in Aliq spectrum to 2.88 ppm after DES formation or H1 shifts from 2.87 ppm in LMet spectrum to 2.74 ppm in the spectrum of DES). The characteristic peak of the hydroxyl group in the LMet spectrum shifts from 3.52 to 4.05 ppm after DES formation in agreement with the presence of H-bonds in DES Aliq:LMet (3:7). [31].

To study the effect of the synthesis method on the properties of the DESs the density and viscosities were evaluated. Both properties are determinant for the application of DESs. The density value of DESs oscillate between 1.0 and 1.3 g cm^{-3} at 25 ^{o}C [7]. Table 6 show the densities for the DESs

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synthesised from the different methods. The results obtained show that the densities are similar, indicating that the synthesis method does not influence the density of the compounds obtained.

Table 7 show bibliographic results of densities for the different DESs. The densities obtained are similar to the bibliographic ones, the slight differences observed may be due to the methods used to measure the densities or the presence of impurities in the compounds.

Table 5. ^{1}H NMR chemical shifts of LMet, Aliq and the hydrophobic DES Aliq:LMet (3:7). The spectra were recorded at 333 K using deuterated DMSO as the external reference.

		δ (ppm)		
		L-Menthol	**Aliquat 336 TG**	**Aliq:LMet (3:7)**
L-Menthol	H1	2.87 (1H)		2.74 (7H)
	H2	0.67 (1H)		0.67 (7H)
	H3a	1.22 (1H)		1.19-1.16
	H3b	0.41 (1H)		0.53-0.35
	H4a	1.14 (1H)		1.12
	H4b	0.54 (1H)		0.53-0.35
	H5	0.93 (1H)		0.95-0.86
	H6a	1.51 (1H)		1.58 (7H)
	H6b	0.52 (1H)		0.53-0.35
	H7	1.83 (1H)		1.86 (7H)
	CH_3 5a	0.47 (3H)		0.45
	CH_3 7a	0.36 (3H)		0.36
	CH_3 7b	0.47 (3H)		0.45
	OH	3.52 (1H)		4.05 (7H)
Aliquat-336 TG	$^{+}$N-C**H**$_3$		2.94 (3H)	2.88 (9H)
	$^{+}$N**CH$_2$**CH$_2$(CH$_2$)$_n$CH$_3$		3.18 (6H)	3.01 (18H)
	$^{+}$NCH$_2$**CH$_2$**(CH$_2$)$_n$CH$_3$		1.34 (5H)	1.28
	$^{+}$NCH$_2$CH$_2$(**CH$_2$**)$_n$CH$_3$		0.95-0.86 (34H)	0.95-0.86
	$^{+}$NCH$_2$CH$_2$(CH$_2$)$_n$**CH$_3$**		0.45 (9H)	0.45

Aliq-LMet (3:7)

Table 6. Densities of hydrophilic and hydrophobic DESs measured at 25ºC.

DES	Density (g/cm^3) Heating and stirring	Density (g/cm^3) Ultrasound
Hydrophilic DES		
ChCl: U (1:2)	1.1846±0.0060	1.1646±0.0016
ChCl:EG (1:2)	1.0931±0.0010	1.1024±0.0045
ChCl:EG (1:3)	1.0953±0.0021	1.1050±0.0072
ChCl:EG (1:4)	1.0995±0.0035	1.1026±0.0109
ChCl: Ox (1:1)	1.2289±0.0034	1.2103±0.0012
Hydrophobic DES		
Aliq: LMet (3:7)	0.8862±0.0025	0.8877±0.0018
Lid:Ac.Dec (1:2)	0.9466±0.0020	0.9489±0.0012

Table 7. Bibliographic densities obtained for 25ºC for hydrophilic and hydrophobic DESs.

