

# Glycerol as a source of designer solvents: physico-chemical properties of low melting mixtures containing glycerol ethers and ammonium salts

Alejandro Leal-Duaso,<sup>a,b</sup> Pascual Pérez,<sup>c</sup> José A. Mayoral,<sup>b</sup> Elisabet Pires,<sup>b</sup> and José I. García\*<sup>a</sup>

In this work we report the preparation of mixtures of several alkyl glyceryl ethers, as hydrogen bond donor compounds, with two ammonium salts, choline chloride and *N,N,N*-triethyl-2,3-dihydroxypropan-1-aminium chloride. The stability of the mixtures at different molar ratios and temperatures has been evaluated in order to determine the formation of low melting mixtures. Liquid and stable mixtures have been characterized and their physical properties such as density, viscosity, refractive index, conductivity and surface tension have been measured in the temperature range of 293.15 K to 343.15 K. Comparison of the mixtures prepared herein with the ones containing glycerol and choline chloride evidences the possibility of tuning the physical properties by changing the substitution pattern in the hydrogen bond donor compound or in the ammonium salt, thus broadening the scope of application of these mixtures.

## Introduction

The vast majority of chemical industry processes, with perhaps the noticeable exception of petrochemical industry, rely on the use of conventional organic solvents. Although there are undisputable advantages in the use of these kinds of solvents, not least their easy availability and low price, there are also important drawbacks, such as their (eco)toxicity, volatility or flammability. For this reason, developing cost-effective, harmless and environmentally benign alternative solvent systems is a research area of great interest. Desirable features of the so-called green solvents are, among others: renewable origin, easy availability and biodegradability, and low (eco)toxicity, volatility, flammability and price. About twenty years ago ionic liquids (IL) were proposed as a green alternative to the conventional hazardous volatile organic solvents due to their low flammability, essentially null volatility, and very special physicochemical properties.<sup>1,2</sup> Since year 1998, a great attention has been devoted to these kinds of solvents, as illustrated by the increasing number of publications appeared

in this area.<sup>3</sup> Nevertheless, some drawbacks have also been enlightened about some IL, for instance their high price, their sometimes difficult synthesis/purification, or their significant (eco)toxicity in many cases.<sup>4,5</sup> Very recently, Low Melting Mixtures (LMM), very often named as Deep Eutectic Solvents (DES) in the literature, have been suggested as greener analogues of ionic liquids.<sup>6-9</sup> This claim is based on their easy preparation, usually just requiring the mixing of two easily available components, their renewable origin in most cases, and the low toxicity of its components.<sup>10</sup>

Most DES are formed by a hydrogen bond donor compound (HBD) and an ammonium salt. The formation of hydrogen bonds between the HBD component and the anion of the salt disrupts the crystallinity of the latter and is responsible for the decrease in the melting point of the mixture relative to their individual components. The stronger the interaction between both components, the larger will be the decrease with regard to the ideal behaviour of the mixture. Unfortunately, terminology used in the literature is not always clear when talking of DES and many of the publications refer to DES when they actually are working with LMM,<sup>11</sup> as the eutectic point corresponds to the single composition of the mixture showing the minimum melting point.

Description of DES preparation, properties and applications has recently been reviewed by Smith *et al.*<sup>12</sup> Some other specialized reviews have also appeared dealing with the use of DES and LMM in organic synthesis,<sup>7,13,14</sup> in nanotechnology,<sup>15,16</sup> and as polymerization media.<sup>17</sup>

Concerning DES compositions, choline chloride is almost universally used as ammonium salt due to its easy accessibility (it is produced on the MTon scale as a chicken feed additive) and low price (*ca.* 2 € per kilogram), but the use of other compounds, such as tetraalkylammonium salts, has also been described.<sup>18-20</sup> It is worth mentioning that the renewable origin

<sup>a</sup> Dr. J. I. García, A. Leal-Duaso  
Instituto de Síntesis Química y Catálisis Homogénea (ISQCH)  
CSIC-University of Zaragoza  
Calle Pedro Cerbuna, 12. E-50009 Zaragoza, Spain  
E-mail: ji.garcia@csic.es

<sup>b</sup> Dr. J. A. Mayoral, Dr. E. Pires  
Department of Organic Chemistry. Faculty of Science  
University of Zaragoza  
Calle Pedro Cerbuna, 12. E-50009 Zaragoza, Spain.

<sup>c</sup> Dr. P. Pérez  
Department of Physical Chemistry. Faculty of Science  
University of Zaragoza  
Calle Pedro Cerbuna, 12. E-50009 Zaragoza, Spain.

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of choline chloride is often claimed as a “green credential”. However, at present most of this chemical is industrially produced from ethylene oxide, and hence from fossil sources. Polyols, urea and its derivatives, carboxylic acids or amides have been described as the HDB component for the formation of DES or LMM. Glycerol is among the most used compounds within this category. Some authors have studied the physical properties of glycerol-containing LMM with different ammonium salts.<sup>21–23</sup> Furthermore, Abbott *et al.* have described the use of glycerol eutectics as sustainable solvent systems in glycerol esterification processes.<sup>8</sup>

On the other hand, glycerol derivatives have attracted great attention as renewable green solvents in different applications.<sup>24–26</sup> In particular, glycerol ethers have shown to be promising candidates for solvent substitution, given that their physicochemical properties can be modulated through the number, size and nature of their alkyl groups, leading to a wide range of polarities, among other properties.<sup>27–30</sup> Some preliminary toxicity studies indicate that most of them display low acute toxicity for widely used biomarkers.<sup>31,32</sup>

In this work, we present a systematic study of the physical properties of mixtures composed of alkyl glyceryl ethers as HBD components and two different ammonium salts: choline chloride and *N,N,N*-triethyl-2,3-dihydroxypropan-1-aminium chloride ([N.0.0]Cl). In the latter case both components can be obtained using glycerol as a platform molecule. The final aim of the work is the fine tuning of the physicochemical properties of the mixture by changing the length and nature of the alkyl chain of the glycerol ether and the ammonium salt.

## Experimental

### Materials and methods

Glycidol, 3-chloropropane-1,2-diol and triethylamine were purchased from Sigma–Aldrich. MeOH, EtOH, <sup>1</sup>PrOH, potassium or sodium hydroxide were purchased from Scharlab. BuOH, 2,2,2-trifluoroethanol, phenol, 2-methoxyphenol and choline chloride were purchased from Alfa Aesar. ChCl was recrystallized from absolute ethanol, filtered and dried at 323.15 K under vacuum prior to use. The alcohols were dried and distilled over calcium hydride previous to use.

<sup>1</sup>H-, <sup>13</sup>C- and <sup>19</sup>F-NMR spectra (DMSO-*d*<sub>6</sub>,  $\delta$  ppm, *J* Hz) were obtained using a Bruker AV-400 instrument with TMS as standard. HRMS spectra were obtained using a Bruker MicroTof-Q spectrometer with electrospray ionization. Solvent boiling points were determined using differential scanning calorimetric (DSC) analysis in a DSC-Q20 TA Instruments, calibrated with indium, using micropore aluminium pans, in a range of 298.15–673.15 K, at atmospheric pressure. Gas chromatography was carried out in a Hewlett Packard 7890 Series II Chromatograph using a column of phenyl silicone 5.5% (Zebron ZB-5HT Inferno 30 m x 0.25 mm x 0.25  $\mu$ m) and Helium as carrier gas, equipped with a flame ionization detector (FID).

