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Influence of water and ethanol in the physical properties of choline glycinate at several temperatures

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ABSTRACT

In this study, a physical characterization (density (ρ), refractive index (n_D), speed of sound (u) and dynamic viscosity (η)) as a function of temperature (298.15–343.15 K) of choline glycinate (ChGly) and its binary mixtures with water or/and methanol over the entire composition range was performed from 298.15 K to 323.15 K. Several derived properties of the pure ionic liquid and excess molar volume (V_m^E) changes of refractive index on mixing (Δn_D), deviations in isentropic compressibility ($\Delta\kappa_S$) and viscosity deviations ($\Delta\eta$) have been calculated using the experimental data in the selected temperature range. These experimental data of ChGly have been positively correlated using polynomial equations and the derived magnitudes were successfully fitted to Redlich-Kister equation. Finally, different models have been implemented for the first time to predict the density of the selected binary mixtures as a function of the temperature.
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1. Introduction

The growing interest of ionic liquids during the last years has been mostly centred in the imidazolium and pyridinum families. In this sense, imidazolium ionic liquids were the first family applied at industrial scale and they were already registered under REACH regulation on chemicals (e.g. [C_2C_1im] and [C_4C_1im] cations combined with Cl, [C_2SO_4], [C_1SO_3], [O_2CMe] and [NTf_2] anions). This regulation indicates that their high chemical and thermal stability suggest potential problems related to their toxicity, degradation and persistence in both the aquatic and soil environment. Taking into account this fact, their 'green' label is being questioned by the scientific community [1]. Nevertheless, it is well-known that one of the advantages offered by ionic liquids is the possibility of creating millions of combinations cation–anion to find more sustainable alternatives [2].

Nowadays, the search of industrial applications of ionic liquids has boosted the design of biocompatible options, even bearing pharmaceutical and biological properties [3,4], in line with the idea suggested by Hough and coworkers [5] who stressed the need of strengthening the bonds between industry and biology. Thus, ammonium [6] and phosphonium [7] have recently attracted the attention of the scientific community as more environmentally friendly ionic liquid families [8]. More specifically, choline-based ionic liquids have emerged as promising candidates in very different research fields such as medicine [9], chemistry [10] or even as precursors of a new generation of greener chemicals named Deep Eutectic Solvents [11].

The analysis of ecotoxicological effects of different choline-based ionic liquids with amino acid anions in aquatic organisms indicates that ChGly is practically harmless [3]. Among the possible anions available to build biocompatible ionic liquids, amino acids entail a high hydrogen bonding capacity and viscosity because of specific interactions between ions. On the one hand, the proposed functionalized ionic liquids are hydrophilic at room temperature which reveals their potential to be formulated as biocompatible extractants. Moreover, additional remarkable properties associated with amino acids as anions were concluded by Ohno and Fukumoto [12], since the combination of these anions with phosphonium cations involved hydrophobic and chiral compounds that are miscible in water at room temperature but they are immiscible when cooled. Furthermore, their cheap and abundant character compared to others chiral compounds favours that aminoacid ionic liquids play a major role in the context of green and sustainable chemistry [13]. Finally, the interest of the scientific community in these novel ionic liquids is also based on the greenness of their synthesis where choline hydroxide as cation and amino acids as

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anions are vigorously mixed at room temperature, just getting water as by-product [14].

The physical characterization (density (ρ), refractive index (n_D), speed of sound (u) and dynamic viscosity (η)) of the ionic liquid based on ammonium cation and glycinate anion, at different temperatures (298.15 to 343.15 K), is the main goal pursued in this work. So, density and dynamic viscosity are decisive to properly evaluate the mass transfer in processes involving phase segregation for industrial applications. In this particular case, some experimental results have already been reported for this ionic liquid [15,16] and the differences should be analysed. The experimental determination of these intensive properties will be the basis to estimate relevant thermodynamic properties such as isobaric thermal expansivity, α, molecular volume, V, molar refraction, R_m, molecular polarizability, α_0, and free volume, f_m.

In addition to the thermodynamic characterization of ChGly, the physical properties of this ionic liquid in the most popular solvents (water and methanol) will allow scientific community to understand their interactions and will assist them in optimizing different procedures mainly in bio-tech industries, where this type of compounds would presumably be consumed as solvents. So, the densities, refractive indices, speeds of sound and dynamic viscosities of the binary mixtures of ChGly with water or methanol from 298.15 to 323.15 K and atmospheric pressure were measured over the entire composition range. Excess and derived properties have been calculated from the experimental data and a function of the mole fraction and Redlich-Kister equation was used to fit these derived values.

