Journal of Molecular Liquids 383 (2023) 122024

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Full Length Article

Physico-chemical characterization of methanolic mixtures of cholinium dihydrogen phosphate-based DES

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ARTICLE INFO

Keywords:
Deep Eutectic Solvents, Choline dihydrogen phosphate
Ethyleneglycol
Glycerol
Methanol, Physical properties

ABSTRACT

The biocompatibility of three deep eutectic solvents based on cholinium dihydrogen phosphate for their use in lipase-catalyzed reactions was recently demonstrated, so the possible application as cosolvents with methanol in transesterification processes demands an exhaustive characterization of the physical properties. Thus, in this work binary and ternary deep eutectic solvents composed of the abovementioned salt as hydrogen bond acceptor and ethyleneglycol and/or glycerol as hydrogen bond donors were synthesized and mixed with methanol. The density, refractive index, electrical conductivity and dynamic viscosity were determined between 293.15 K and 323.15 K. The experimental data were correlated with different well-known equations and derived magnitudes like excess molar volumes, changes of refractive index on mixing and viscosity deviations were inferred in order to get an in-depth characterization of the studied mixtures with cholinium dihydrogen phosphate-based DES. The most intriguing data observed is the great peak measured for ionic conductivity at very high methanol concentration, which is difficult to explain even with the most recent theoretical models.

1. Introduction

During the last years, a booming interest in the research of more sustainable solvents has been translated into the synthesis and application of a great number of ionic liquids. These salts, with melting temperatures under 100 °C, were firstly reported by Walden a century ago [1] and they are characterized by their negligible vapor pressure [2], non-flammability [3], thermal stability [4] and tunability [5], thus being applied in an array of applications like biocatalysis [6], separation processes [7] and electrochemistry [8]. These compounds are considered to be the parents of a new kind of substances discovered by Abbot and coworkers in 2001 [9], who opened-up a completely new research field on what were named as Low Transition Temperature Mixtures or Deep Eutectic Solvents (DES). DES are composed of hydrogen bond acceptors (HBA), like ammonium-based salts, amino acids, or lactic acid, and hydrogen bond donors (HBD) like organic acids or polyols [10].

These compounds share many of the advantages of ionic liquid to replace the about 600 existing volatile organic compounds currently employed, although they stand out due to their distinct features and advantages like their inexpensiveness, easy synthesis, biodegradability, and low toxicity [11]. Due to this, they are employed in a plethora of fields like gas capture, metallurgy, nanotechnology or biotechnology [12]. More specifically, their suitability to be used as solvents in biocatalysis has been firstly demonstrated in 2008 by Kazlauskas et al. [13] and since them, different DES were successfully employed with lipases, lyases, peroxidases, catalases or dehalogenases [14].

In our research group, we have recently demonstrated the suitability of three novel DES to be employed in lipase extraction and biocatalysis, so the physical properties of cholinium dihydrogen phosphate combined with ethyleneglycol and/or glycerol were recently determined [15,16]. Therefore, the combination of these DES and lipases for transesterification reactions can be optimum for biodiesel production, as also recently demonstrated by our research group [17]. However, the reaction medium containing typical acyl acceptors like methanol should be characterized prior to develop this process, as these data are crucial for process simulation and its subsequent industrial implementation.

Therefore, in this research work we have thermodynamically characterized methanolic mixtures of three DES (cholinium dihydrogen

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https://doi.org/10.1016/j.molliq.2023.122024
Received 23 February 2023; Received in revised form 21 April 2023; Accepted 3 May 2023
Available online 9 May 2023
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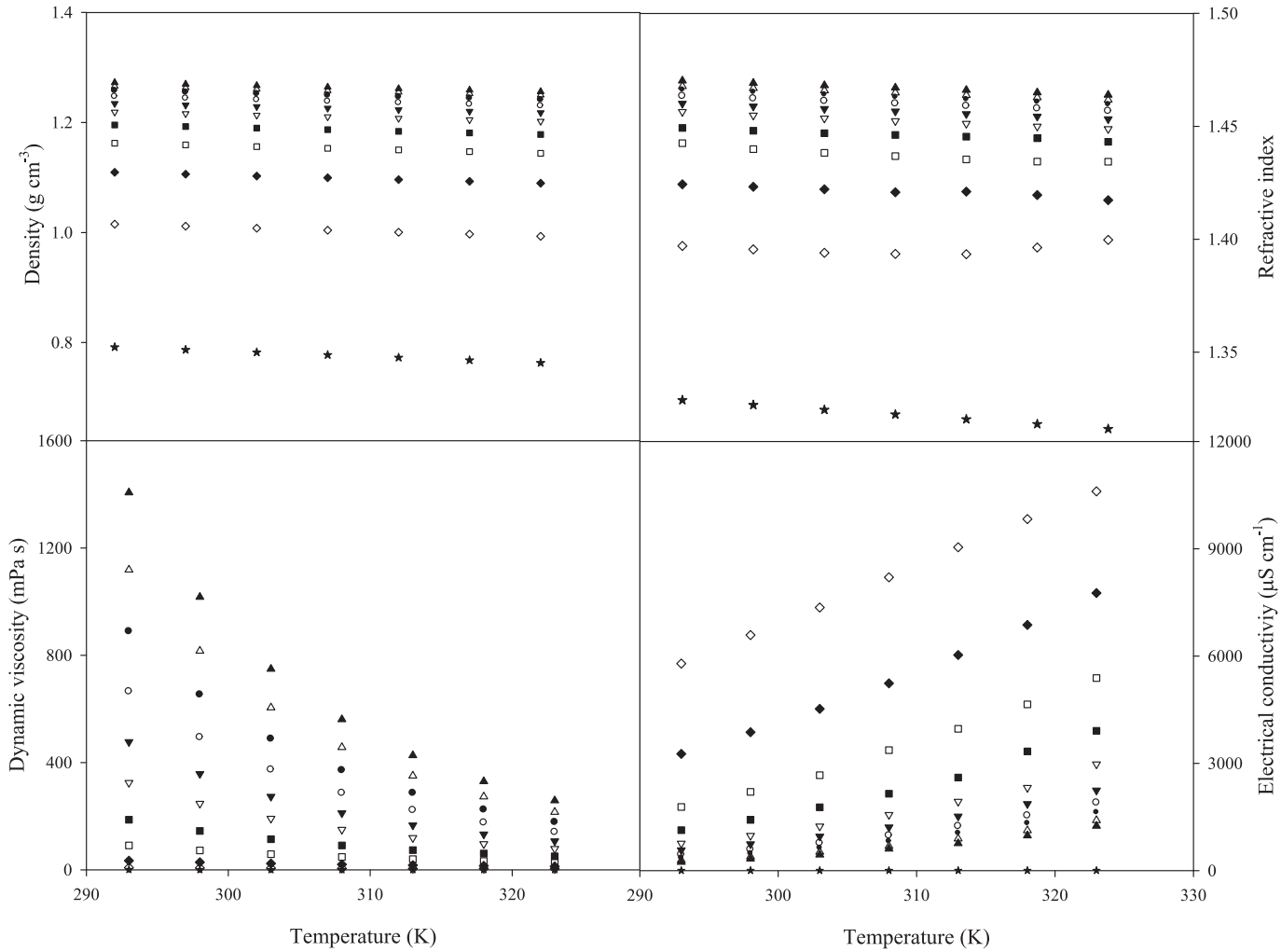

Fig. 1. Experimental densities (ρ), viscosities (η), refractive indices (n_D) and electrical conductivities (κ) of methanolic mixtures of DES ChDHP:EG at different temperatures and molar fractions: (△) $x_2 = 0.000$, (ρ) $x_2 = 0.1030$, (●) $x_2 = 0.2016$, (○) $x_2 = 0.3082$, (▽) $x_2 = 0.4050$, (▲) $x_2 = 0.4991$, (■) $x_2 = 0.6029$, (□) $x_2 = 0.7015$, (◆) $x_2 = 0.8007$, (◆) $x_2 = 0.8993$, (*) $x_2 = 1.0000$, for temperatures comprised between 293.15 K and 323.15 K.

phosphate combined with ethyleneglycol, glycerol or both compounds) for their future applications in biocatalysis, chemical reactions or extraction processes, among others. Thus, density ρ, electrical conductivity κ, refractive index n_D, and dynamic viscosity η of the synthesized DES were experimentally ascertained at temperatures comprised between 293.15 K and 323.15 K and atmospheric pressure over all dilution range, but with special attention at very diluted methanolic DES mixtures. There are different models in literature that have been proposed to describe physical properties, like perturbed-chain statistical associating fluid theory [18,19], or even associated with the free volume theory [20], so well-known mathematical expressions were proposed to correlate the experimental data and several derived magnitudes were calculated in order to gain fundamental knowledge about methanolic mixtures of cholinium dihydrogen phosphate-based DES. Special attention has been given to electrical conductivity data due to an unexpected sharp peak measured at high dilution (with molar fraction of methanol about 0.95).

2. Experimental

2.1. Materials

Methanol (CAS 67–59–1, mass fraction purity > 0.99), glycerol (GLY) (CAS 56–81–5, mass fraction purity > 0.99) and ethyleneglycol (EG) (CAS 107–21–1, mass fraction purity > 0.99) were acquired from Sigma-Aldrich. Cholinium dihydrogen phosphate (ChDHP) (CAS 83846–92–8, mass fraction purity > 0.98) was purchased from IoLiTec. To remove potential traces of solvents and moisture of the salt, vacuum drying ($2 \cdot 10^{-1}$ Pa) and moderate temperature (T = 323.15 K) were applied for several days. The water content of liquids reagents was determined by Karl-Fischer titration and was lower than 0.001 (w/w).