### Synthesis of glycerol monoethers, [R.0.0]

The appropriate amount of alcohol (1500% mol with respect to glycidol) and potassium hydroxide (20% mol with respect to

glycidol) were placed into a round-bottomed flask. The reaction was stirred and heated at 338 K under argon until total dissolution of the catalyst. Then, glycidol (1 mol) was added dropwise. The reaction was monitored at different times by extracting samples that were neutralized with HCl 0.3 M previous to injection in GC. After total consumption of glycidol, the reaction was quenched with HCl 0.3 M and filtered off. After reaction work-up, the corresponding glycerol monoether was purified by vacuum distillation, or by column chromatography in the case of aromatic monoethers.

### Synthesis of *N,N,N*-triethyl-2,3-dihydroxypropan-1-aminium chloride, [N.0.0]Cl

42.4 mL of 3-chloropropane-1,2-diol (0.51 mol) were added to a solution of triethylamine (105 mL, 0.76 mol) in methanol (80 mL) in a round bottomed flask. The reaction was stirred and heated at 338 K under argon atmosphere for 12 hours. Then, triethylamine was eliminated by vacuum distillation and the resulting oil was washed with ether until appearance of a white precipitate. This solid was filtered off, washed with acetone and dried under vacuum.

### DES Preparation

The mixtures were formed by stirring the two components, the glycerol ether and the ammonium salt (ChCl or [N.0.0]Cl), under argon at 343 K for 10 hours approximately. In the correct molar proportion, a homogeneous colourless liquid was obtained, its composition being checked by NMR.

### Physicochemical properties measurements

**Density and sound speed.** Both properties were simultaneously determined by an Anton Paar DSA 5000 M which is equipped with a density and sound speed cells. Both chambers are temperature controlled by an internal Peltier thermostat at  $\pm 0.001$  K. After the appropriated calibration, the sample is introduced into a U-shaped glass tube and the density is obtained from its frequency of vibration with an uncertainty of  $\pm 5 \cdot 10^{-3}$  Kg m<sup>-3</sup>. Correction due to kinematic viscosity of the liquid is made automatically. Sound speed of the sample is calculated by the determination of sound waves through the cell with an uncertainty of  $\pm 0.1$  m s<sup>-1</sup>.

**Static dielectric permittivity and dipole moment.** Static dielectric permittivity, or dielectric constant, data were calculated from capacitance values measured with a WTW (DM01) dipolemeter (Kahlsico) at 2MHz. The apparatus works using the superposition method, by which the oscillations of two high frequency oscillators are brought to superposition in a mixing section. Two cylindrical condensers type sample holding cells were used in order to cover the entire range of experimental data. Cell DFL2 covered the dielectric constant range from 1 to 7 and cell MFL2/MS from 6 to 23. Both cells were provided with a metal jacket and held at constant temperature by a water circulating external bath and they were previously calibrated with high purity and low water content reference liquids. Relative uncertainty in dielectric constant values is estimated to be better than 0.05%. Dielectric constant of liquid [3F.0.0] was only measured at 298.15 K by the time domain reflectometry (TDR) technique using the first reflection

method, due to its high dielectric constant was out of the range of the MFL2/MS cell.

From the dielectric constant, refractive index and density experimental data, an average of dipole moment  $\langle \mu^2 \rangle^{1/2}$  for every pure liquid was calculated through the Onsager's equation:<sup>33</sup>

$$\langle \mu^2 \rangle = \frac{9kT}{4\pi N_A} \cdot \frac{M}{\rho} \frac{(\epsilon - n_D^2)(2\epsilon + n_D^2)}{\epsilon \cdot (n_D^2 + 2)^2}$$

where:

$k$  = Boltzman's constant

$T$  = temperature in K

$M$  = molar mass

$N_A$  = Avogadro's number

$\rho$  = density

$n_D$  = refractive index

$\epsilon$  = dielectric permittivity

**Refractive index.** An Abbe refractometer ZUZI 315 with temperature controlled and a sodium lamp as light source was used to refractive index measurements, with an uncertainty of  $\pm 0.0001$ .

**Viscosities.** A set of three Ubbelohde viscometers with suspending ball level (Schott) and relatively long flow time were used in order to cover the entire range of experimental values. In each experiment the flow time was measured at least three times with differences not greater than  $\pm 0.3$  s. The viscometers models were: 501 11/la, 501 23/IIc and 501 30/III, whose constants  $k$  were 0.04957, 0.3157 and 1.000  $\text{mm}^2\text{s}^{-2}$ , respectively. The kinematic viscosities were calculated from the equation:

$$\nu = k(t - \Delta_{HC})$$

where  $\nu$  is the kinematic viscosity,  $k$  the viscometer constant,  $t$  the average flow time and  $\Delta_{HC}$  the kinetic energy correction.

The viscometers were placed in a thermostated bath using a suitable support. The relative uncertainty in kinematic viscosity data is around 0.6%. Dynamic viscosity was calculated according the equation:

$$\eta = \nu\rho$$

where  $\eta$  is the dynamic viscosity,  $\rho$  the density and  $\nu$  the kinematic viscosity as defined above.

**Conductivity.** The ionic conductivity measurements were carried out with a Crison GLP31 conductimeter. The apparatus was calibrated by using two KCl reference solutions of 1413  $\mu\text{S cm}^{-1}$  and 12.88  $\text{mS cm}^{-1}$ . The liquid and the conductivity cell were set in a glass container equipped with a thermostated jacket. The experimental values have a relative uncertainty better than 0.5%.

In the process of measurement of the above-mentioned properties: dielectric constant, refractive index, conductivity and kinematic viscosity, temperature was controlled by means of a Haake F6 thermostat with stability better than 0.01 K.

**Surface tension.** A drop volume tensiometer Lauda TVT-2, which is able to measure the volume of a drop with high precision, was used to obtain surface tension of sample liquids at a fixed temperature with a relative uncertainty not worse

than 0.5%. A Lauda E-200 thermostat allowed to maintain the sample temperature within  $\pm 0.01$  K.

For all liquids and properties measured, the temperature was registered by means of a digital thermometer AΣΛ with a Pt sensor with resolution of 0.001 degree and uncertainty of  $\pm 0.01$  K.

## Results and discussion

In the last years we have focussed our attention in the synthesis, characterization, use and toxicity study of alkyl glyceryl ethers.<sup>28,31,32,34-36</sup> These promising solvents have some advantages like being relatively inert from a chemical point of view (differently from other glycerol derivatives, such as esters, ketals or carbonate), non-volatile and less viscous than glycerol. Moreover, their physicochemical and toxicological properties can be tuned by simply changing the number, size and nature of the alkyl chains. As an evidence of the stability of these glycerol derivatives, semi quantitative analysis of peroxides (Quantofix®) in samples of solvents stored in our laboratory showed less than 1  $\text{mg}\cdot\text{L}^{-1}$  of  $\text{H}_2\text{O}_2$  in two years old ether samples and less than 3  $\text{mg}\cdot\text{L}^{-1}$  in solvents stored for 12 years.