Since the volumetric properties of amino-acid based ionic liquids are scarce in the literature, the development of predictive methods is an important task to complement the available experimental data and one of the aspects that has been investigated in this work. Thus, the experimental density and refractive index of the pure components have been used to estimate the density of the mixture. In the same line, several predictive models such as Riedel, Narsimham, Bradford-Thodos, Yen-Woods, Rackett, Spencer-Danner and Hankinson-Thomson (COSTALD) equations [7] have been used to satisfactorily predict the density of the mixtures at several temperatures.

2. Experimental

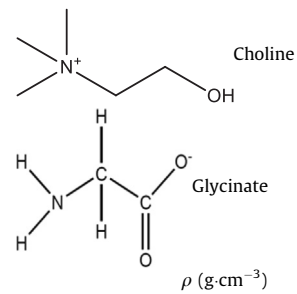
2.1. Chemicals

Methanol (99 wt%, CAS 67-59-1) was provided by Sigma-Aldrich. In the experiments milli Q-water was used. The pure aminoacid-based ionic liquid (ChGly) has been previously synthetized in our lab as reported elsewhere [17]. The obtained ionic liquid was dried for several days under vacuum and moderate temperature (40 °C and 0.5 mbar). The water content was determined by Coulometric Karl-Fischer titrations (Metrohm 899) and the values are over 5 wt%. Specific information of the reagents is listed in Table 1.

2.2. Apparatus and procedure

The binary mixtures were prepared into stoppered bottles to prevent preferential evaporation. A Sartorius CubisMSA balance (125P-100-DA) balance (precision of 10^{-5} g) was used to determine the amount of the pure solvents that are transferred via syringe to the vials. The combined expanded uncertainty in mole fractions of all the samples was estimated ±0.02.

Table 1
Structure, physical properties and comparison with literature data of ChGly at 298.15 K.



	ρ (g·cm^{-3})	n_D	η (mPa·s)
ChGly	1.14628	1.49224	500.96
	1.15560[1]	1.5012[1]	12,301
	1.14520[2]	1.5224[2]	182.3[2]

[1] S. De Santis, G. Masci, F. Casciotta, R. Caminiti, E. Scarpellini, M. Campetella, L. Gontrani, Phys. Chem. Chem. Phys. 17 (2015) 20687–20698.
[2] D. Tao, Z. Cheng, F. Chen, Z. Li, N. Hu, X. Chen, J. Chem. Eng. Data 58 (2013) 1542–1548.

2.2.1. Densities and speeds of sound

The density and speed of sound were obtained by using an Anton Paar DSA-5000M digital vibrating tube densimeter. The apparatus was calibrated with Millipore quality water and ambient air according to the instructions. The instrument automatically corrects the effect of viscosity on density and speed of sound values. The combined expanded uncertainties with a level of confidence = 0.95, k = 2 associated with measurements of density and speed of sound were found to be $5{\cdot}10^{-4}$ g·cm^{-3} and 0.5 m·s^{-1}, respectively.

2.2.2. Refractive indices

The refractive indices were determined by the automatic refractometer ABBEMAT-WR Dr. Kernchen with an uncertainty in the experimental measurements of $4 \cdot 10^{-5}$. The apparatus was calibrated by measuring the refractive index of Millipore quality water before each series of measurements according to instructions.

2.2.3. Dynamic viscosities

Dynamic viscosities were measured by using Anton Paar Lovis 2000M falling ball automated viscometer. Capillaries with a diameter of 1.59 mm (extended dynamic viscosity range = 0.3–90 mPa·s) and 2.5 mm (extended dynamic viscosity range = 12–10,000 mPa·s) were used for measurements.

Standards N-50 and N-80 were employed to calibrate the capillaries The combined expanded uncertainties with a level of confidence = 0.95, k = 2 associated with measurement of viscosity were found to be as Uc(η) (<1 mPa·s) = 0.20 mPa·s, Uc(η) (1–10 m Pa·s) = 0.60 mPa·s and Uc(η) (11–50 mPa·s) = 0.80 mPa·s. The temperature was kept constant with a precision of 0.01 K.

3. Results and discussion

3.1. Experimental determination of ChGly physical properties

Density (ρ) measurements of ChGly were carried out at temperatures ranging from (298.15 to 323.15) K and the experimental data obtained are listed in Table S1. The analysis of the results reveals that, as expected, the densities linearly decrease with increasing temperature. The comparison with literature data [16] indicates that the addition of different groups to the anion causes

a significant effect in the density. In this particular case, L-Alanine and β-Alanine (addition of a methyl group) and Proline (addition of an ethyl alcohol) present lower values of this property for the selected temperature range. However, Serine anion shows higher density values than the other amino acids. The main differences are based on the fact that this compound contains a carboxylic group connected to a pyrrolidine with a secondary amine. In this case, the elongation of the Serine anion promotes the appearance of different polar domains in comparison with the alkyl side chain of Alanine and Proline, which means that it does not favour the packing of the polar network in amino-acid based ionic liquids so that the volumetric properties are increased [18]. Additionally, it is significant that ChGly shows similar density values that C_2-MIMGly [19]. This fact is very common in ionic liquids where the influence of the cation is less drastic compared to that observed when the anion is modified [20].