2.2. DES preparation

The amount of HBA (ChDHP) and HBD (GLY and/or EG) were determined with a Sartorius Cubis MSA balance (125P-100-DA, $\pm 10^{-5}$ g) and three different DES were prepared: ChDHP:EG (ratio of 1:2), ChDHP:GLY (ratio of 1:2) and ChDHP:EG:GLY (ratio of 1:1:1). They were prepared in glass tubes with screw tops and heated up to 348.15 K with constant magnetic agitation until a clear liquid was obtained (about one hour). Afterwards, the obtained DES was submitted to vacuum-drying (2×10^{-1} Pa and 323.15 K) for two days. Karl-Fisher titration allowed ascertaining the water mass fraction content for each DES ($2.4 \cdot 10^{-3}$ for ChDHP:EG, $1.9 \cdot 10^{-3}$ for ChDHP:GLY and $2.1 \cdot 10^{-3}$ for ChDHP:EG:GLY).

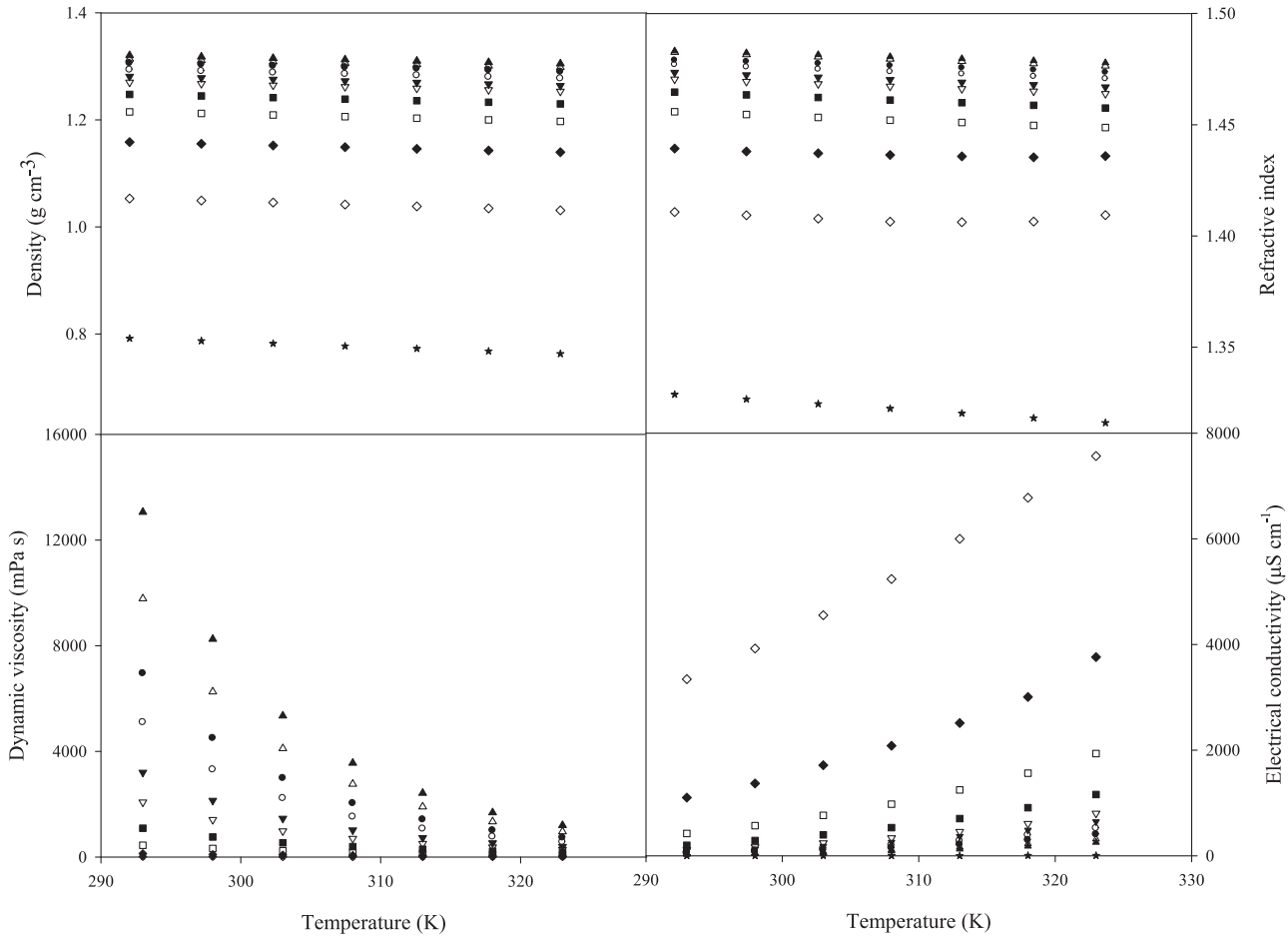

Fig. 2. Experimental densities (ρ), viscosities (η), refractive indices (n_D) and electrical conductivities (κ) of methanolic mixtures of DES ChDHP:GLY at different temperatures and molar fractions: (△) $x_2 = 0.000$, (ρ) $x_2 = 0.1030$, (●) $x_2 = 0.2016$, (○) $x_2 = 0.3082$, (▽) $x_2 = 0.4050$, (▽) $x_2 = 0.4991$, (■) $x_2 = 0.6029$, (□) $x_2 = 0.7015$, (◆) $x_2 = 0.8007$, (◆) $x_2 = 0.8993$, (*) $x_2 = 1.0000$, for temperatures comprised between 293.15 K and 323.15 K.

2.3. Density and viscosity

Density (ρ) and dynamic viscosity (η) were determined with an Anton Paar Stabinger SVM 3000 at different temperatures (293.15 to 323.15) K. The expanded uncertainty in the measurement of density is about 0.5 kg·m^{-3}, while for viscosity, the relative standard uncertainty is 4·10^{-3} of the measured value. Mixtures were thermostated with an internal Peltier cell (uncertainty of ± 0.02 K).

2.4. Refractive index

Refractive index data (n_D) were measured with an ABBEMAT-WR Dr. Kernchen refractometer after calibrating it with tetrachloroethylene and Millipore quality water. The combined expanded uncertainty (level of confidence = 0.95, $k = 2$) for the measurements was calculated to be $U_c(n_D) = 4 \times 10^{-5}$.

2.5. Electrical conductivity

Electrical conductivities (κ) were ascertained using a Crison GLP3 conductimeter, with a relative standard uncertainty of less than 0.005 in a temperature range from 293.15 to 323.15 K. The conductimeter works with an alternating current of 500 Hz and a voltage of 0.5 V_{rms} and the reference fluids used to calibrate the measurement instrument were those called as P/N L7W9710.99 and P/N L7W9700.99. The samples were thermostated in an external bath with an uncertainty of 0.1 K and measured at atmospheric pressure.

3. Results and discussion

3.1. Characterization of methanolic mixtures of DES

As stated in the introduction, determining the physical properties [21] of methanolic mixtures of the synthesized DES is paramount prior to their implementation at industrial scale.

Therefore, density (ρ), refractive indices (n_D), dynamic viscosities (μ) and electrical conductivities (κ) of the methanolic binary mixtures with DES from 293.15 to 323.15 K and atmospheric pressure were determined over the entire composition range, with special attention at very diluted methanolic DES mixtures. These data are presented in Figs. 1-3 and Tables S1-S4 in order to compare the differences between the synthesized DES. In all cases, the differences recorded for the whole composition range between pure DES and methanol are lower than 0.3 g·cm^{-3}, with the most outstanding variations for the molar composition of methanol (x_2) > 0.8. Usually, DES density is higher than that of water, although the selected HBD and HBA decisively influence the density values with variations > 0.5 g cm^{-3} when ChCl:GLY or $ZnCl_2$:Urea are studied [22,23]. In the present case where the HBA is kept the same, it can be noted how HBD affects density, and the use of ethyleneglycol involves lower densities than glycerol, which means that the increase of hydroxyl groups involves a greater capacity of hydrogen bond formation, thus leading to a more compact structure, in line with previous studies [24]. On the other hand, the comparison with other DES containing the same HBD but different HBA, like ChCl:EG and ChCl:GLY, [22] evidences the existence of higher density values when ChDHP is