The evidence that glycerol can be used as the HBD component in LMM<sup>21-23</sup> prompted us to study the possibility of using the alkyl glyceryl ethers as components of LMM together with different ammonium salts. For this study we have chosen mono- and dialkyl glyceryl ethers with alkyl chains of increasing length, alkyl chains containing fluorine, and simple aryl substituents (Fig. 1), in order to study the influence of these structural factors both on the mixtures formation and on the physicochemical properties of the stable mixtures.

As ammonium salts we chose choline chloride (ChCl) (Fig. 1), in order to compare the properties of our mixtures to the ones previously described. We also included in the study an ammonium salt that can be prepared using glycerol as platform molecule, namely the *N,N,N*-triethyl-2,3-dihydroxypropan-1-aminium chloride (henceforth [N.0.0]Cl), so as both components of the DES come from the same renewable source.

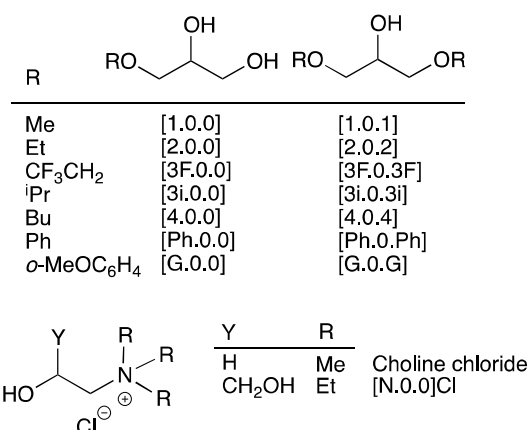
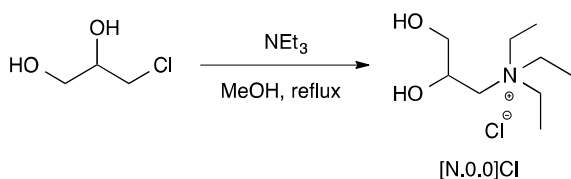


Fig. 1 alkyl glyceryl ethers and ammonium salts used in this study.

In our case, this compound was easily obtained from the reaction of 3-chloropropane-1,2-diol with triethylamine (Scheme 1).



Scheme 1 Synthetic procedure for the preparation of [N.0.0]Cl.

### Preparation and stability of the mixtures

First, a complete study of the formation of the mixtures and their stability was carried out. HBD and ammonium salt components were mixed at 343 K in different molar ratios: 2.5:1, 2:1, 1.5:1 and 1:1. The main purpose was obtaining homogeneous liquid mixtures at moderated or low temperatures, capable of being used as solvents. Not all the combinations tested yielded homogeneous mixtures at the working temperature. Diethers [1.0.1], [2.0.2], [4.0.4], [3i.0.3i], [3F.0.3F], [Ph.0.Ph], and one triether ([1.1.1]) when mixed with both salts, led to heterogeneous solid-liquid systems depending on the temperature and the nature of the ammonium salt. Thus, in the case of ChCl, solid-liquid phases were obtained in the overall range of temperature considered (from 258 to 343 K).

In the case of [N.0.0]Cl, although homogeneous liquid mixtures were formed at 343 K, solid phases segregated from all mixtures as soon as the temperature started to decrease. On the other hand, monoethers of glycerol ([1.0.0], [2.0.0], [4.0.0], [3i.0.0], [3F.0.0], [Ph.0.0] and [G.0.0]) were able to form homogeneous colourless liquid mixtures at working temperature at all the proportions tested with both ammonium salts. However, after cooling to room temperature the homogeneity in the liquid mixtures was kept only in those mixtures having a 2:1 HBD:ammonium salt molar ratio. In the case of [N.0.0]Cl, some stable liquid mixtures were also obtained at a 2.5:1 molar ratio. These results point to the need of having at least two hydroxyl groups in the HBD molecule and a molar ratio *ca.* 2:1 of this component in the mixture in order to allow strong interactions with the chloride anion of the ammonium salt, leading to stable low melting mixtures. As a consequence of these results we decided to continue the study only with those components and molar ratios leading to homogeneous and stable liquid phases.

Using the abovementioned seven [R.0.0] ethers and the two ammonium salts, up to 14 new LMM could be formed in the molar

proportion 2:1. However, the range of stability of these mixtures was not the same. Some mixtures, including [2.0.0], [4.0.0], [3i.0.0] and [G.0.0] displayed a “critical stability temperature” below which some solid phase appears. This temperature was characteristic of the HBD component used, and increases as the R chain length does. In the case of ChCl mixtures, their values were 306, 325, 333, 347 and 313 K for [1.0.0], [2.0.0], [3i.0.0], [4.0.0], and [G.0.0], respectively. On the other hand, [N.0.0]Cl mixtures are more stable, and the “critical temperatures” were lower, mixtures with [1.0.0], [2.0.0], [3F.0.0] and [Ph.0.0] being totally stable in the whole range of temperature (from 298 to 343 K).

The homogeneous mixtures were cooled below 248 K, and the formation of different glass phases was observed. In no case liquid-crystal transitions were observed. For this reason, only in the case of mixing solid [Ph.0.0] (m. p. = 327–330 K) or [G.0.0] (m. p. = 350–354 K) with either of the two salts, ChCl (m.p. = 575 K) or [N.0.0]Cl (m.p. = 373–423 K) the homogeneous liquid mixtures obtained could be properly named as DES from a physicochemical point of view. For the rest of mixtures, where the HBD component is already liquid at room temperature, the name of LMM would be more appropriate.

### Physical property measurements

The majority of properties characterizing solvents were measured in a temperature range of 298.15–343.15 K, except in those cases in which the above-mentioned critical temperature falls within this interval, and experimental data obtained were fitted to model equations.

**Density.** Density ( $\rho$ ) is a very important property of solvents, essential for many chemical and engineering industrial applications. Fig. 2 shows the density measurements in all studied solvents in the temperature range of 298.15–343.15 K. For comparative purposes, the densities of pure glycerol monoethers are also included, together with those of their mixtures with ChCl and [N.0.0]Cl. As usual in organic solvents, densities decrease when increasing temperature, due to the thermal expansion. The influence of the R alkyl chain of the glycerol ether on this property can also be ascertained from Fig.2. As the R chain length increases, the corresponding density value decreases, most probably because the lengthening of the alkyl chains results in an increase of the volume occupied by molecules in the liquid. The branched alkyl ether [3i.0.0] displays densities similar to those of [4.0.0]. As expected, the fluorinated ether [3F.0.0] displays higher densities, due to the higher atomic mass of fluorine atoms.