The speed of sound (u) was measured for the first time at several temperatures from (298.15 to 343.15) K and the experimental values are compiled in Table S1. As seen in this table, this property was found to be linearly decreasing when the temperature is increased. These experimental data are scarce but they are required to obtain valuable information about thermophysical properties such as the isentropic compressibility. Thus, the experimental determination of this physical property is pertinent and has been carried out in this research work.

The refractive indices (n_D) were measured over the temperature range from (298.15 to 343.15) K and the experimental data are listed in Table S1. In general terms, the refractive index for the ionic liquids also exhibits a similar linear trend as that followed by the density, since the increase of temperature involves a reduction of the refractive index. Additionally, the results suggest that optical properties are not so drastically influenced by the anion, contrarily to the findings concluded for the density. Analogous results were also recorded for ionic liquids composed of imidazolium cation and glycinate anion [19].

Dynamic viscosity (η) is one of the decisive transport properties allowing to get a proper understanding of ChGly in terms of mass transfer, and was thus experimentally determined over the selected temperature range. From the data presented in Table S1, it becomes patent that this property decrease exponentially with the temperature [7,15,16]. The analysis of literature [16] values suggests that dynamic viscosity data are strongly influenced by the introduction of a methyl, hydroxyethyl or pyrrolidine group in the anion moiety (alaninate, prolinate and serinate). This behaviour can be rationalized in terms of intermolecular interactions (hydrogen bonding and/or van der Waals interactions) and size of the amino acid.

A comparison of these experimental data (ρ, n_D and η) at the selected temperatures with those existing in literature [16]. In this case, low deviations in the refractive indices and densities are found, contrarily to the values obtained for the dynamic viscosity, especially at low temperatures. This fact could indicate the presence of some amounts of water or the use of different experimental methods, as it has been frequently reported in literature [21].

3.2. Correlation of ChGly physical properties

After having concluded a linear relationship between temperature and physical properties, ρ, n_D and u were fitted to a polynomic equation of the form:

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

where Q is the physical property (ρ, n_D and u), T is the temperature in K, A_i are the fitting parameter and m = 1 is the degree of the polynomial expansion. This one was optimized applying the F-test. The A_i parameters calculated using Eq. (1) are listed in Table 2, together with their root mean standard deviations (σ) determined using the following equation:

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

where the property values and the number of experimental data are represented by z and n_{DAT}, respectively. The analysis of σ values allows concluding a suitable description of the experimental data for the three physical properties.

The temperature dependence of η was fitted to a Litovitz equation [22]:

$$\eta = \eta_L \cdot \exp\left(\frac{B_L}{T^3} \right) \tag{3}$$

being η_L and B_L the fitting parameters that are listed in Table 2. In the same line, the non-linear relationship between dynamic viscosity and density for different temperatures is evidenced by the data listed in Table S1. This statement made us to bet in the fluidity (η^{-1}) as the viable tool to analyse the reliability of the obtained experimental data.

$$(1/\eta)^{\varphi} = a + bT \tag{4}$$

where T is the temperature in K and a, b and ϕ are adjustable parameters, that are shown in Table 2, together with σ. The analysis of the presented data unveils the reduction of the standard deviation when the parameter ϕ is not fixed to 0.3, as recommended in literature for other ionic liquids [23].

3.3. Derived properties obtained from physical characterization of ChGly

Once the main physical properties have been ascertained, two fundamental derived magnitudes were inferred from the experimental density data in order to shed light on the thermodynamic behaviour of the aminoacid-base ionic liquid. Thus, the isobaric thermal expansivity, α, and the molar volume, V, were calculated as follows,

$$\alpha = \frac{-1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P \tag{5}$$

$$V_m = \frac{M}{\rho} \tag{6}$$

Table 2
Fitting parameters and root mean square deviation (σ) to correlate the physical properties of ChGly as a function of temperature *Fixed value at 0.3.

Physical properties	A_0/η_L	A_1/B_L	ϕ	∇
ρ/(g·cm^{-3})	1.3346	−0.0006		0.0010
n_D	1.5647	−0.0002		0.0001
u/(m·s^{-1})	2900.0	−2.543		0.24
η (mPa·s)	0.6547	1.76 10^8		1.456
η (mPa·s)	−0.7782	0.0031	0.30*	0.003
η (mPa·s)	−0.7784	0.0030	0.35	0.001

where M is the molar mass of ChGly. The calculated values of α and V_m for each temperature are detailed in Table S2. These values ranged about 5 10^{-4} K^{-1} and are similar to the other ionic liquids [15,16,19].