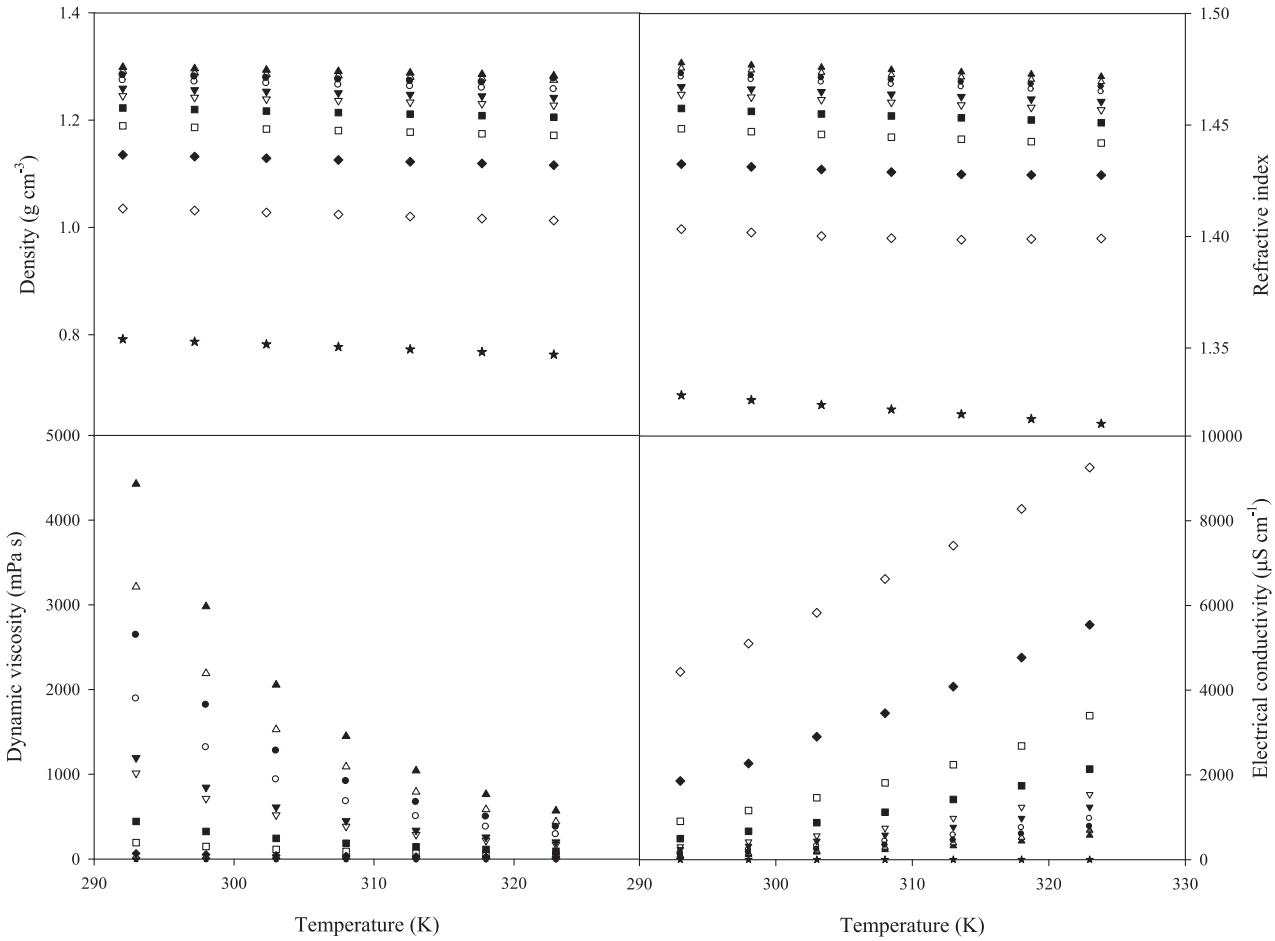

Fig. 3. Experimental densities (ρ), viscosities (η), refractive indices (n_D) and electrical conductivities (κ) of methanolic mixtures of DES ChDHP:EG:GLY at different temperatures and molar fractions: (△) $x_2 = 0.000$, (ρ) $x_2 = 0.1030$, (●) $x_2 = 0.2016$, (○) $x_2 = 0.3082$, (▽) $x_2 = 0.4050$, (▽) $x_2 = 0.4991$, (■) $x_2 = 0.6029$, (□) $x_2 = 0.7015$, (◆) $x_2 = 0.8007$, (◆) $x_2 = 0.8993$, (*) $x_2 = 1.0000$, for temperatures comprised between 293.15 K and 323.15 K.

employed. The reason for such differences could be the different predicted octanol–water partition coefficient (logP) values for chloride and dihydrogen phosphate anions (log P of 0.61 and − 1.02, respectively [26]) that demonstrates the higher ability of DHP to establish hydrogen bonds.

Regarding viscosity, a physical property that has been considered as a relevant barrier for industrial implementation of DES, the data depicted in Figs. 1-3 reveal important differences depending on the HBD, following the order: EG < EG:GLY < GLY. It has already been reported that the establishment of a compact hydrogen bond network between DES components usually results in a reduced mobility of free species within DES, which is ultimately translated into a greater viscosity [27]. Therefore, the higher number of OH groups in glycerol leading to a greater hydrogen bonds formation involves viscosity values almost 10-fold higher than those recorded for EG-based DES (both with EG alone or mixed with GLY). This is analogous with the trends recorded when ChCl:GLY and ChCl:EG DES were characterized [27,28]. Additionally, it is observed in Figs. 1-3 that dynamic viscosity of methanolic mixtures drastically decreases as methanol concentration is increased, so the mixing with this kind of low-viscosity solvents is a tool to make it viable the industrial implementation of these DES.

In relation with the refractive index, there are not many research works focused on the study of DES refractive indices, most of them tackling solvents composed of ChCl as HBA. The data recorded for ChDHP shown in Figs. 1-3 are similar to those obtained when ChCl is employed as HBA [25], and the addition of methanol does not involve significant changes for all the composition range (values comprised between 1.4 and 1.5 for compositions between $x_2 = 0.1$ and 0.9), but some minimal variations. In this sense, it can be observed that some refractive indices are positively correlated with temperature while other follow the contrary trend. Several authors have converged upon the idea that refractive index variation with temperature (dn/dT) may be positive or negative depending on the material. For instance, while lead halide perovskite and plastics displayed negative coefficients, glass substances were positive [29,30]. It has also been reported in these papers that a substance may display changes of thermo-optic coefficient depending on the temperature, going from constant values between 10 and 30 °C to negative results at higher temperatures.

Similarly, almost no data about DES conductivity can be found in literature, so the characterization of the synthesized DES is interesting in terms of fundamental knowledge. In this sense, although the data presented in Figs. 1-3 reveal that all ChDHP-based DES present conductivity values similar to those reported in literature for other Ch-based DES [31], the increase in methanol concentrations up to $x_2 = 0.9$ involves a great increase in conductivity at levels > 20 folds higher than those recorded in the pure DES. Additionally, the use of EG as HBD entails higher conductivity values, probably due to the higher ions mobility in this compound compared with GLY.

3.2. Mathematical modelling of experimental data for methanolic mixtures

An exhaustive characterization of the systems requires the use of mathematical expressions to completely define the relationship between

Table 1
Fitting parameters and standard deviation (σ) for density and refractive index correlation in methanolic mixtures of DES as a function at temperature.