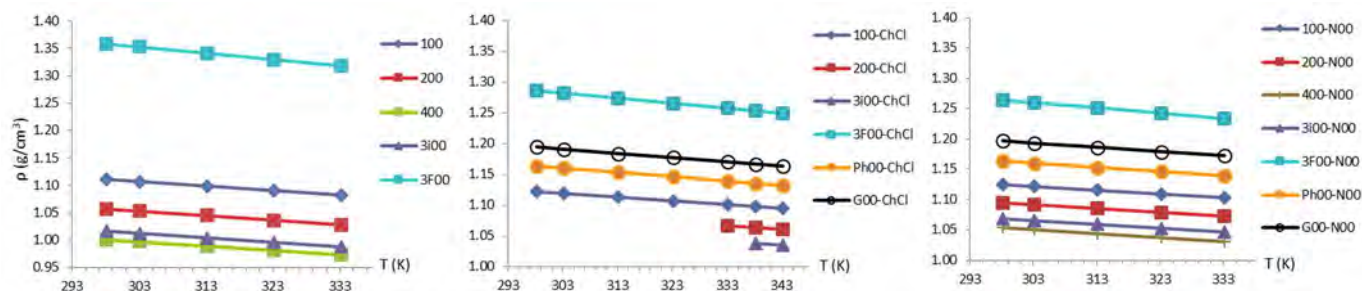


Fig. 2 Densities of Glycerol monoethers [R.0.0] and their mixtures with ChCl and [N.0.0]Cl

Interestingly, the densities of the mixtures are not quite different from those of the pure [R.0.0] ethers, with the exception of [3F.0.0], for which densities of the mixtures are noticeably lower. Another observation from plots in Fig. 2 is that the nature of the ammonium salt does not affect appreciably to the densities of the corresponding mixtures. The density values of these mixtures are ranged (at 298.15 K) in between those of conventional organic solvents ( $0.75\text{--}1.00\text{ g}\cdot\text{cm}^{-3}$ ) and those of the majority of ILs ( $1.21\text{--}1.45\text{ g}\cdot\text{cm}^{-3}$ ), 2:1 ChCl DES (e.g.  $1.24\text{ g}\cdot\text{cm}^{-3}$  for ureline and  $1.18\text{ g}\cdot\text{cm}^{-3}$  for glyceline)<sup>12</sup> or pure glycerol ( $1.261\text{ g}\cdot\text{cm}^{-3}$ ).<sup>28</sup>

The experimental data of the densities obtained at different temperatures were fitted to linear equation 1 ( $r^2 > 0.999$ ):

$$\rho = aT + b \quad (1)$$

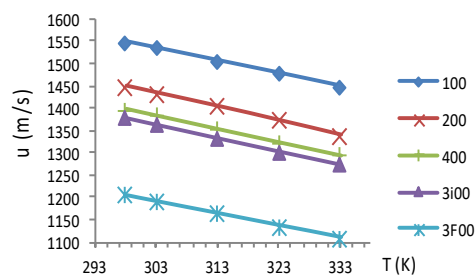
where  $\rho$  is the density in  $\text{g}\cdot\text{cm}^{-3}$ ,  $T$  is the temperature in Kelvin, and  $a$  and  $b$  are constants (related to the molar composition in the case of DES). Full density-temperature model parameters are gathered in Table 1.

An interesting property related to density is the sound propagation speed of the solvent ( $u$ ), very used in refinery.<sup>37</sup> Propagation speed trends versus temperature are very similar to densities trends, with the exception of [3F.0.0], whose low propagation speed can be explained according to the inverse dependence of this property with density. Experimental values are near to those of conventional solvents like water ( $1493\text{ m}\cdot\text{s}^{-1}$  at r.t.). However, this property noticeably increases in the mixtures by the presence of the salt. Higher sound propagation speeds in DES are due to the multiple and stronger interactions formed between the two components in the liquid medium.

**Table 1** Density-temperature model parameter.<sup>a</sup>

	$a$	$b$	$r^2$
[1.0.0]	-0.000808	1.351813	1.0000
[2.0.0]	-0.000834	1.305653	0.9997
[4.0.0]	-0.000789	1.236374	1.0000
[3i.0.0]	-0.000834	1.265385	1.0000
[3F.0.0]	-0.001155	1.702551	1.0000
[1.0.0]:ChCl	-0.000620	1.306844	1.0000
[2.0.0]:ChCl	-0.000525	1.241157	0.9990
[3F.0.0]:ChCl	-0.000815	1.528180	1.0000
[Ph.0.0]:ChCl	-0.000697	1.371036	0.9991
[G.0.0]:ChCl	-0.000700	1.403065	0.9997
[1.0.0]:[N.0.0]Cl	-0.000612	1.307098	0.9998
[2.0.0]:[N.0.0]Cl	-0.000638	1.284867	0.9999
[4.0.0]:[N.0.0]Cl	-0.000645	1.245904	1.0000
[3i.0.0]:[N.0.0]Cl	-0.000653	1.263256	1.0000
[3F.0.0]:[N.0.0]Cl	-0.000842	1.514573	0.9994
[Ph.0.0]:[N.0.0]Cl	-0.000674	1.364079	0.9998
[G.0.0]:[N.0.0]Cl	-0.000696	1.404102	0.9990

<sup>a</sup> All the experimental density values are available in the ESI.



**Fig. 3** Sound propagation speeds of glycerol monoethers [R.0.0].

These experimental data were also fitted to a model equation, as a linear function of temperature (see Table 2):

$$u = aT + b \quad (2)$$

where  $u$  is the sound propagation speed in  $\text{m}\cdot\text{s}^{-1}$ ,  $T$  is the temperature in Kelvin, and  $a$  and  $b$  are the adjustable parameters.

**Table 2** Sound propagation speed-temperature model parameter.<sup>a</sup>

	$a$	$b$	$r^2$
[1.0.0]	-2.860	2401.9	1.0000
[2.0.0]	-3.111	2377.3	0.9998
[4.0.0]	-2.940	2274.1	0.9999
[3i.0.0]	-3.052	2289.5	1.0000
[3F.0.0]	-2.773	2033.3	1.0000
[1.0.0]:ChCl	-2.997	2684.2	0.9997
[2.0.0]:ChCl	-2.696	2481.2	1.0000
[3F.0.0]:ChCl	-2.654	2274.5	1.0000
[Ph.0.0]:ChCl	-3.442	2849.2	0.9991
[G.0.0]:ChCl	-3.263	2818.4	0.9996
[1.0.0]:[N.0.0]Cl	-2.910	2642.7	0.9996
[2.0.0]:[N.0.0]Cl	-3.000	2572.8	0.9994
[4.0.0]:[N.0.0]Cl	-2.973	2464.7	0.9994
[3i.0.0]:[N.0.0]Cl	-3.084	2518.3	0.9991
[3F.0.0]:[N.0.0]Cl	-2.978	2381.5	0.9996
[Ph.0.0]:[N.0.0]Cl	-4.382	3151.2	0.9900

<sup>a</sup> All the experimental sound propagation speed values are available in the ESI.

**Molar Volume.** Molar Volume ( $V_m$ ), for a liquid, is the volume filled by 1 mol of this substance at a given temperature. This parameter is directly correlated to the free volume of a molecule, which is closely related to other properties like viscosity or conductivity. The molar volume of the solvents was calculated according to semi empirical equation 3, where  $M$  is the molar mass and  $\rho$  the solvent density.

$$V_m = \frac{M (\text{g/mol})}{\rho (\text{g/cm}^3)} \quad (3)$$

In a DES,  $M$  is the relative molar mass (and  $x$  the mole fraction):

$$M = x_{\text{HBD}} \cdot M_{\text{HBD}} + x_{\text{HBA}} \cdot M_{\text{HBA}} \quad (4)$$

Molar volume is inversely proportional to density, so it increases as the temperature does. Molar volumes of [R.0.0] and [R.0.0] LMM (fig. 4) are higher than that of glycerol ( $73.03\text{ cm}^3\cdot\text{mol}^{-1}$  at 298.15 K). In addition, molar volumes of the mixtures with [N.0.0]Cl are greater than those of the mixtures with ChCl, due to the different  $M_{\text{HBA}}$  ( $211.73$  vs.  $139.62\text{ g}\cdot\text{mol}^{-1}$ ).