The analysis of the literature data for thermal expansivity reflects a high similarity in the order of magnitude of the values obtained for ChGly in relation to imidazolium, pyridinium and phosphonium ionic liquids when amino acids are employed as anions [19]. However, slight differences with literature data are observed for this ionic liquid [15,16]. The rationale behind this fact is based in the α calculation. In this research work, α values have been numerically obtained by the differential equation of the polynomial fit of the density (Eq. (1)), contrarily to what is found in literature, where a rational function is used to determine this parameter. The authors have evaluated both alternatives and have bet in the theoretical definition of the isobaric thermal expansivity. Then, the best fit of the experimental data is a degree one equation relating density and temperature, taking into account the linearity of the experimental data.

Regarding the molar volume, V_m, it is patently clear that this parameter is negligibly affected by the temperature and a linear trend is demostrated. In this case, the scarcity of experimental density data as a function of the temperature makes it difficult to properly analyse the impact of the amino acid anion paired to the choline cation. However, the obtained values (154.23 $cm^3 \cdot mol^{-1}$) resulting from summing choline cation and glycinate anion are in reasonable agreement with the experimental one measured in this work [15]. In this scenario, the differences between ChGly data and literature data [15] could be attributed to the differences in the experimental density, as can be seen in Table 1.

The relationship between light and mass is an important issue that is worth being analysed due to it provides valuable information about the interplays between molecules [24]. The main way to approach this study is using the experimental refractive index and density of the pure components. In this sense, Lorentz-Lorenz relationship [24] between the refractive index and the electronic polarizability, α_0, leads to the definition of derived molar refraction R_m and free volume f_m:

$$R_m = \left[\frac{n_D^2 - 1}{n_D^2 + 2}\right]\left(\frac{M}{\rho}\right) = \frac{4\pi N_A}{3}\alpha_0 \quad (7)$$

$f_m = V_m - R_m$, (8)

The values of molar refraction, R_m, molecular polarizability, α_0, and free volume, f_m were calculated from the experimental data of ChGly at the selected temperatures and are listed in Table S2. In this particular case, it can be concluded that the derived magnitudes are temperature-independent in the selected range. A comparison of R_m and f_m values for ChGly with those found in the literature for phosphonium-based ionic liquids [24] indicates that the lower free volume of the ammonium-based ionic corresponds to a stronger hydrogen bond network than that observed for phosphonium ionic liquids.

3.4. Experimental determination of the physical properties of binary mixtures at several temperatures

ρ, n_D, u and η of the binary mixtures ChGly with water or methanol through the whole composition range from 298.15 to 323.15 K were measured and the values are given in Tables S3 and S4 and plotted in Figs. 1–4. These data were experimentally determined for the first time in this research work in order to analyze the influence of two polar components as water and methanol in the polar environment of ChCly.

The experimental density values of ChGly with water/methanol increase with the mole fraction of ChGly in the mixture, albeit

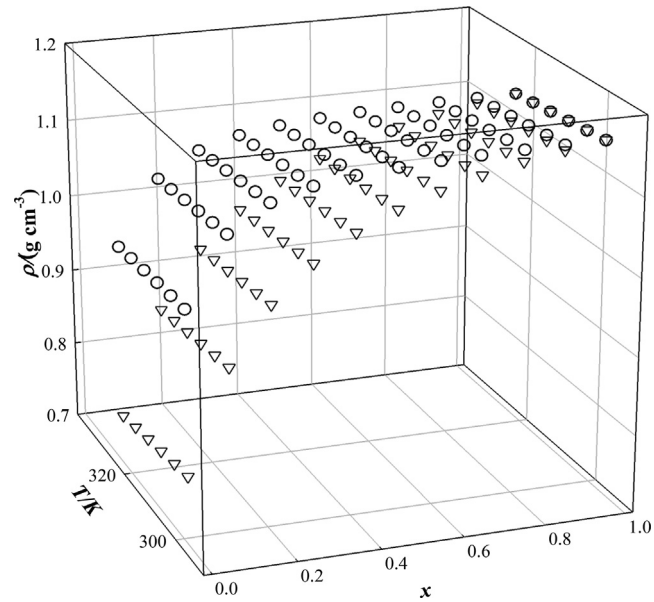


Fig. 1. Experimental density (ρ) of the binary mixture: (○) ChGly (1) + H_2O (2) and (▽) ChGly (1) + CH_3OH (2) as a function of the temperature.