ChDHP:EG (1) + MeOH (2)						
	$\rho(g{\cdot}cm^{-3})$			n_D		
x_2	A_0	A_1	σ	A_0	A_1	σ
0.0000	1.4333	$-5.49\ 10^{-4}$	$3.50\ 10^{-5}$	1.5314	$-2.10\ 10^{-4}$	$1.04\ 10^{-5}$
0.1030	1.4255	$-5.44\ 10^{-4}$	$5.55\ 10^{-5}$	1.5263	$-2.01\ 10^{-4}$	$6.05\ 10^{-5}$
0.2016	1.4197	$-5.53\ 10^{-4}$	$7.56\ 10^{-5}$	1.5296	$-2.16\ 10^{-4}$	$1.37\ 10^{-5}$
0.3082	1.4107	$-5.59\ 10^{-4}$	$7.53\ 10^{-5}$	1.5284	$-2.22\ 10^{-4}$	$8.65\ 10^{-6}$
0.4050	1.3987	$-5.60\ 10^{-4}$	$4.52\ 10^{-5}$	1.5268	$-2.28\ 10^{-4}$	$1.59\ 10^{-5}$
0.4991	1.3835	$-5.61\ 10^{-4}$	$3.74\ 10^{-5}$	1.5269	$-2.41\ 10^{-4}$	$3.72\ 10^{-4}$
0.6029	1.3656	$-5.80\ 10^{-4}$	$1.53\ 10^{-6}$	1.5045	$-1.89\ 10^{-4}$	$2.24\ 10^{-4}$
0.7015	1.3421	$-6.13\ 10^{-4}$	$3.45\ 10^{-5}$	1.5215	$-2.73\ 10^{-4}$	$6.85\ 10^{-5}$
0.8007	1.3031	$-6.61\ 10^{-4}$	$4.37\ 10^{-5}$	1.4925	$-2.32\ 10^{-4}$	$1.47\ 10^{-4}$
0.8993	1.2303	$-7.34\ 10^{-4}$	$5.46\ 10^{-5}$	1.4992	$-3.48\ 10^{-4}$	$2.30\ 10^{-4}$
1.0000	1.0708	$-9.52\ 10^{-4}$	$6.02\ 10^{-5}$	1.4531	$-4.24{\cdot}10^{-4}$	$1.87\ 10^{-5}$
ChDHP:GLY (1) + MeOH (2)						
	$\rho(g{\cdot}cm^{-3})$			n_D		
x_2	A_0	A_1	σ	A_0	A_1	σ
0.0000	1.4722	$-5.18\ 10^{-4}$	$2.04\ 10^{-5}$	1.5338	$-1.73{\cdot}10^{-4}$	$5.55\ 10^{-5}$
0.1065	1.4676	$-5.24\ 10^{-4}$	$4.21\ 10^{-5}$	1.5419	$-2.03{\cdot}10^{-4}$	$2.63\ 10^{-5}$
0.2024	1.4619	$-5.29\ 10^{-4}$	$6.75\ 10^{-5}$	1.5325	$-1.82{\cdot}10^{-4}$	$9.45\ 10^{-5}$
0.3004	1.4531	$-5.44\ 10^{-4}$	$4.84\ 10^{-5}$	1.5390	$-2.12{\cdot}10^{-4}$	$2.43\ 10^{-5}$
0.4058	1.44924	$-5.72\ 10^{-4}$	$7.61\ 10^{-5}$	1.5375	$-2.18{\cdot}10^{-4}$	$2.43\ 10^{-5}$
0.5005	1.4378	$-5.71\ 10^{-4}$	$5.30\ 10^{-5}$	1.5330	$-2.13{\cdot}10^{-4}$	$4.80\ 10^{-5}$
0.5992	1.4199	$-5.88\ 10^{-4}$	$3.98\ 10^{-5}$	1.5336	$-2.35{\cdot}10^{-4}$	$2.09\ 10^{-5}$
0.7010	1.3898	$-5.94\ 10^{-4}$	$3.39\ 10^{-5}$	1.5249	$-2.36{\cdot}10^{-4}$	$8.57\ 10^{-5}$
0.7998	1.3429	$-6.29\ 10^{-4}$	$3.52\ 10^{-5}$	1.4811	$-1.44{\cdot}10^{-4}$	$2.35\ 10^{-4}$
0.9003	1.2680	$-7.34\ 10^{-4}$	$2.77\ 10^{-5}$	1.4810	$-2.41{\cdot}10^{-4}$	$2.72\ 10^{-4}$
1.0000	1.0706	$-9.52\ 10^{-4}$	$6.02\ 10^{-5}$	1.4531	$-4.24{\cdot}10^{-4}$	$1.87\ 10^{-5}$
ChDHP:EG:GLY (1) + MeOH (2)						
	$\rho(g{\cdot}cm^{-3})$			n_D		
x_2	A_0	A_1	σ	A_0	A_1	σ
0.0000	1.4545	$-5.31\ 10^{-4}$	$5.72\ 10^{-5}$	1.5379	$-2.05{\cdot}10^{-4}$	$1.49\ 10^{-5}$
0.1014	1.4498	$-5.42\ 10^{-4}$	$4.93\ 10^{-5}$	1.5346	$-2.02{\cdot}10^{-4}$	$3.70\ 10^{-5}$
0.2040	1.4449	$-5.50\ 10^{-4}$	$5.15\ 10^{-5}$	1.5296	$-1.93{\cdot}10^{-4}$	$2.69\ 10^{-5}$
0.2975	1.4382	$-5.60\ 10^{-4}$	$4.95\ 10^{-5}$	1.5348	$-2.17{\cdot}10^{-4}$	$2.23\ 10^{-5}$
0.4061	1.4264	$-5.70\ 10^{-4}$	$6.23\ 10^{-5}$	1.5320	$-2.21{\cdot}10^{-4}$	$6.43\ 10^{-6}$
0.5011	1.4157	$-5.81\ 10^{-4}$	$9.15\ 10^{-5}$	1.5312	$-2.30{\cdot}10^{-4}$	$2.42\ 10^{-5}$
0.5998	1.3914	$-5.75\ 10^{-4}$	$5.96\ 10^{-5}$	1.5163	$-2.02{\cdot}10^{-4}$	$9.82\ 10^{-5}$
0.7001	1.3641	$-5.96\ 10^{-4}$	$2.47\ 10^{-5}$	1.5135	$-2.23{\cdot}10^{-4}$	$9.76\ 10^{-5}$
0.7998	1.3251	$-6.47\ 10^{-4}$	$2.57\ 10^{-5}$	1.4995	$-2.29{\cdot}10^{-4}$	$5.50\ 10^{-5}$
0.9007	1.2521	$-7.40\ 10^{-4}$	$4.52\ 10^{-5}$	1.4702	$-2.30{\cdot}10^{-4}$	$2.55\ 10^{-4}$
1.0000	1.0706	$-9.52\ 10^{-4}$	$6.02\ 10^{-5}$	1.4531	$-4.24{\cdot}10^{-4}$	$1.87\ 10^{-5}$

Table 2
Fitting parameters and standard deviation (σ) for viscosity and conductivity VTF correlations of methanolic mixtures of DES as a function of temperature.

ChDHP:EG (1) + MeOH (2)					
x_2	*0*	*0.1*	*0.2*	*0.3*	*0.4*
η_∞	0.0384	0.0386	0.0386	0.0390	0.0396
B_η	1642	1613	1579	1540	1491
T_η	137.0	136.2	136.0	135.1	134.5
σ (mPa·s)	0.76	0.64	0.36	0.36	0.1
κ_∞	$7.6{\cdot}10^{-6}$	$1.5{\cdot}10^{-4}$	$1.9{\cdot}10^{-4}$	$1.8{\cdot}10^{-4}$	$1.7{\cdot}10^{-4}$
B_κ	−5390	−4814	−4950	−5282	−5797
T_κ	607	622	632	649	676
σ (μS/cm)	66	30	37	37	48
x_2	*0.5*	*0.6*	*0.7*	*0.8*	*0.9*
η_∞	0.0531	0.0585	0.0569	0.0541	0.0480
B_η	1346	1243	1161	1072	892
T_η	138.7	139.1	135.7	126.7	117.5
σ (mPa·s)	0.0	0.031	0.012	0.010	0.045
κ_∞	$7.1{\cdot}10^{-5}$	$7.7{\cdot}10^{-5}$	$9.7{\cdot}10^{-5}$	$7.1{\cdot}10^{-5}$	$4.6{\cdot}10^{-5}$
B_κ	−6577	−7301	−8550	−12048	−18443
T_κ	698	734	802	900	1280
σ (μS/cm)	38	64	125	375	167
ChDHP:GLY (1) + MeOH (2)					
x_2	*0*	*0.1*	*0.2*	*0.3*	*0.4*
η_∞	0.0381	0.0383	0.0384	0.0385	0.0394
B_η	1681	1650	1602	1547	1506
T_η	161.3	160.6	160.8	162.0	159.9
σ (mPa·s)	30	20	13	6.2	6.0
κ_∞	$1.4{\cdot}10^{-6}$	$1.4{\cdot}10^{-5}$	$1.7{\cdot}10^{-4}$	$1.7{\cdot}10^{-4}$	$1.6{\cdot}10^{-4}$
B_κ	−5390	−2788	−2880	−3087	−3387
T_κ	607	513	519	530	546
σ (μS/cm)	9.5	7	9.1	13	17
x_2	*0.5*	*0.6*	*0.7*	*0.8*	*0.9*
η_∞	0.0385	0.0577	0.0561	0.0531	0.0464
B_η	1470	1276	1187	1078	907
T_η	158.2	163.6	160.9	154.8	137.1
σ (mPa·s)	3.0	1.5	0.54	0.29	0.008
κ_∞	$6.8{\cdot}10^{-5}$	$7.3{\cdot}10^{-5}$	$9.4{\cdot}10^{-5}$	$3.1{\cdot}10^{-6}$	$4.7{\cdot}10^{-5}$
B_κ	−4058	−4697	−5573	−12048	−13005
T_κ	572	606	654	900	1011
σ (μS/cm)	19	28	41	120	110
ChDHP:EG:GLY (1) + MeOH (2)					
x_2	*0*	*0.1*	*0.2*	*0.3*	*0.4*
η_∞	0.0684	0.0546	0.0554	0.0602	0.0593
B_η	1478	1505	1479	1413	1359
T_η	159.7	156.1	155.9	156.7	156.0
σ (mPa·s)	8.3	5	4.1	2.9	1.6
κ_∞	$3.3{\cdot}10^{-6}$	$5.0{\cdot}10^{-5}$	$5.2{\cdot}10^{-5}$	$5.0{\cdot}10^{-5}$	$4.9{\cdot}10^{-5}$
B_κ	−5390	−2788	−2880	−3087	−3387
T_κ	607	513	519	530	546
σ (μS/cm)	9.5	7	9.1	13	17
x_2	*0.5*	*0.6*	*0.7*	*0.8*	*0.9*
η_∞	0.0583	0.0583	0.0567	0.0542	0.0461
Bη	1326	1248	1164	1057	897
Tη	157.3	153.5	150.1	144.5	133.2
σ (mPa·s)	1.3	0.39	0.13	0.067	0.023
κ_∞	$4.8{\cdot}10^{-5}$	$4.8{\cdot}10^{-5}$	$4.1{\cdot}10^{-5}$	$4.8{\cdot}10^{-6}$	$4.6{\cdot}10^{-5}$
Bκ	−5530	−6397	−7370	−12047	−14780
Tκ	643	686	727	900	1096
σ (μS/cm)	36.2	47.3	41.2	121	97.9

temperature and physical properties. First of all, from the data depicted in Figs. 1-3, it is evident a linear relationship between temperature and density/refractive index, so the experimental data were fitted to the following expression:

$$Q = \sum_{i=0}^{m} A_i T^i = A_0 + A_1 T \tag{1}$$

where Q is the physical property (ρ and n_D), T is the temperature in K, A_i are the model parameters and $m = 1$ is the degree of the polynomial expansion. The values of the fitting parameters were calculated after minimizing the standard deviations (σ) with solver tool in Microsoft excel:

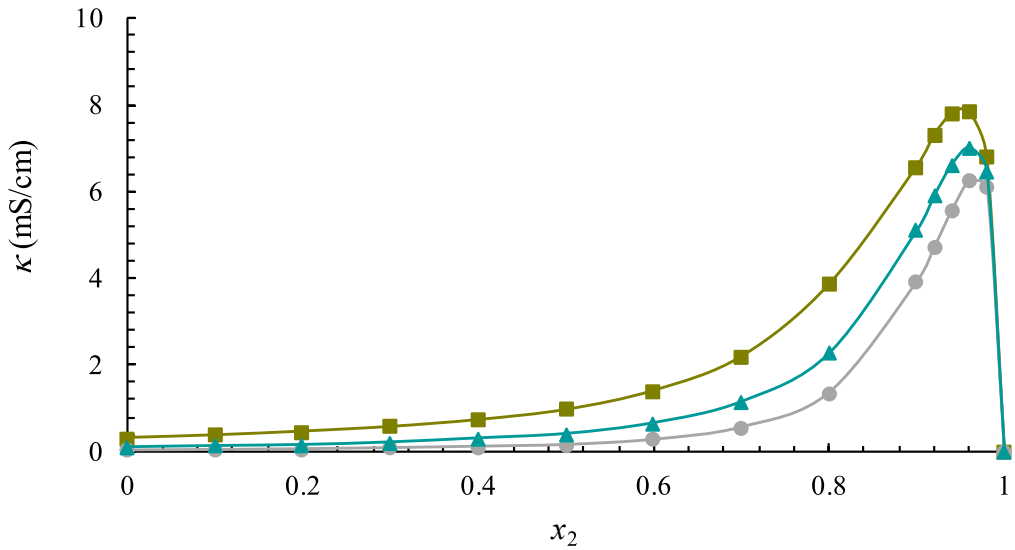

Fig. 4. Electrical conductivity of methanolic mixtures of DES at 298.15 K. ChDHP:EG (■), ChDHP:GLY (●) and ChDHP:EG:GLY(△). () are guides to the eye.

$$\sigma = \left(\frac{\sum_i^{n_{DAT}} (z_{\exp} - z_{pred})^2}{n_{DAT}}\right)^{1/2} \quad (2)$$

where $z_{\exp}$ and z_{pred} represent the empirical and theoretical values, respectively, and n_{DAT} stands for the number of experimental points. The obtained data are presented in Table 1 together with the standard deviations (σ). It can be concluded that density and refractive index are successfully correlated with the proposed mathematical expression as supported by the lower standard deviation values for the two physical properties.

On the other hand, the viscosity and conductivity data presented in Table S4, as well as in Figs. 1-3 evidence a non-linear relationship between temperature and these physical properties. Although Arrhenius type equations could be used as it have been demonstrated to be useful in binary mixtures of DES and methanol [32], in this case we have bet in a Vogel-Tamman-Fulcher (VTF) relationship [33–35], which reads,

$$F = F_\infty \cdot \exp\{B_F/(T - T_F)\} \quad (3)$$

where F is the physical property (η or κ,). For viscosity, η_∞, is the limiting value of the magnitude, B_η is a coefficient related with the activation energy of hopping and T_η is the so called Vogel temperature, which is near the glass transition point [33]. The obtained parameters from the fitting of our data are listed in Table 2, together with the standard deviation (obtained from Eq. (2)) of the VTF fit. As observed, the B_η parameter decreases when methanol concentration increases, which means that activation energy for the mass transport also decreases. As noted above, the most interesting result obtained is the giant peak in the electrical conductivity observed at very high methanol concentration, with.

$x_2 = 0.95$ (i.e., twenty methanol molecules for each DES unity), presented in Fig. 4 for the three methanolic mixtures studied at 298.15 K. As observed, the maximum conductivity is about 20 times higher than that of the corresponding pure DES.

3.3. Calculation of excess molar volumes, refractive index on mixing and viscosity deviations

Excess molar volume (V_m^E), changes of refractive index on mixing (Δn_D) and viscosity deviations ($\Delta\eta$) were calculated for all the temperatures under study by using the following mathematical expressions:

$$V_m^E = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (4)$$

Table 3
Fitting parameters. α_i. calculated from Eq (4). Eq (5). Eq (6) and Eq (7). and standard deviations. σ. for the binary mixture: ChDHP:EG (1) + MeOH (2) at several temperatures.

$V_m^E\left(cm^3 mol^{-1}\right)$						
293.15 K	$\alpha_0 =$ -5.9646	$\alpha_1 =$ -4.8659	$\alpha_2 =$ -1.5892	$\alpha_3 =$ -4.0289	$\alpha_4 =$ -8.4288	$\sigma =$ 0.012
298.15 K	$\alpha_0 =$ -6.1606	$\alpha_1 =$ -5.1604	$\alpha_2 =$ -1.4742	$\alpha_3 =$ -4.0779	$\alpha_4 =$ -8.7852	$\sigma =$ 0.014
303.15 K	$\alpha_0 =$ -6.3730	$\alpha_1 =$ -5.4393	$\alpha_2 =$ -0.9091	$\alpha_3 =$ -4.0789	$\alpha_4 =$ -10.006	$\sigma =$ 0.014
308.15 K	$\alpha_0 =$ -6.6451	$\alpha_1 =$ -5.6165	$\alpha_2 =$ -0.9596	$\alpha_3 =$ -4.2911	$\alpha_4 =$ -10.274	$\sigma =$ 0.013
313.15 K	$\alpha_0 =$ -6.9119	$\alpha_1 =$ -5.6896	$\alpha_2 =$ -1.0427	$\alpha_3 =$ -4.4115	$\alpha_4 =$ -10.694	$\sigma =$ 0.014
318.15 K	$\alpha_0 =$ -7.1546	$\alpha_1 =$ -5.8403	$\alpha_2 =$ -0.8634	$\alpha_3 =$ -4.7110	$\alpha_4 =$ -11.604	$\sigma =$ 0.016
323.15 K	$\alpha_0 =$ -7.4370	$\alpha_1 =$ -5.9683	$\alpha_2 =$ -0.6604	$\alpha_3 =$ -4.8096	$\alpha_4 =$ -12.500	$\sigma =$ 0.016
Δn_D						
293.15 K	$\alpha_0 =$ 0.2272	$\alpha_1 =$ 0.1766	$\alpha_2 =$ 0.1351	$\alpha_3 =$ 0.1668	$\alpha_4 =$ 0.1161	$\sigma =$ 0.0008
298.15 K	$\alpha_0 =$ 0.2277	$\alpha_1 =$ 0.1726	$\alpha_2 =$ 0.1312	$\alpha_3 =$ 0.1782	$\alpha_4 =$ 0.1349	$\sigma =$ 0.0005
303.15 K	$\alpha_0 =$ 0.2292	$\alpha_1 =$ 0.1730	$\alpha_2 =$ 0.1303	$\alpha_3 =$ 0.1819	$\alpha_4 =$ 0.1419	$\sigma =$ 0.0004
308.15 K	$\alpha_0 =$ 0.2315	$\alpha_1 =$ 0.1728	$\alpha_2 =$ 0.1192	$\alpha_3 =$ 0.1940	$\alpha_4 =$ 0.1752	$\sigma =$ 0.0006
313.15 K	$\alpha_0 =$ 0.2354	$\alpha_1 =$ 0.1740	$\alpha_2 =$ 0.1082	$\alpha_3 =$ 0.2132	$\alpha_4 =$ 0.2154	$\sigma =$ 0.0005
318.15 K	$\alpha_0 =$ 0.2369	$\alpha_1 =$ 0.1669	$\alpha_2 =$ 0.0865	$\alpha_3 =$ 0.2631	$\alpha_4 =$ 0.3066	$\sigma =$ 0.0011
323.15 K	$\alpha_0 =$ 0.2382	$\alpha_1 =$ 0.1641	$\alpha_2 =$ 0.0966	$\alpha_3 =$ 0.3244	$\alpha_4 =$ 0.3640	$\sigma =$ 0.0011
$\Delta\eta$ (mPa s)						
293.15 K	$\alpha_0 =$ -1525.3	$\alpha_1 =$ -209.26	$\alpha_2 =$ 122.68	$\alpha_3 =$ 385.17	$\alpha_4 =$ -175.38	$\sigma =$ 1.080
298.15 K	$\alpha_0 =$ -1053.7	$\alpha_1 =$ -182.42	$\alpha_2 =$ 62.884	$\alpha_3 =$ 258.52	$\alpha_4 =$ -90.556	$\sigma =$ 0.804
308.15 K	$\alpha_0 =$ -525.52	$\alpha_1 =$ -134.80	$\alpha_2 =$ 8.5287	$\alpha_3 =$ 140.86	$\alpha_4 =$ -38.408	$\sigma =$ 0.513
313.15 K	$\alpha_0 =$ -378.90	$\alpha_1 =$ -109.16	$\alpha_2 =$ -14.555	$\alpha_3 =$ 90.410	$\alpha_4 =$ -1.2385	$\sigma =$ 0.314
318.15 K	$\alpha_0 =$ -276.58	$\alpha_1 =$ -89.813	$\alpha_2 =$ –23.568	$\alpha_3 =$ 65.370	$\alpha_4 =$ 13.567	$\sigma =$ 0.258
323.15 K	$\alpha_0 =$ -203.93	$\alpha_1 =$ -74.221	$\alpha_2 =$ -27.756	$\alpha_3 =$ 46.284	$\alpha_4 =$ 0.8153	$\sigma =$ 0.217

Table 4
Fitting parameters. α_i. calculated from Eq (4). Eq (5). Eq (6) and Eq (7). and standard deviations. σ. for the binary mixture: ChDHP:GLY (1) + MeOH (2) at several temperatures.