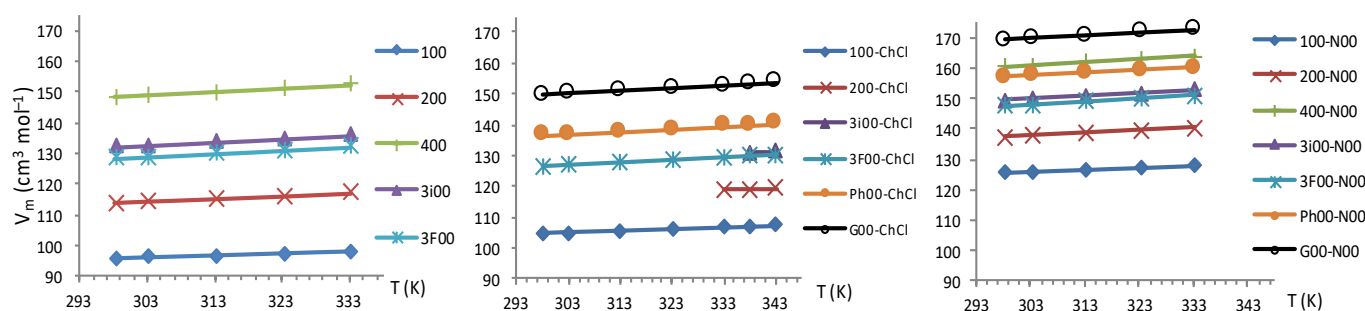


Fig. 4 Molar Volume values of Glycerol monoethers [R.0.0] and their mixtures with ChCl and [N.0.0]Cl.

**Solvent Polarity.** Different physical and chemical parameters can be used to estimate the polarity of the solvents. In this work we have decided to determine dielectric permittivity ( $\epsilon$ ) and dipole moment ( $\mu$ ) as indicators of the polarity of the solvents. Unfortunately, these parameters can only be measured for nonionic substances, which excludes the study of the mixtures.

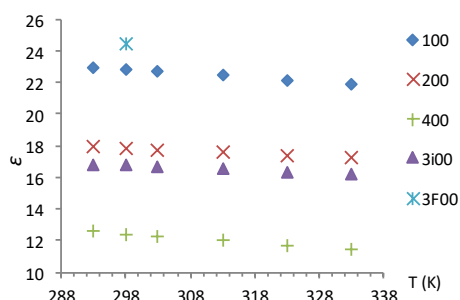


Fig. 5 Dielectric permittivities of Glycerol monoethers solvents [R.0.0].

Permittivity values indicate that the shorter the alkyl chain of the glycerol ether, the higher the polarity. Again, there is an exception in the case of the fluorinated solvent. The dielectric permittivity of this solvent is so high (24.5) that it could only be measured at 298.15 K using a different method (see details in the Experimental section). In general, the  $\epsilon$  values measured are similar to those of other conventional alcohols (for instance ethanol 24.3 or isopropanol 17.9 at 298.15 K), but much lower than that of glycerol (46.5 at 298.15 K) or even ethylene glycol (37.7 at 298.15 K). The equation describing the inverse variation of the permittivity with temperature (eq. 5) is the following:

$$\epsilon = a T + b \quad (5)$$

where  $\epsilon$  is the dielectric permittivity of the solvent, T is the temperature in Kelvin, and  $a$  and  $b$  are adjustable parameters.

Using the dielectric permittivity and other properties like densities and refractive indexes it is possible to calculate the dipole moment ( $\mu$ ) of a molecule using the Onsager's equation (see Experimental section). As can be seen in Table 4, calculated dipole moments of the glycerol ethers show the same trend already observed for dielectric permittivities. However, dipole moments of glycerol ethers are

higher than those of conventional solvents, including glycerol and water, indicating their high capacity to solvate ionic and dipolar solutes.

	$a$	$b$	$r^2$
[1.0.0]	-0.0247	30.19	0.9999
[2.0.0]	-0.0177	23.15	0.9988
[4.0.0]	-0.0294	21.21	0.9992
[3i.0.0]	-0.0144	21.06	0.9988

<sup>a</sup> All the experimental dielectric permittivity values are available in the ESI.

Table 4 Calculated dipole moment  $\mu$  (in Debye) of selected glycerol ether and other conventional solvents (using the Onsager's equation) at 298.15 K

	<b>[1.0.0]</b>	<b>[2.0.0]</b>	<b>[4.0.0]</b>	<b>[3i.0.0]</b>	<b>[3F.0.0]</b>
<b>Glycerol</b>	2.56	3.49	3.35	3.13	3.51
<b>Hexane</b>	<b>Et<sub>2</sub>O</b>	<b>DCM</b>	<b>MeOH</b>	<b>THF</b>	<b>Water</b>
	0.00	1.38	1.60	1.70	1.75
			1.70	1.75	1.85

**Refractive index.** Another physical property of a solvent, and related with its purity, is the refractive index (RI or  $n_D$ ). In general, RI is a precise measure of the polarizability of the molecules. RI values were determined in the temperature range of 298.15–348.15 K. In the case of [R.0.0] ethers,  $n_D$  values are closely similar in all cases, with the exception of [3F.0.0]. In fact, as the alkyl chain length increases,  $n_D$  slightly increases too, as expected, given the higher global polarizability. The low RI of the fluorinated ether is explained because of the lower polarizability of this molecule due to the electronegative fluorine atoms.

Concerning the mixtures, as it is shown in Fig. 6, they always have higher RI than the corresponding [R.0.0] monoethers, due to the salt presence. Refractive indices are similar for the mixtures regardless of the nature of the ammonium salt (ChCl or [N.0.0]Cl), although there are slightly higher in the case of [N.0.0]Cl. In all the cases, the  $n_D$  values are analogous to those of conventional solvents (1.32–1.50) and glycerol (1.47). It is worth mentioning that the mixtures of both aromatic ethers have noticeably high RI ( $n_D > 1.53$ ),



much closer to those of aromatic solvents like toluene and xylene, or sugar-based DES.<sup>38</sup>

Interestingly, in the mixtures the variation of  $n_D$  with the length of R follows the opposite trend observed for pure glycerol ethers. This can be explained because the existence of two opposed physical effects. On the one hand, as mentioned above, the polarizability of

the [R.0.0] component increases with the R length, leading to an increase of RI. On the other hand, a longer R chain results in a lower density of the mixture, so light propagation speed increases and RI decreases accordingly. It is clear that this second mechanism overrules the first one in the case of the mixtures.