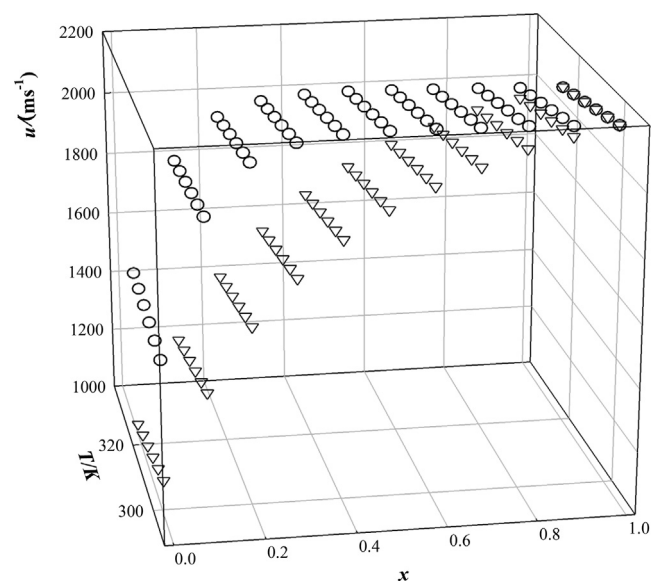


Fig. 2. Experimental speed of sound (u) of the binary mixture: (○)ChGly (1) + H_2O (2) and (▽) ChGly (1) + CH_3OH (2) as a function of the temperature.

these data decrease with greater temperatures. It is interesting to note that the presence of water in the binary mixture favours the interactions with the polar network of the aminoacid-ionic liquid resulting in a high value of the density (Fig. 2). However, these cohesive forces are lower when methanol is employed as solvent. The differences between the hydrogen-bond capacity of water with respect to methanol could be a plausible explanation when considering hydrotope effects. In this case, a previous work of our group [18] sustains that aqueous solutions of ChGly promote aggregates formation and their corresponding interactions affect to volumetric properties. The different intensity of these interactions is diminished when water or methanol concentrations are lower (mole fraction higher than 0.8) and the presence of ChGly determines the interactions. The same trend is observed in Fig. 2 when the speed of sound is determined at several temperatures and the

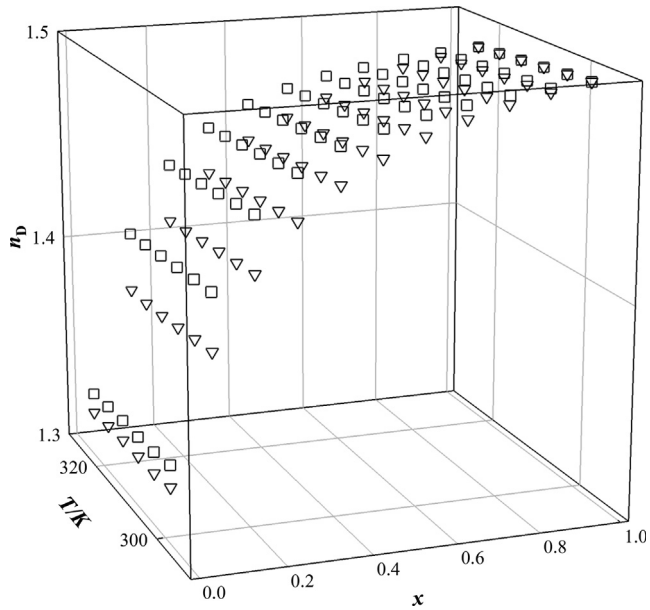


Fig. 3. Experimental refractive index (n_D) of the binary mixture: (○)ChGly (1) + H_2O (2) and (▽) ChGly (1) + CH_3OH (2) as a function of the temperature.