$V_m^E\left(cm^3mol^{-1}\right)$						
293.15 K	α_0 = -6.8743	α_1 = -7.9655	α_2 = -0.7565	α_3 = -0.3443	α_4 = -10.093	σ = 0.036
298.15 K	α_0 = -7.6774	α_1 = -7.7356	α_2 = 0.4424	α_3 = -1.3654	α_4 = -10.668	σ = 0.031
303.15 K	α_0 = -7.6438	α_1 = -7.3345	α_2 = -0.5189	α_3 = -2.6034	α_4 = -12.105	σ = 0.035
308.15 K	α_0 = -7.8167	α_1 = -7.6233	α_2 = 0.4609	α_3 = -2.6564	α_4 = -12.632	σ = 0.038
313.15 K	α_0 = -7.9234	α_1 = -7.5799	α_2 = -0.9462	α_3 = -3.3668	α_4 = -10.768	σ = 0.037
318.15 K	α_0 = -8.0394	α_1 = -8.1380	α_2 = -0.2170	α_3 = -2.8128	α_4 = -12.955	σ = 0.042
323.15 K	α_0 = -8.4846	α_1 = -9.0570	α_2 = -1.2668	α_3 = -2.0101	α_4 = -10.574	σ = 0.036
Δn_D						
293.15 K	α_0 = 0.2592	α_1 = 0.2040	α_2 = 0.1085	α_3 = 0.2262	α_4 = 0.3009	σ = 0.0008
298.15 K	α_0 = 0.2605	α_1 = 0.2043	α_2 = 0.1136	α_3 = 0.2307	α_4 = 0.2966	σ = 0.0008
303.15 K	α_0 = 0.2617	α_1 = 0.2061	α_2 = 0.1202	α_3 = 0.2353	α_4 = 0.2911	σ = 0.0007
308.15 K	α_0 = 0.2629	α_1 = 0.2079	α_2 = 0.1273	α_3 = 0.2403	α_4 = 0.2863	σ = 0.0006
313.15 K	α_0 = 0.2645	α_1 = 0.2078	α_2 = 0.1282	α_3 = 0.2582	α_4 = 0.3051	σ = 0.0007
318.15 K	α_0 = 0.2661	α_1 = 0.2059	α_2 = 0.1249	α_3 = 0.2848	α_4 = 0.3386	σ = 0.0007
323.15 K	α_0 = 0.2680	α_1 = 0.1999	α_2 = 0.1148	α_3 = 0.3432	α_4 = 0.4172	σ = 0.0009
$\Delta\eta$ (mPa s)						
293.15 K	α_0 = -17830	α_1 = 4132.1	α_2 = -3247.6	α_3 = -226.62	α_4 = -6521.7	σ = 65.29
298.15 K	α_0 = -10857	α_1 = 2309.8	α_2 = -2605.0	α_3 = -453.47	α_4 = 5074.6	σ = 35.64
303.15 K	α_0 = -6773.8	α_1 = 1202.5	α_2 = -1758.0	α_3 = -354.03	α_4 = 3507.2	σ = 23.97
308.15 K	α_0 = -4327.7	α_1 = 664.07	α_2 = -1315.5	α_3 = -330.52	α_4 = 2578.5	σ = 14.79
313.15 K	α_0 = -2821.4	α_1 = 356.37	α_2 = -981.61	α_3 = -295.21	α_4 = 1903.2	σ = 9.553
318.15 K	α_0 = -1875.1	α_1 = -179.97	α_2 = -719.26	α_3 = -240.24	α_4 = 1376.3	σ = 6.438
323.15 K	α_0 = -1272.1	α_1 = -87.095	α_2 = -543.12	α_3 = -192.18	α_4 = 1011.8	σ = 4.630

Table 5
Fitting parameters. α_i. calculated from Eq (4). Eq (5). Eq (6) and Eq (7). and standard deviations. σ. for the binary mixture: ChDHP:EG:GLY (1) + MeOH (2) at several temperatures.

$V_m^E\left(cm^3mol^{-1}\right)$						
293.15 K	α_0 = -5.9947	α_1 = -5.0966	α_2 = -3.5036	α_3 = -7.6408	α_4 = -4.1423	σ = 0.051
298.15 K	α_0 = -6.1671	α_1 = -5.3088	α_2 = -3.6460	α_3 = -7.6095	α_4 = -4.6666	σ = 0.049
303.15 K	α_0 = -6.2651	α_1 = -5.6109	α_2 = -4.1048	α_3 = -7.3436	α_4 = -4.8035	σ = 0.049
308.15 K	α_0 = -6.3927	α_1 = -5.8598	α_2 = -4.9551	α_3 = -7.9128	α_4 = -3.3881	σ = 0.055
313.15 K	α_0 = -6.5934	α_1 = -6.7545	α_2 = -3.3952	α_3 = -5.5653	α_4 = -8.2510	σ = 0.041
318.15 K	α_0 = -6.7978	α_1 = -6.7946	α_2 = -4.0648	α_3 = -6.8315	α_4 = -6.4737	σ = 0.052
323.15 K	α_0 = -7.1382	α_1 = -7.0131	α_2 = -4.1472	α_3 = -5.9828	α_4 = -7.9885	σ = 0.050
Δn_D						
293.15 K	α_0 = 0.2418	α_1 = 0.1837	α_2 = 0.1248	α_3 = 0.2164	α_4 = 0.1943	σ = 0.0006
298.15 K	α_0 = 0.2432	α_1 = 0.1847	α_2 = 0.1275	α_3 = 0.2184	α_4 = 0.1959	σ = 0.0005
303.15 K	α_0 = 0.2448	α_1 = 0.1862	α_2 = 0.1312	α_3 = 0.2198	α_4 = 0.1946	σ = 0.0005
308.15 K	α_0 = 0.2467	α_1 = 0.1873	α_2 = 0.1305	α_3 = 0.2263	α_4 = 0.2060	σ = 0.0006
313.15 K	α_0 = 0.2490	α_1 = 0.1897	α_2 = 0.1302	α_3 = 0.2330	α_4 = 0.2195	σ = 0.0007
318.15 K	α_0 = 0.2511	α_1 = 0.1891	α_2 = 0.1296	α_3 = 0.2566	α_4 = 0.2498	σ = 0.0007
323.15 K	α_0 = 0.2526	α_1 = 0.1900	α_2 = 0.1389	α_3 = 0.2785	α_4 = 0.2629	σ = 0.0007
$\Delta\eta$ (mPa s)						
293.15 K	α_0 = -5609.0	α_1 = -291.30	α_2 = 1510.6	α_3 = 3606.3	α_4 = -4561.2	σ = 24.97
298.15 K	α_0 = -3589.1	α_1 = -271.38	α_2 = 503.87	α_3 = 2286.6	α_4 = -2303.37	σ = 17.22
303.15 K	α_0 = -2355.9	α_1 = -287.50	α_2 = 106.98	α_3 = 1623.4	α_4 = -1270.3	σ = 8.924
308.15 K	α_0 = -1591.7	α_1 = -257.65	α_2 = 78.426	α_3 = 1108.5	α_4 = -886.11	σ = 6.628
313.15 K	α_0 = -1101.5	α_1 = -214.29	α_2 = 83.593	α_3 = 768.31	α_4 = -668.63	σ = 3.946
318.15 K	α_0 = -746.84	α_1 = -196.39	α_2 = -130.30	α_3 = 591.93	α_4 = -241.99	σ = 3.248
323.15 K	α_0 = -545.27	α_1 = -155.52	α_2 = 42.691	α_3 = 393.41	α_4 = -361.41	σ = 2.918

$$\Delta n_D = n_D - \sum_{i=1}^{N} x_i n_{Di} \tag{5}$$

$$\Delta\eta = \eta - \sum_{i=1}^{N} (\eta_i^o \cdot x_i) \tag{6}$$

Where M_i is the molecular weight of each pure component and x_i is the molar concentration of the pure DES and methanol. In all cases, a Redlich-Kister type equation [36] was used to model these excess and derived properties:

$$\Delta Q = x_1 \cdot (1 - x_1) \sum_{i=0}^{m} A_i \cdot (2x_1 - 1)^i \tag{7}$$

being ΔQ the excess or derived property and A_i the adjustable parameters. Once the standard deviations were minimized with Eq (2), their values and those of the obtained parameters were compiled in Tables 3, 4 and 5. Additionally, Figs. 5, 6 and 7 allow visualizing how the Redlich-Kister-type fittings describe the obtained data.

Regarding the excess volumes, it can be noticed that all the systems display negative-valued excess molar volumes, with a minimum placed at methanol molar concentrations around 0.8, no matter the temperature under study. This suggests that small species are included in the void spaces of the mixture, without breaking DES pseudo-lattice order, a behavior coincident with what has been detected in previous research works focused on choline chloride as HBA [37]. It can also be observed that higher temperatures lead to a weakening of the hydrogen bonds in methanolic solutions, as excess molar volumes are more negative at increased temperatures [38]. The comparison between EG and GLY-based DES reveals a great homology with what has been concluded previously for ethaline and glyceline (DES composed of ChCl and EG and GLY, respectively) [25], as GLY involves more negative excess volumes than EG.

Contrarily to excess volumes, Δn_D values for methanolic mixtures of the synthesized DES are always positive for all the compositions and temperatures under study. This is due to a weakening of the interplays between species when they bear different polarities, as it has been reported previously [39].