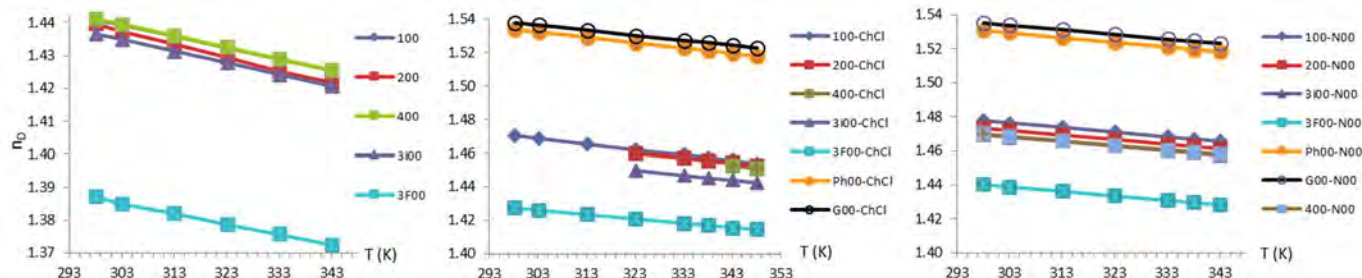


Fig. 6 Refractive indices of studied solvents: Glycerol monoethers [R.0.0] and their mixtures with ChCl and [N.0.0]Cl.

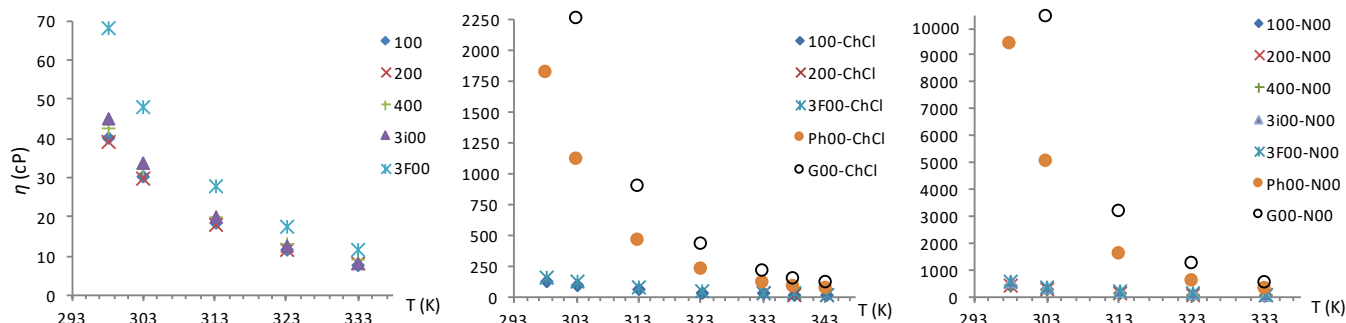


Fig. 7 Dynamic viscosities of studied solvents: Glycerol monoethers [R.0.0] and their mixtures with ChCl and [N.0.0]Cl.

Dependence of the refractive index with temperature is quite similar in all glycerol monoethers, as can be seen in Table 5, which gathers the excellent fittings ( $r^2 > 0.999$ ) of the experimental  $n_D$  data to the linear model shown in equation 6 (with T in Kelvin, a in  $K^{-1}$  and b unitless):

$$n_D = aT + b \quad (6)$$

The molar refractivity ( $R_m$ ) of the studied solvents can be calculated using the Lorentz equation, from the molar volume and the  $n_D$  values:

$$R_m = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot V_m \quad (7)$$

where  $R_m$  is in  $cm^3 \cdot mol^{-1}$ ,  $n_D$  is the measured refractive index and  $V_m$  is the molar volume in  $cm^3 \cdot mol^{-1}$ . As  $n_D$  is measured with radiation of optical frequency,  $R_m$  is related to the mean electronic polarizability and it may be considered as a measure of the capacity of molecular orbitals to be deformed by an electric field. All molar refractivity values of the glycerol solvents are available in the Electronic Supplementary Information.

**Viscosity.** Viscosity is a very important solvent property as it determines some of its possible uses. In this work we have measured kinematic viscosity ( $\nu$ , in cSt) in the temperature range of 298.15–343.15 K. The dynamic viscosity ( $\eta$ , in cP) can be derived from kinematic viscosity and densities values.

Aliphatic glycerol monoethers have viscosities much lower (35–45 cP at r.t.) than glycerol (1200 cP at r.t.), probably because substitution of a hydroxyl group by an alkoxide group has a remarkable effect on the strength of intermolecular interactions.

The high viscosity of glycerol is indeed a problem in many applications, due to the higher operational and energy costs. When comparing the viscosity values of glycerol ethers with different R chain lengths, we observe that the longer the alkyl chain, the higher the viscosity. The presence of a ramification in the substituent leads to an increase in the viscosity of the monoether ([3i.0.0] vs. [4.0.0], Fig. 7). A singular case is that of [3F.0.0], whose viscosity is almost double than its non-fluorinated homologue [2.0.0]. This may be due to the higher density of [3F.0.0] and hence to its lower free volume. According to the hole theory,<sup>12</sup> as this solvent has low free volume, the flow of a molecule of [3F.0.0] through a hole inside the liquid is more difficult, which results in a higher viscosity.

The viscosities of the mixtures of glycerol ethers with ChCl or [N.0.0]Cl increase moderately with regard to that of pure [R.0.0] monoethers. Abbott *et al.* stated that whereas the viscosity of the mixtures glycerol:ChCl decreases as the salt concentration increases, the opposite is true in the case of diols. Thus, the situation of glycerol monoethers seems to be analogous to that of diols.

**Table 5** Refractive index-temperature model parameter.<sup>a</sup>

	<i>a</i>	<i>b</i>	<i>r</i> <sup>2</sup>
[1.0.0]	-0.000346	1.5441	0.9998
[2.0.0]	-0.000402	1.5596	0.9990
[4.0.0]	-0.000345	1.5439	0.9999
[3i.0.0]	-0.000354	1.5422	0.9999
[3F.0.0]	-0.000317	1.4813	0.9987
[1.0.0]:ChCl	-0.000325	1.5672	0.9993
[2.0.0]:ChCl	-0.000299	1.5566	0.9992
[4.0.0]:ChCl	-0.000155	1.5055	0.9990
[3i.0.0]:ChCl	-0.000291	1.5439	0.9992
[3F.0.0]:ChCl	-0.000262	1.5056	0.9995
[Ph.0.0]:ChCl	-0.000315	1.6275	0.9997
[G.0.0]:ChCl	-0.000308	1.6297	0.9992
[1.0.0]:[N.0.0]Cl	-0.000267	1.5570	0.9997
[2.0.0]:[N.0.0]Cl	-0.000269	1.5536	0.9999
[4.0.0]:[N.0.0]Cl	-0.000266	1.5489	0.9996
[3i.0.0]:[N.0.0]Cl	-0.000263	1.5477	0.9999
[3F.0.0]:[N.0.0]Cl	-0.000259	1.5173	0.9999
[Ph.0.0]:[N.0.0]Cl	-0.000288	1.6168	0.9996
[G.0.0]:[N.0.0]Cl	-0.000270	1.6161	0.9991

<sup>a</sup> All the experimental refractive index values are available in the ESI.