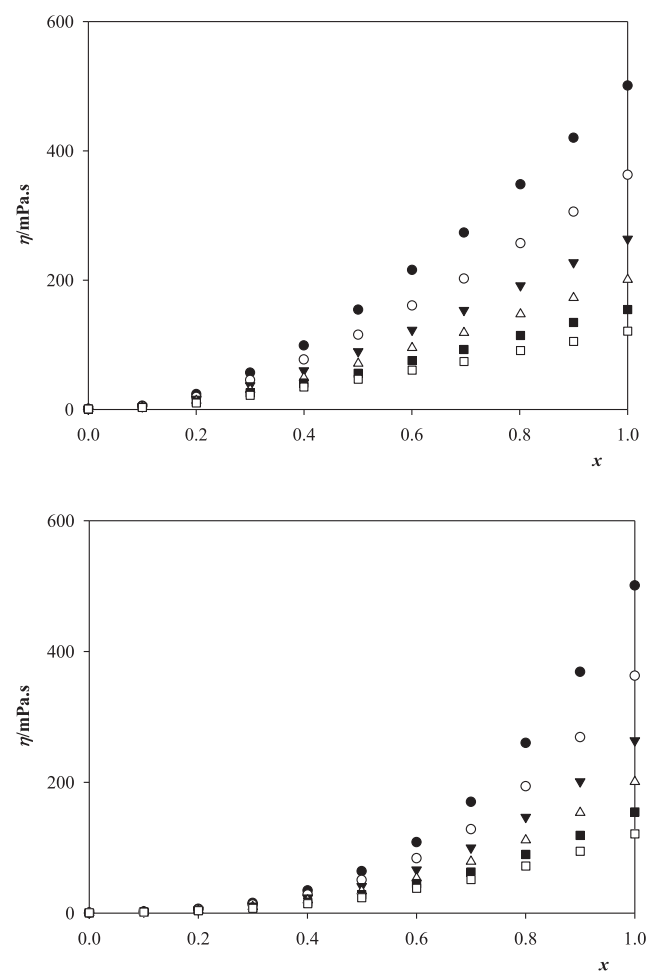


Fig. 4. Experimental dynamic viscosity (η) of the binary mixture: (top) ChGly (1) + H_2O (2) and (bottom) ChGly (1) + CH_3OH (2) at: (●) 298.15 K, (○) 303.15 K, (▽) 308.15 K, (Δ) 313.15 K, (■) 318.15 K and (□) 323.15 K.

effect of compression and decompression regulates the degree of packing of the polar solvent and ChGly.

The influence in the light propagation in a media composed of water or methanol plus ChGly is possible to be quantified by the experimental determination of the refractive index. In this case, the experimental data plotted in Fig. 3 indicate that the interactions between the components do not entail significant differences and the values are very similar no matter the solvent under study.

Finally, in Fig. 5 the experimental values of the dynamic viscosity are represented as a function of the mole fraction and temperature. In this case, the influence of decisive intermolecular interactions such as hydrogen bonding, dispersive forces and columbic interactions is patently clear [25]. The experimental η values of the binary mixtures are similar and increase with the ChGly concentration but decrease at elevated temperatures. This trend is supported by the role of the abovementioned intermolecular forces, because stronger interactions between ChGly and

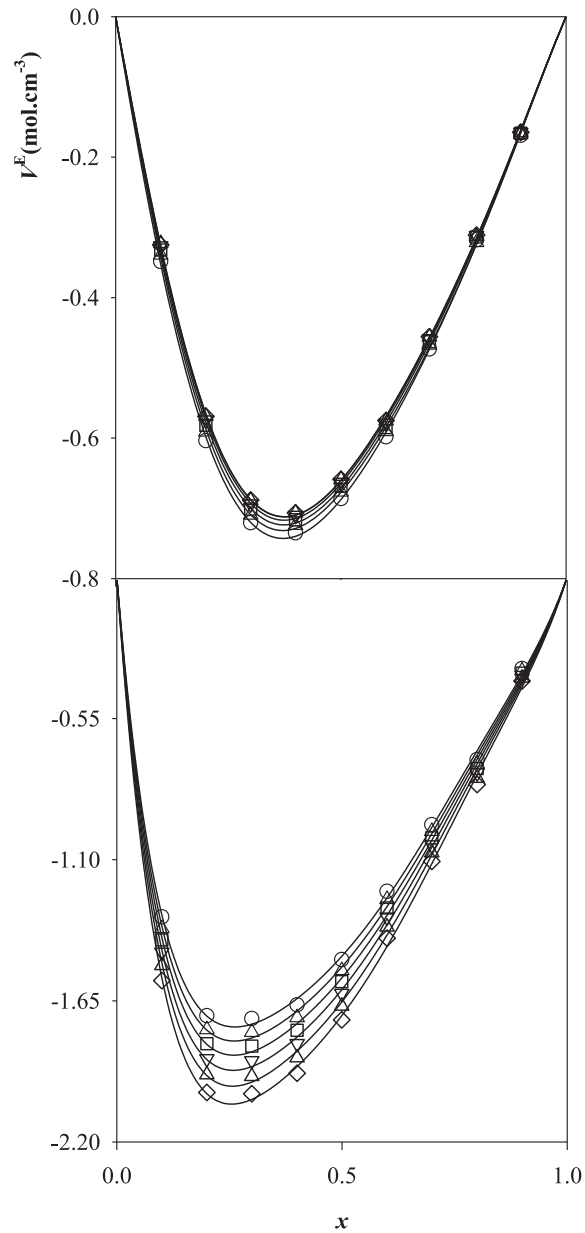


Fig. 5. Excess molar volumes (V^E) of the binary mixture: (top) ChGly (1) + H_2O (2) and (bottom) ChGly (1) + CH_3OH (2) at: (○) 298.15 K, (Δ) 303.15 K, (□) 308.15 K, (▽) 313.15 K, (☆) 318.15 K and (◆) 323.15 K.

water/methanol are responsible of the resistance against flowing of the binary mixtures.