Hydrophilic DES	Density (g/cm^3)	Reference
ChCl:EG (1:2)	1.12	[40]

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ChCl:EG (1:3)	1.12	[41]
ChCl:EG (1:4)	1.11	[42]
ChCl:U (1:2)	1.21	[43]
ChCl:U (1:2)	1.25	[44]
ChCl:Ox (1:1)	1.15	[11]
Hydrophofic DES		
Aliq:LMet (3:7)	0.88	[31]
Lid:Ac.Dec (1:2)	0.89	[45]

The DES viscosity is a fundamental parameter that influences on the transport properties and can be used to define their potential applications [7]. DESs are usually quite viscous fluids when compared with organic solvents. Viscosity changes significantly as a function of temperature, the hydrogen bond donor type and the mixture composition. Figure 8 shows the viscosity values of the DESs prepared by the two methods at different temperatures.

It is observed that the viscosity decreases with increasing temperature in all cases for DESs obtained by both synthesis methods. This behaviour is explained using Hole's theory. Abbott and co-workers first applied this theory to DESs. [41,44]. Viscosity and electrical conductivity depend on the presence of holes in the liquids that facilitate the mobility of the compounds in the final network.

These holes of different sizes and location are in continuous movement. At lower temperatures, the size of the holes is small compared to the size of the DESs components, which therefore fit with difficulty into the holes, reducing the free mobility of the components and increasing the viscosity of the system. This behaviour is reversed at high temperatures, the average hole size increases with temperature and is comparable to the size of the components, thus increasing their mobility [42,46]. According to this theory, viscosity is controlled by volumetric factors or steric effects that influence the intermolecular interactions between HBA and HBD, rather than by the stronger interaction between the two components.

The results obtained shows that the viscosities of the hydrophilic DESs is affected by the synthesis method. The viscosity values are higher to the DESs prepared by heating and stirring than those of the same DES prepared by ultrasound. The main differences are obtained to the ChCl:U (1:2) and ChCl:Ox (1:1). The viscosity differences could be due to a higher water content in the ultrasonically obtained samples because the synthesis was carried out in a water bath [11]. Higher water contents imply a decrease in hydrogen bonds between the HBA and HBD of the DES [47].

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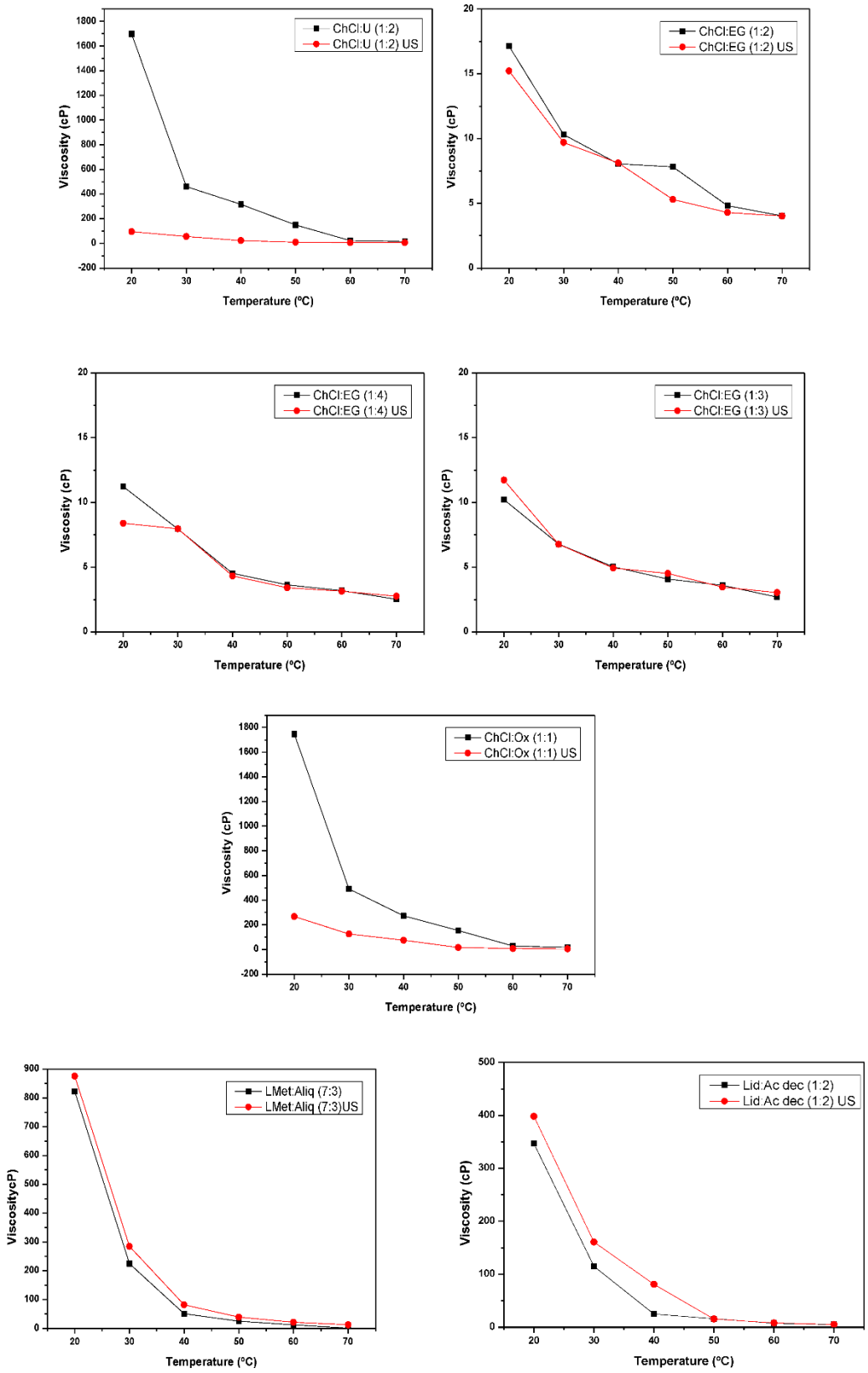