Apart from this, [N.0.0]Cl mixtures are three times more viscous than their homologous containing ChCl. This seems to be due to the additional interactions (particularly hydrogen bonds) established by the former, which has a longer carbon chain and an additional hydroxyl group. Regardless the ammonium salts used, the viscosity order observed is: [1.0.0] < [2.0.0] < [4.0.0] < [3i.0.0] < [3F.0.0] <<< [Ph.0.0] << [G.0.0]. Explanation for this order has been mentioned above. Mixtures of aliphatic ethers with [N.0.0]Cl show viscosities close to DES ones (>400 cP at 298.15 K) and they are quite similar to those shown in mixtures between glycerol and ChCl (in the same 2:1 ratio).<sup>8</sup> Mixtures of aliphatic ethers with ChCl display a viscosity (≈150 cP at 298.15 K) higher than conventional solvents, but lower than other reported DES (750 cP at 298 K for urea:ChCl or 1124 cP for malonic acid:ChCl). Finally, mixtures containing aromatic ethers present extremely high viscosities, which can be explained by the stronger aromatic rings π-π and π-OH intermolecular interactions.

Viscosity is a very temperature-dependent property. When the temperature increases molecular mobility increases too, resulting in an exponential decrease of viscosity. The experimental data have been fitted to an Arrhenius-type equation 8,<sup>39</sup> which describes adequately the viscosity behaviour with temperature:

$$\ln \eta = \frac{E_{\eta}}{RT} + b \quad (8)$$

where  $\eta$  is the dynamic viscosity in cP,  $T$  is the temperature in Kelvin,  $R$  is the gas constant (8.31445 J·K<sup>-1</sup> mol<sup>-1</sup>),  $E_{\eta}$  is the energy for activation of viscous flow and  $b$  is a constant. The values of  $E_{\eta}$  show the different trends mentioned above, being <40 kJ·mol<sup>-1</sup> for the pure monoethers and 36–87 kJ·mol<sup>-1</sup> for the different mixtures (36–51 kJ·mol<sup>-1</sup> for aliphatic ethers and 63–87 kJ·mol<sup>-1</sup> for aromatic ones). As can be observed in table 6, [R.0.0]/[N.0.0]Cl mixtures have  $E_{\eta}$  values higher than that of glycerol:ChCl (45.1 kJ·mol<sup>-1</sup>).<sup>8</sup>

**Table 6** Viscosity-temperature model parameter.<sup>a</sup>

	$E_{\eta}$ / kJ·mol <sup>-1</sup>	<i>b</i>	<i>r</i> <sup>2</sup>
[1.0.0]	39.043	-12.087	0.9994
[2.0.0]	37.946	-11.667	0.9987
[4.0.0]	37.418	-11.370	0.9990
[3i.0.0]	40.344	-12.491	0.9991
[3F.0.0]	41.838	-12.707	0.9972
[1.0.0]:ChCl	36.940	-10.056	0.9984
[2.0.0]:ChCl	34.137	-8.923	0.9996
[3i.0.0]:ChCl	36.164	-9.529	0.9974
[3F.0.0]:ChCl	37.063	-9.912	0.9987
[Ph.0.0]:ChCl	63.892	-18.334	0.9977
[G.0.0]:ChCl	66.480	-18.695	0.9994
[1.0.0]:[N.0.0]Cl	50.209	-14.179	0.9980
[2.0.0]:[N.0.0]Cl	49.884	-14.053	0.9983
[4.0.0]:[N.0.0]Cl	49.012	-13.707	0.9990
[3i.0.0]:[N.0.0]Cl	51.469	-14.484	0.9985
[3F.0.0]:[N.0.0]Cl	51.118	-14.345	0.9982
[Ph.0.0]:[N.0.0]Cl	85.149	-25.267	0.9976
[G.0.0]:[N.0.0]Cl	87.177	-25.368	0.9992

<sup>a</sup> All the experimental viscosity values are available in the ESI.

**Ionic conductivity.** The ionic conductivity ( $\kappa$ ) is a physical property typically determined for DES. This property is very important for these kinds of solvents because of their interesting electrochemical applications.<sup>12</sup> Temperature is again an essential parameter influencing the conductivity. Conductivity values measured in the temperature range 298.15–343.15 K have been fitted to an Arrhenius-type equation<sup>40</sup> very similar to that employed with viscosity:

$$\ln \kappa = \frac{E_{\kappa}}{RT} + b \quad (9)$$

where  $\kappa$  is the ionic conductivity in  $\mu\text{S}\cdot\text{cm}^{-1}$ ,  $T$  in Kelvin,  $R$  is the gas constant,  $E_{\kappa}$  the energy for conduction activation and  $b$  is a constant.

In this case  $E_{\kappa}$  values are quite similar to the values reported for ionic liquids,<sup>41–43</sup> but slightly higher than those measured with usual DES, including glycerol:ChCl (−27.9 kJ·mol<sup>-1</sup>).<sup>8</sup> Conductivity has an inverse variation with viscosity, as is shown in the inverse relation existing between both activation energies,  $E_{\eta}$  and  $E_{\kappa}$ . The higher the solvent viscosity, the more difficult the flow of ions, resulting in a decrease of ionic conductivity. A strong interaction between the HBD component of the mixture and the chloride anion increases the effective size of the latter, making it difficult ion mobility and thus decreasing ionic conductivity.

In Fig. 8 we can see this inverse behaviour exhibited by conductivity with regard to viscosity: Conductivity in the mixtures containing ChCl (at 298.15 K) is three times higher than in the ones of [N.0.0]Cl. Regardless the ammonium salts in the mixture, the conductivity order is: [1.0.0] > [3F.0.0] > [2.0.0] > [3i.0.0] > [4.0.0] > [Ph.0.0] > [G.0.0]. The longer R chain in the ether is the lower the conductivity. In the very viscous mixtures containing aromatic ethers the conductivity is quite low, with values comparable to those of viscous ILs.



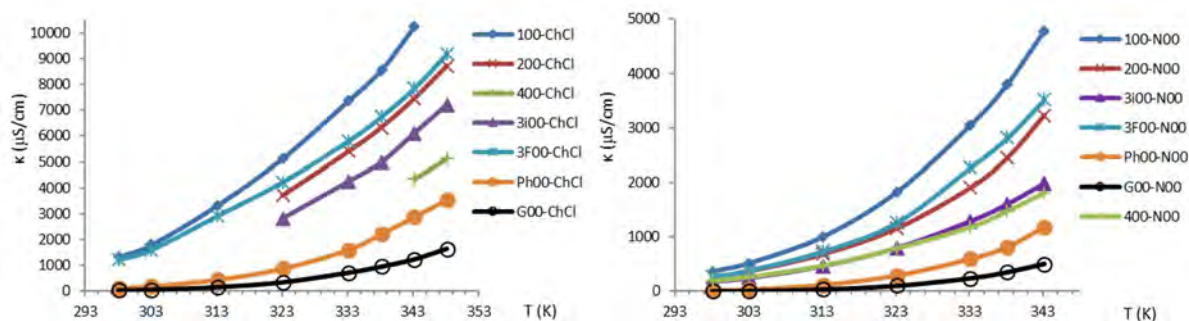


Fig. 8 Ionic conductivities of mixtures of glycerol monoethers [R.0.0] and ChCl or [N.0.0]Cl.