3.5. Correlation of physical properties of the binary mixtures at several temperatures

Excess molar volume (V_m^E), changes of refractive index on mixing (Δn_D), isentropic compressibility (κ_S), determined by means of Laplace equation, ($\kappa_S = \rho^{-1} \cdot u^{-2}$), deviations in isentropic compressibility ($\Delta\kappa_S$) and viscosity deviations ($\Delta\eta$) from 298.15 to 323.15 K were calculated using the experimental values of the binary mixtures, as follows:

$$V_m^E = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}) \tag{9}$$

Table 3
Fitting parameters, A_i, calculated from Eq. (13) and standard deviations, σ for the binary mixture: ChGly (1) + H_2O (2) at several temperatures.

$V_m^E\left(cm^3 mol^{-1}\right)$						
298.15 K	A_1 = −2.7505	A_2 = 1.5560	A_3 = −0.6155	A_4 = −0.3886	A_5 = 0.6720	σ = 0.004
303.15 K	A_1 = −2.7096	A_2 = 1.5166	A_3 = −0.6851	A_4 = −0.4428	A_5 = 0.8153	σ = 0.003
308.15 K	A_1 = −2.6833	A_2 = 1.5026	A_3 = −0.6150	A_4 = −0.4636	A_5 = 0.7728	σ = 0.004
313.15 K	A_1 = −2.6593	A_2 = 1.4919	A_3 = −0.5991	A_4 = −0.5044	A_5 = 0.7767	σ = 0.003
318.15 K	A_1 = −2.6420	A_2 = 1.4820	A_3 = −0.6014	A_4 = −0.5438	A_5 = 0.7814	σ = 0.003
323.15 K	A_1 = −2.6432	A_2 = 1.4786	A_3 = −0.5664	A_4 = −0.5081	A_5 = 0.7124	σ = 0.003
Δn_D						
298.15 K	A_1 = 0.2559	A_2 = −0.1953	A_3 = 0.1438	A_4 = −0.1908	A_5 = 0.1585	σ = 0.0003
303.15 K	A_1 = 0.2581	A_2 = −0.1960	A_3 = 0.1433	A_4 = −0.2015	A_5 = 0.1711	σ = 0.0004
308.15 K	A_1 = 0.2581	A_2 = −0.1957	A_3 = 0.1412	A_4 = −0.2027	A_5 = 0.1769	σ = 0.0004
313.15 K	A_1 = 0.2559	A_2 = −0.1938	A_3 = 0.1406	A_4 = −0.1993	A_5 = 0.1714	σ = 0.0004
318.15 K	A_1 = 0.2556	A_2 = −0.1934	A_3 = 0.1411	A_4 = −0.2007	A_5 = 0.1710	σ = 0.0003
323.15 K	A_1 = 0.2560	A_2 = −0.1930	A_3 = 0.1389	A_4 = −0.2052	A_5 = 0.1792	σ = 0.0004
$\Delta k_s\left(TPa^{-1}\right)$						
298.15 K	A_1 = −524	A_2 = 434	A_3 = −346	A_4 = 864	A_5 = −874	σ = 2.14
303.15 K	A_1 = −506	A_2 = 420	A_3 = −329	A_4 = 818	A_5 = −830	σ = 1.92
308.15 K	A_1 = −489	A_2 = 408	A_3 = −327	A_4 = 776	A_5 = −775	σ = 1.83
313.15 K	A_1 = −475	A_2 = 397	A_3 = −319	A_4 = 743	A_5 = −735	σ = 1.72
318.15 K	A_1 = −463	A_2 = 388	A_3 = −311	A_4 = 714	A_5 = −703	σ = 1.60
323.15 K	A_1 = −452	A_2 = 380	A_3 = −306	A_4 = 686	A_5 = −672	σ = 1.54
$\Delta\eta$ (mPa s)						
298.15 K	A_{11} = −387.0	A_{21} = 139.2	A_{31} = −93.0	A_{41} = −59.1	A_{51} = 69.6	σ = 1.00
303.15 K	A_{11} = −263.6	A_{21} = 98.1	A_{31} = −29.8	A_{41} = −19.0	A_{51} = −21.6	σ = 0.89
308.15 K	A_{11} = −169.3	A_{21} = 82.5	A_{31} = −28.1	A_{41} = 10.2	A_{51} = 12.8	σ = 0.58
313.15 K	A_{11} = −118.8	A_{21} = 57.9	A_{31} = −19.0	A_{41} = 13.8	A_{51} = −17.4	σ = 0.44
318.15 K	A_{11} = −82.2	A_{21} = 35.4	A_{31} = −23.8	A_{41} = 37.9	A_{51} = 1.35	σ = 0.51
323.15 K	A_{11} = −55.0	A_{21} = 25.4	A_{31} = -26.9	A_{41} = 33.9	A_{51} = 6.23	σ = 0.46

Table 4
Fitting parameters, A_i, calculated from Eq. (13) and standard deviations, σ for the binary mixture: ChGly (1) + CH_3OH (2) at several temperatures.