Figure 8. Viscosity (η) values at different temperatures of the DESs prepared by different methods.

+ Ebehaviour is different for hydrophobic DES. The viscosity values are slightly higher for DESs prepared by ultrasound than for DES prepared by heating and stirring.

It is observed that in the case of DESs ChCl:EG, prepared in different molar ratios (1:2, 1:3 and 1:4), the viscosity, in general, decreases with increasing concentration of the donor compound (EG)

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[42]. Low viscosity is beneficial for mass transfer between solute and solvent [48]. This decrease in viscosity is an interesting property to achieve low-viscosity metal leachates with which to work without problems.

The model commonly used to DESs to study the effect of temperature on viscosity is the Arrhenius model. This equation gives a correlation between the viscosity and temperatures:

$$\ln \eta = \ln \eta_0 + E_\eta/RT \quad (1)$$

where ln η is logarithm of viscosity, η_0 is a pre-exponential constant and E_η is the energy for activation of viscous flow, R is the universal gas constant and T is the temperature.

Figure 9 shows that all of the data obey equation (1) well ($R^2 > 0.9673$) (Figure 9a: heating and stirring method), ($R^2 > 0.9673$) (Figure 9b: ultrasonic assisted synthesis).

Tables 8 show the activation energy values obtained for each DES and the corresponding values of η_0. Less viscous DESs show low Ea values such as ChCl:EG (1:4), whereas highly viscous DESs have larger Ea, such as ChCl:U (1:2). It is observed that the DESs that present the highest activation energy are the obtained by the heating and stirring method. Hence, calculated data of Ea perfectly correlate with the measured values of viscosity.

The activation energy of DESs formed by ChCl and EG, in the three molar ratios studied (1:2, 1:3 and 1:4), presents lower energy independently of the synthesis method used. The DESs that shows the greatest difference in activation energy according to the synthesis method used is the ChCl: U 1:2. E_η = 79.04 KJ/mol using the heating and stirring method y E_η = 53.30 KJ/mol using ultrasonic assisted synthesis.