In addition, $\Delta\eta$ is negative for all the concentrations under study, and an increase in temperature is translated into greater viscosity deviation values for the three synthesized DES. This behavior has been also observed in the study of the viscosity deviations in methanolic mixtures of cholinium-based ionic liquids [40], and has been attributed to the existence of a more compact structure due to methanol inclusion into the

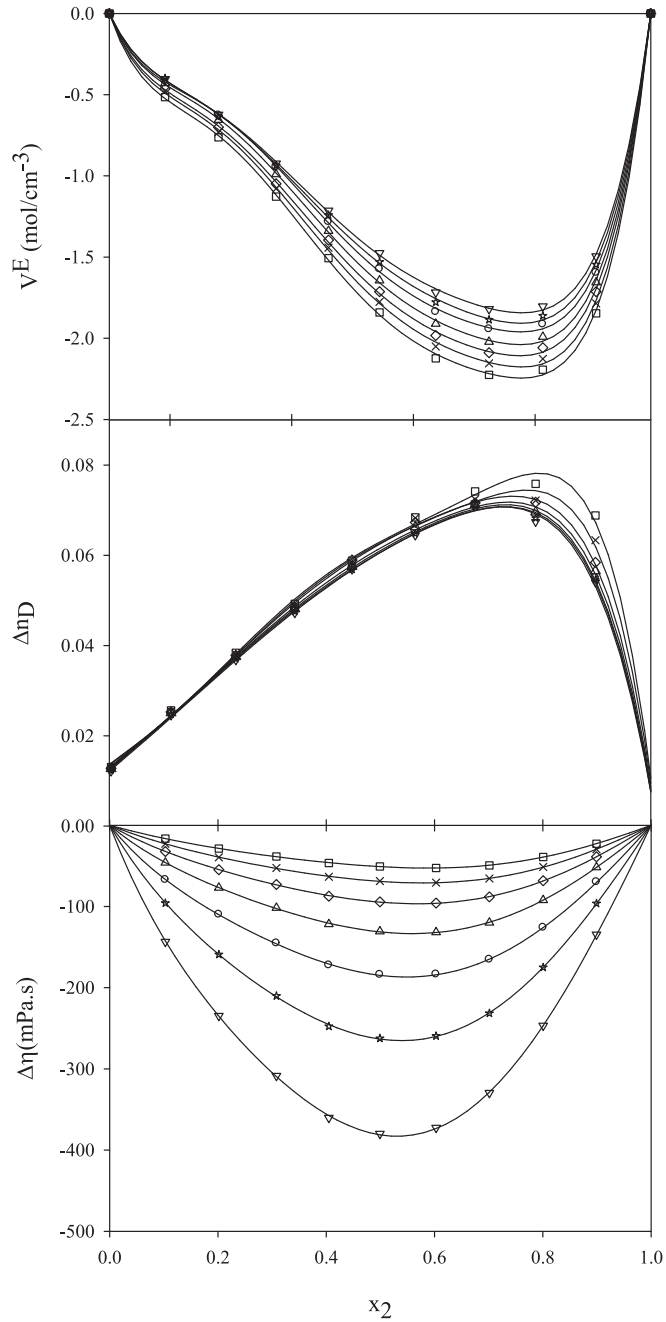

Fig. 5. Excess molar volumes (V_m^E), changes of refractive index on mixing (Δn_D) and viscosity deviations ($\Delta\eta$) of the binary mixture containing ChDHP:EG (1) and CH_3OH (2), at 293.15 K (▽), 298.15 K (*), 303.15 K (○), 308.15 K (△), 313.15 K (◆), 318.15 K (×) 323.15 K (□).

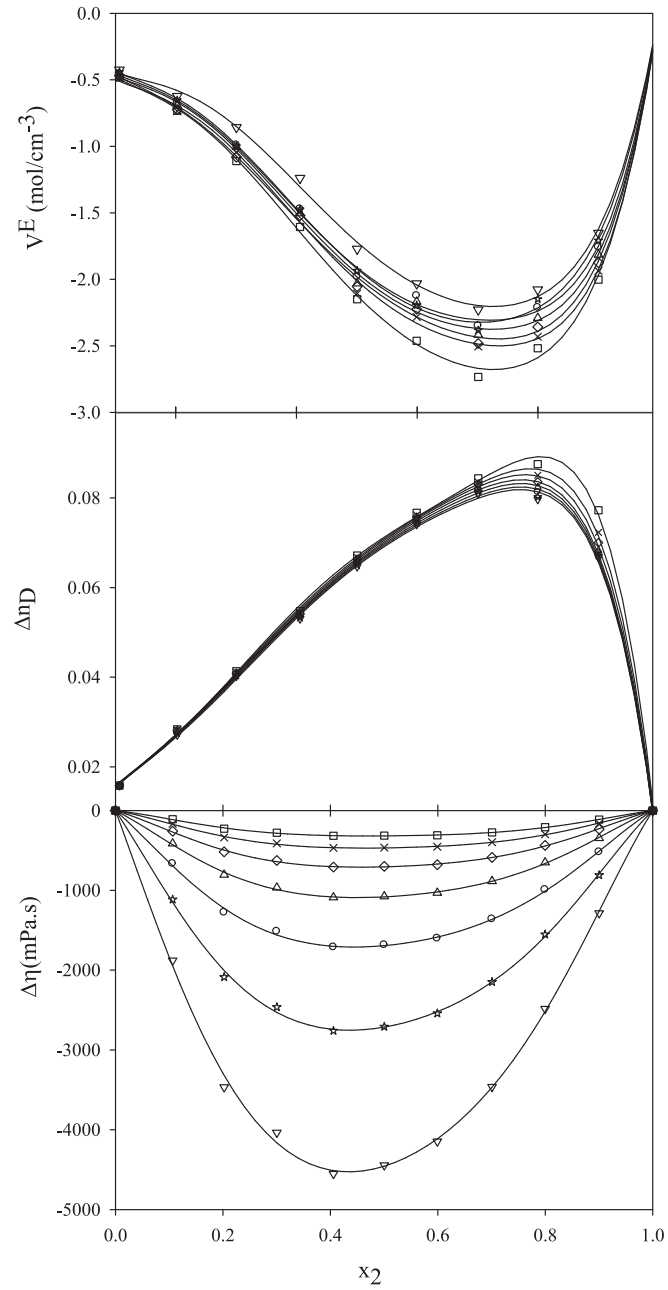

Fig. 6. Excess molar volumes (V_m^E), changes of refractive index on mixing (Δn_D) and viscosity deviations ($\Delta\eta$) of the binary mixture containing ChDHP:GLY (1) and CH_3OH (2), at 293.15 K (▽), 298.15 K (*), 303.15 K (○), 308.15 K (△), 313.15 K (◆), 318.15 K (×) 323.15 K (□).

cavities of the ionic liquid.

Also, we have observed that refractive index and density values in the mixtures are related and the former depends on the value of the latter. Thus, we have observed that the refractive index can be obtained from the relationship, $n_D = 0.29 \cdot \rho(g/cm^3) + 1.10$, independently of the DES used in the mixture or its temperature, as shown in Fig. 8 for the three mixtures at 293.15 K, 298.15 K and 308.15 K. Note that at the highest temperatures used refractive index data for the most diluted mixtures is not accurate due to the solvent evaporation in the refractometer, so enriching the mixture with DES. Independently, we have observed that the classical Newton relationship giving refractive index of the mixture, in terms of the values of density and refractive index of both pure compounds [41].

Regarding electrical conductivity data, there is no point to obtain the excess magnitude as for the other properties, because its value in a mixture is never ideal (in fact there is no formal definition of ideal mixture relative to conductivity). Conductivity value not only depend on the number of free ions, but their mobility, which increases with de decreasing ions concentration. Thus, it is typical to obtain a peak in the conductivity curve, being the maximum at the concentration where the mobility of the ions respecting its number is optimal [42]. The unusual behavior obtained here is the sharp peak observed at very low DES concentration ($x_1 = 0.05$), which represents about 20 solvent molecules per ionic pair. This behavior is not universal for DES mixtures, since there are previous reports where there no peak in the conductivity was found for any concentration in mixtures of choline chloride with dimethyl sulfoxide [43], while other authors have observed a peak for