Table 7 Conductivity-temperature model parameter.<sup>a</sup>

	$E_k / \text{kJ}\cdot\text{mol}^{-1}$	$b$	$r^2$
[1.0.0]:ChCl	-38.216	22.688	0.9925
[2.0.0]:ChCl	-31.869	20.093	0.9993
[4.0.0]:ChCl	-30.845	19.282	0.9927
[3i.0.0]:ChCl	-35.198	21.046	0.9986
[3F.0.0]:ChCl	-34.960	21.282	0.9895
[Ph.0.0]:ChCl	-59.605	28.912	0.9972
[G.0.0]:ChCl	-67.371	30.896	0.9980
[1.0.0]:[N.0.0]Cl	-48.916	25.660	0.9987
[2.0.0]:[N.0.0]Cl	-46.401	24.326	0.9995
[4.0.0]:[N.0.0]Cl	-41.688	22.137	0.9984
[3i.0.0]:[N.0.0]Cl	-45.148	23.451	0.9988
[3F.0.0]:[N.0.0]Cl	-48.787	25.303	0.9991
[Ph.0.0]:[N.0.0]Cl	-77.392	34.306	0.9928
[G.0.0]:[N.0.0]Cl	-81.381	34.827	0.9974

<sup>a</sup> All the experimental conductivity values are available in the ESI.

**Surface tension.** The last measured property is the surface tension ( $\gamma$ ), which provides interesting information (*e.g.* for emulsions and surfactants applications) about the cohesive forces operating in the solvent. The intermolecular attractive forces in the liquid reduces the surface area of the liquid-air interface, increasing the necessary energy for enlarge the surface.<sup>23</sup> As shown in Fig. 9, surface tension values of [R.0.0] are in between 25 and 40  $\text{mN}\cdot\text{m}^{-1}$ , quite similar to those of *n*-alkanols (*e.g.* 25.1 for BuOH), THF (28.2), halogenated solvents (29.5 for DCM) or aromatic solvents (29.6 for benzene). In general, the longer the R alkyl chain, the lower the surface tension. The most probable mechanism for this structure-property relationship is related with the ability of the glycerol ethers to form strong intermolecular hydrogen bonds. Pure glycerol has a high surface tension (63.4), which diminishes when one of the hydroxyl

groups is blocked. Besides this, longer alkyl substituents probably disturb the intermolecular hydrogen bonding network, leading to lower surface tensions.

Table 8 Surface tension-temperature model parameter.<sup>a</sup>

	$a$	$b$	$r^2$
[1.0.0]	-0.0766	61.54	0.9999
[2.0.0]	-0.0673	52.80	1.0000
[4.0.0]	-0.0571	45.94	0.9995
[3i.0.0]	-0.0690	48.45	0.9992
[3F.0.0]	-0.0608	45.69	0.9999
[1.0.0]:ChCl	-0.0361	52.47	0.9994
[3F.0.0]:ChCl	-0.0414	43.60	0.9988
[Ph.0.0]:ChCl	-0.0632	63.12	0.9991
[1.0.0]:[N.0.0]Cl	-0.1151	79.06	0.9998
[3F.0.0]:[N.0.0]Cl	-0.0878	59.36	0.9994
[Ph.0.0]:[N.0.0]Cl	-0.2013	109.43	0.9982

<sup>a</sup> All the experimental surface tension values are available in the ESI.

In the mixtures with ammonium salts, an increase in surface tension is observed with regard to pure glycerol ethers. The values are higher for [N.0.0]Cl, due to stronger intermolecular interactions. The experimental values for the mixtures range between 30 and 50  $\text{mN}\cdot\text{m}^{-1}$ , similar to the majority of IL reported in the literature.<sup>38</sup> Again, maximum values are found for aromatic ether DES. Even so, reported surface tension values are lower than that of water (72.8), pure glycerol or glycerol:ChCl DES ( $\approx 52$ ).<sup>8</sup>

Surface tension diminishes linearly with temperature (fitting to Eq. 10), due to the decreasing of the liquid cohesive forces.

$$\gamma = aT + b \quad (10)$$

where  $\gamma$  is the surface tension in  $\text{mN}\cdot\text{m}^{-1}$ ,  $T$  is temperature in Kelvin, and  $a$  and  $b$  are fitting constants (Table 8).

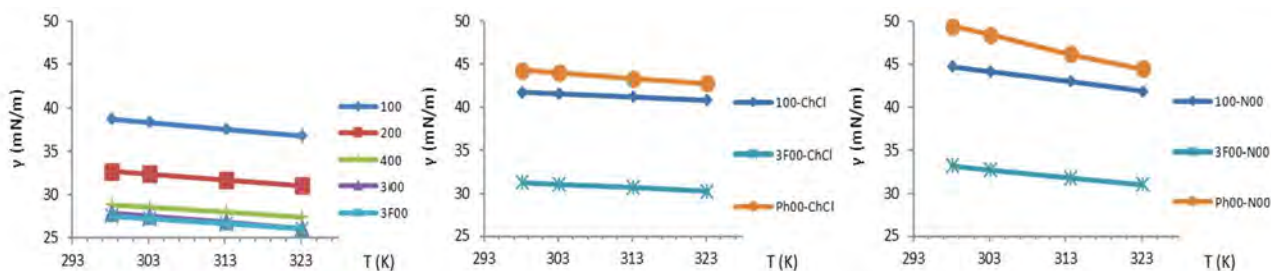


Fig. 9 Surface tension of solvents: Glycerol monoethers [R.0.0] and their mixtures with ChCl and [N.0.0]Cl.

## Conclusions

Mixtures of several monoalkyl glyceryl ethers with two ammonium salts bearing hydroxyl groups, choline chloride and *N,N,N*-triethyl-2,3-dihydroxypropan-1-aminium chloride, have been prepared. These mixtures display a wide temperature range of liquid state and can be considered as Low Melting Mixtures LMM. In the case of the mixtures containing [Ph.0.0] or [G.0.0], both solids at room temperature, the mixtures can be referred to as deep eutectic solvents DES. *N,N,N*-triethyl-2,3-dihydroxypropan-1-aminium chloride has been used for the first time to prepare these kinds of solvents. Its use leads to DES coming formally from the same renewable source, glycerol, thus enlarging the possibilities of this platform molecule as a source of solvents with very different features.

Liquid and stable mixtures have been characterized and a series of critical physicochemical properties, such as density, viscosity, refractive index, conductivity and surface tension, have been measured in most cases within the temperature range of 298 to 343 K, adequate for the applications of a green solvent in soft conditions. The range of values measured for the above-mentioned properties evidences the possibility of fine tuning the physical properties of the solvent by changing the substitution pattern in the hydrogen bond donor compound (glycerol ether) or in the ammonium salt, thus broadening the scope of application of these mixtures, and allowing their *à la carte* preparation. Comparison of the mixtures prepared herein with the ones containing HBD compounds and choline chloride, as well as with commonly used ionic liquids reveals that these new mixtures cover a similar and wide range of physicochemical properties with a much more homogeneous origin and consistent preparation procedure, and therefore they can be used in substitution of many previously described IL and DES.

Some practical applications of these solvents, as reaction media for catalytic processes or as extraction solvents, are currently being explored in our group.

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