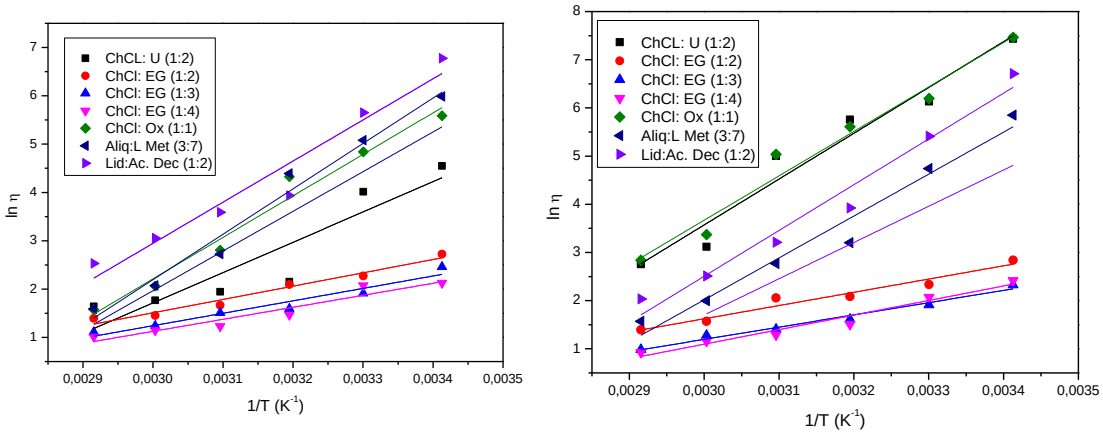

Figure 9. Plots of ln viscosity vs. inverse of temperature for different DESs synthesized by the two methods studied: a) heating and stirring method, b) ultrasonic assisted synthesis.

Table 8. Activation energy values obtained for each DES and values of η_0.

Hydrophilic DES	E_η (KJ/mol)	η_0
ChCl: U (1:2)	79.04	1.46E-11
ChCl: U (1:2) US	53.30	2.94E-08
ChCl:EG (1:2)	22.85	1.33E-03
ChCl:EG (1:2) US	22.93	1.15E-03
ChCl:EG (1:3)	21.13	1.62E-03
ChCl:EG (1:3) US	21.38	1.54E-03
ChCl:EG (1:4)	25.11	3.48E-04
ChCl:EG (1:4) US	20.67	1.77E-03
ChCl: Ox (1:1)	76.68	3.77E-11
ChCl: Ox (1:1) US	71.40	5.90E-11

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Hydrophobic DES		
Aliq: LMet (3:7)	78.97	5.17E-12
Aliq: LMet (3:7) US	71.48	1.29E-10
Lid: Ac.Dec (1:2)	72.33	3.48E-11
Lid: Ac.Dec (1:2) US	78.14	5.11E-12

3. Materials and Methods

3.1. Materials and Reagents

The hydrophilic and hydrophobic DESs were synthesized using choline chloride (ChCl, high purity grade), urea >99 (N), ethylene glycol (EG) pure, oxalic acid 2-hydrate (Ox) 99%, L-menthol (LMet) 99%, Aliquat 336 TG (Aliq), lidocaine (Lid) 97.5% and decanoic acid (Ac Dec) 99%. The description of the chemical reagents used for the synthesis of the DESs is shown in Table 9. The proportions for the synthesis of each of the DESs are shown in Table 10.

Table 9. Chemical reagents used for the synthesis of the DESs.

Chemical reagents	Reagent name	Manufacturer	Mass fraction purity
$C_5H_{14}NOCl$	Choline chloride	PanReac AppliChem	High purify grade
$CO(NH_2)_2$	Urea	PanReac AppliChem	>99% (N)
CH_2OH-CH_2OH	Ethylene glycol	PanReac AppliChem	Pure
$H_2C_2O_4.2H_2O$	Oxalic acid 2-hidrate	PanReac AppliChem	99%
$C_{10}H_{20}O$	L-Menthol	Thermo Fisher Scientific	99%
$[CH_3(CH_2)_7]_3NCH_3Cl$	Aliquat 336 TG	Thermo Fisher Scientific	-
$C_{14}H_{22}N_2O$	Lidocaine	Thermo Fisher Scientific	97.5%
$CH_3(CH_2)_8COOH$	Decanoic acid	Thermo Fisher Scientific	99%

Table 10. Ratios for the synthesis of hydrophilic and hydrophobic DESs.