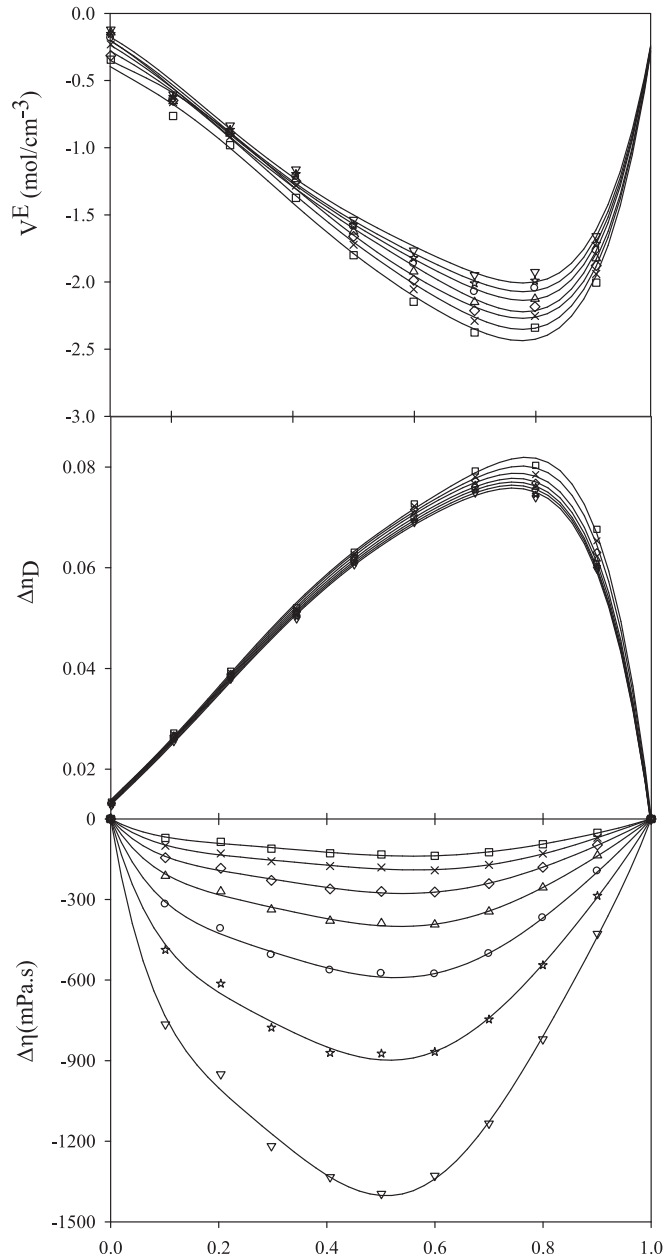

Fig. 7. Excess molar volumes (V_m^E), changes of refractive index on mixing (Δn_D) and viscosity deviations ($\Delta\eta$) of the binary mixture containing ChDHP:EG:GLY (1) and CH_3OH (2), at 293.15 K (▽), 298.15 K (*), 303.15 K (○), 308.15 K (△), 313.15 K (◆), 318.15 K (×) 323.15 K (□).

the conductivity in aqueous mixtures of different DES (as glucose–choline chloride, sucrose–choline chloride, 1,2-propanediol–choline chloride, lactic acid:glucose) at about a 60 % of water concentration, except for the mixture with proline:malic acid, where the peak appeared at a very high water concentration as a 80 % in weight [44]. Respecting mixtures of DES with methanol some results have been published showing a peak but at lower methanol concentration (with $x_2 = 0.8$) [45,46]. Also, in those references the observed increase in the conductivity value with solvent addition depends on the pair DES-solvent used, ranging from 10 to 100 times higher at the peak concentration respecting its value when pure.

We have tried to fit the obtained conductivity curve using the recently proposed expression based in a pseudo-lattice structure in the mixture for all the concentration range. This model is capable of fitting the majority of electrolytes, including those formed by ionic liquids

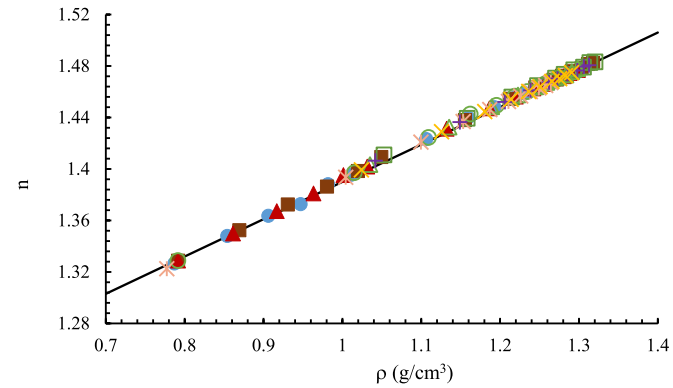

Fig. 8. Plot of refractive index vs density for the binary mixtures studied. ChDHP:EG and CH_3OH at 293.15 K (○), 298.15 K (●), 308.15 K (*); ChDHP:GLY and CH_3OH at 293.15 K (□), 298.15 K (■), 308.15 K (+); ChDHP:EG:GLY and CH_3OH at 293.15 K (△), 298.15 K (△), 308.15 K (×).The straight line is the best fit of all data shown.

[45], which are dissociated when the solvent concentration is so high that solvent molecules cannot occupy the interionic space (so giving place to a negative excess molar volume). This equation reads [47],

$$\kappa = \kappa_0\left(\phi_0\phi_S\nu_B + \phi_0^2 + \phi_0^2\phi_S\Delta\nu\right) \tag{8}$$

where κ_0 is the electrical conductivity of the pure IL, ϕ_0 and ϕ_S the molar partial volume of the pure DES and the solvent respectively (obviously $\phi_0 + \phi_S = 1$ in a binary mixture). In Equation (8), the term ν_B represent the jumping frequency of ion hopping between adjacent cells, while $\Delta\nu$ takes into account the different frequencies of jumping depending on the cell type, and both will be used as free parameters to fit the corresponding data. The resulting curves for the three methanolic mixtures of DES at 298.15 K have been plotted in Fig. 9, where we observe that even this recently proposed equation cannot fit the giant peak measured, nor determine the concentration where it appears. We guess that a novel charge transport mechanism is present in these systems, which could be the Grotthuss mechanism of proton conduction already observed in protic ILs [34]. This mechanism explains that protons move through a medium by jumping from one water molecule to another by quickly breaking and forming hydrogen bonds. Since hydrogen bonds are relatively weak protons can move rapidly through a medium by hopping from one water molecule to another, by breaking and forming hydrogen bonds. Regarding the existence of outliers, it could be hypothesized that the presence of impurities could further or hinder the establishment of hydrogen bonds of protons while moving through the solvent.

4. Conclusions

In this study, most important physicochemical properties like density, refractive index, viscosity and electrical conductivity of three novel cholinium dihydrogen phosphate-based DES have been determined in detail as they were measured for their methanolic mixtures over the entire range of compositions at atmospheric pressure and T = (293.15 to 323.15) K. Their derived properties V_m^E, Δn_D, and $\Delta\eta$ have been calculated for the binary mixtures at the proposed temperatures in order to identify the influence of the molecular interactions in these mixtures and they were correlated by the Redlich-Kister type equation. The negative values of excess molar volume and derived viscosity, excepting for derived refractive index, could be associated to the strong interactions of DES and methanol, highlighting the more negative excess volumes when the HBD compound is glycerol. Furthermore, the two transport properties (η and κ) for saturated electrolytes have a Vogel-Tamman-Fulcher temperature behavior, observing that the three methanolic mixtures presented a 20 times higher conductivity observed at high methanol

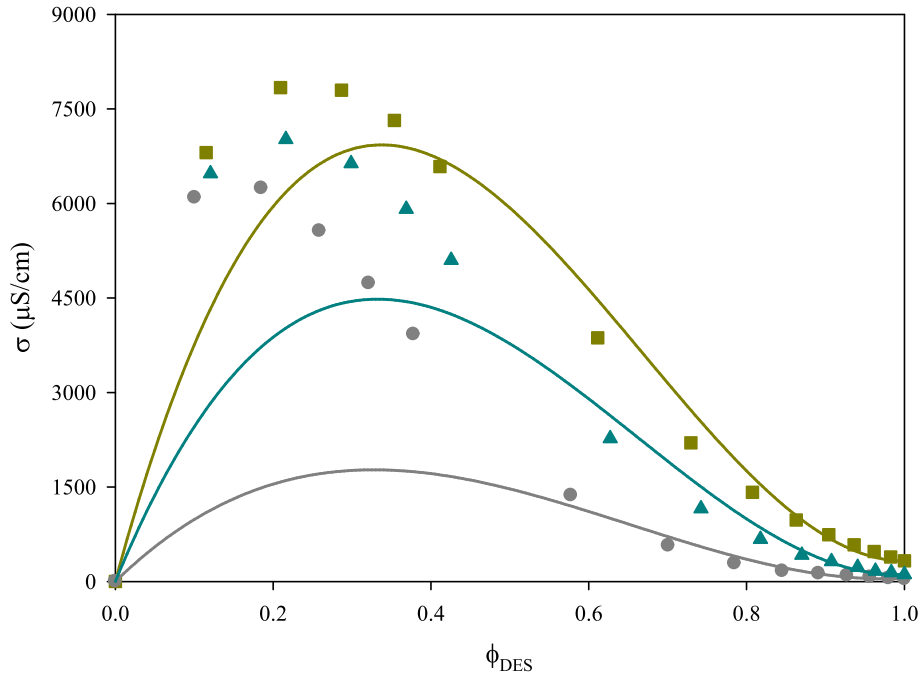

Fig. 9. Electrical conductivity versus partial molar volume of DES for the three methanolic mixtures studied at 298.15 K. ChDHP:EG and CH_3OH (■), ChDHP:GLY (●) and ChDHP:EG:GLY(△). The lines are the best fit of the Bahe-Varela equation given in Eq. (8).

concentration than of the corresponding pure DES. Finally, the Grotthuss mechanism of proton conduction could explain the charge transport in these methanolic mixtures of studied DES.

CRediT authorship contribution statement

María S. Álvarez: Conceptualization, Investigation, Formal analysis, Writing – original draft, Writing – review & editing, Funding acquisition. **Francisco J. Deive:** Formal analysis, Validation, Writing – original draft, Writing – review & editing, Funding acquisition. **María A. Longo:** Validation, Writing – review & editing, Funding acquisition. **Ana Rodríguez:** Validation, Writing – review & editing. **Luisa Segade:** Validation, Writing – review & editing. **Oscar Cabeza:** Formal analysis, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The authors are grateful to Spanish Ministry of Science, Innovation and Universities for the financial support through the project RTI2018-094702-B-I00. The authors thank Xunta de Galicia and ERDF for funding through a postdoctoral grant (ED481D-2019/017) and Universidade de Vigo/CISUG for funding open access charge.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2023.157461.

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