DES	HBA	HBD	HBA:HBD ratios
ChCl: U (1:2)	Choline chloride	Urea	1:2
ChCl:EG (1:2)	Choline chloride	Ethylene glicol	1:2
ChCl:EG (1:3)	Choline chloride	Ethylene glicol	1:3
ChCl:EG (1:4)	Choline chloride	Ethylene glicol	1:4
ChCl: Ox (1:1)	Choline chloride	Oxalic acid	1:1
Aliq: LMet (3:7)	Aliquat 336	L-Menthol	3:7
Lid: Ac Dec (1:2)	Lidocaine	Decanoic acid	1:2

3.2. Synthesis Method

The synthesis of DESs by heating-stirring method was carried out by mixing the two respective components under continuous stirring (at 600 rpm) at a fixed temperature. The components of each DES were placed in an Erlenmeyer flask and immersed in a silicone oil bath with immersion thermostat (model DIGITERM TFT-200, J.P. SELECTA, Scharlab S.L.).

The ultrasound synthesis of DESs was carried out in an ultrasound bath (A&J Tecno Ultrasound). The respective amount of components was mixed in a Erlenmeyer flask until a homogeneous liquid was obtained.

3.3. Physical-Chemical Characterization of the DESs

The infrared spectra of the DESs synthesized by the two methods studied, as well as the initial reagents, were obtained using a Nicolet iS50 FT-IR Spectrometer of Thermo Scientific™, operated in

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attenuated total reflectance (ATR) mode, in the range from 4000 to 400 cm^{-1}, with spectral resolution of 4 cm^{-1} and accumulation of 64 scans.

^1H NMR spectra of samples obtained by heating-stirring methods were conducted using a Bruker Avance DRX500 spectrometer operating at 500 MHz. The NMR parameters employed included a 30° pulse, an acquisition time of 3.1719 seconds, a relaxation delay of 1 second, and a total of 16-32 scans. All samples were placed in capillary tubes inside a 5 mm NMR glass tubes and analysed using deuterated chloroform ($CDCl_3$) or dimethyl sulfoxide (DMSO-d6) as an external reference. The spectra were acquired after setting the temperature to 298 or 333 K using a Bruker Variable Temperature BVT 3000.

Measurements of the densities of the DESs were made by difference in weight in a Ohaus Explorer Analytical 110G Balance, for which 6 measurements were carried out in which the standard deviation of the samples were calculated.

The viscosities of the DESs were determined using a viscometer PCE-RVI2. The analyses were performed at different temperatures (20 - 70 ºC). Temperature control was carried out in a water bath.

4. Conclusions

The ultrasound method is one of the most promising methods to synthesize DESs in terms of yield and energy. According to the results, it is possible to obtain hydrophilic ChCl: U (1:2), ChCl: Ox (1:1), ChCl:EG (1:2), (1:3) and (1:4) and hydrophobic Lid: Ac. Dec (1:2), Aliq: LMet (3:7) DESs using the ultrasound method, which means lower reaction times and temperatures. The formation of DESs by the ultrasound method is confirmed by the frequency shift in certain bands associated with the formation of hydrogen bonds. The NMR spectra of DESs obtained by heating-stirring methods revealed DES formation. The DESs composed by mixtures of carboxylic acids and ChCl were found to evolve into the respective ester derivatives. The method used to DES synthesis does not affect density values. However, a decrease in the viscosity of the hydrophilic DESs obtained by ultrasound is observed, mainly in ChCl: U (1:2) and ChCl: Ox (1:1), this could be due to a higher water content in the ultrasound DESs. The Arrhenius model fit the correlation between viscosity and temperature.

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