$V_m^E\left(cm^3 mol^{-1}\right)$						
298.15 K	A_1 = −5.9036	A_2 = 3.9246	A_3 = −2.8314	A_4 = 4.0547	A_5 = −4.0947	σ = 0.018
303.15 K	A_1 = −6.0703	A_2 = 4.0758	A_3 = −2.9253	A_4 = 4.1879	A_5 = −4.2694	σ = 0.019
308.15 K	A_1 = −6.2403	A_2 = 4.2240	A_3 = −3.0201	A_4 = 4.3340	A_5 = −4.4329	σ = 0.019
313.15 K	A_1 = −6.4230	A_2 = 4.3750	A_3 = −3.1068	A_4 = 4.5163	A_5 −4.6374	σ = 0.020
318.15 K	A_1 = −6.6145	A_2 = 4.5237	A_3 = −3.2209	A_4 = 4.7251	A_5 = −4.8112	σ = 0.020
323.15 K	A_1 = −6.8273	A_2 = 4.6794	A_3 = −3.3729	A_4 = 4.9819	A_5 = −5.0199	σ = 0.020
Δn_D						
298.15 K	A_1 = 0.2235	A_2 = −0.1452	A_3 = 0.0957	A_4 = −0.0900	A_5 = 0.0600	σ = 0.0002
303.15 K	A_1 = 0.2244	A_2 = −0.1483	A_3 = 0.0979	A_4 = −0.0894	A_5 = 0.0625	σ = 0.0003
308.15 K	A_1 = 0.2224	A_2 = −0.1502	A_3 = 0.1049	A_4 = −0.0761	A_5 = 0.0388	σ = 0.0002
313.15 K	A_1 = 0.2204	A_2 = −0.1503	A_3 = 0.1065	A_4 = −0.0671	A_5 = 0.0275	σ = 0.0002
318.15 K	A_1 = 0.2196	A_2 = −0.1491	A_3 = 0.1033	A_4 = −0.0696	A_5 = 0.0343	σ = 0.0003
323.15 K	A_1 = 0.2195	A_2 = −0.1462	A_3 = 0.0947	A_4 = −0.0833	A_5 = 0.0614	σ = 0.0004
$\Delta k_s\left(TPa^{-1}\right)$						
298.15 K	A_1 = −1428	A_2 = 1100	A_3 = −834	A_4 = 1400	A_5 = −1260	σ = 2.68
303.15 K	A_1 = −1489	A_2 = 1148	A_3 = −873	A_4 = 1481	A_5 = −1331	σ = 2.84
308.15 K	A_1 = −1553	A_2 = 1199	A_3 = −912	A_4 = 1567	A_5 = −1417	σ = 3.02
313.15 K	A_1 = −1622	A_2 = 1254	A_3 = −955	A_4 = 1662	A_5 = −1507	σ = 3.23
318.15 K	A_1 = −1693	A_2 = 1311	A_3 = −1003	A_4 = 1761	A_5 = −1600	σ = 3.44
323.15 K	A_1 = −1767	A_2 = 1371	A_3 = −1048	A_4 = 1864	A_5 = −1703	σ = 3.65
$\Delta\eta$ (mPa s)						
298.15 K	A_{11} = −747.7	A_{21} = −275.7	A_{31} = −5.6	A_{41} = 73.0	A_{51} = 77.2	σ = 0.72
303.15 K	A_{11} = −524.9	A_{21} = −174.9	A_{31} = 6.3	A_{41} = 35.1	A_{51} = 29.5	σ = 0.87
308.15 K	A_{11} = −364.6	A_{21} = −102.4	A_{31} = 8.76	A_{41} = 41.1	A_{51} = 52.6	σ = 0.35
313.15 K	A_{11} = −267.0	A_{21} = −67.7	A_{31} = −17.1	A_{41} = 8.3	A_{51} = 52.7	σ = 0.22
318.15 K	A_{11} = −196.1	A_{21} = −34.1	A_{31} = −3.1	A_{41} = −10.8	A_{51} = 19.9	σ = 0.57
323.15 K	A_{11} = −146.7	A_{21} = −17.9	A_{31} = −6.4	A_{41} = −12.1	A_{51} = 23.6	σ = 0.52

$$\Delta n_D = n_D - \sum_{i=1}^{N} x_i n_{Di} \tag{10}$$

$$\Delta k_S = k_S - \sum_{i=1}^{N} x_i k_{S,i} \tag{11}$$

$$\Delta \eta = \eta - \sum_{i=1}^{N} (\eta_i^o \cdot x_i) \tag{12}$$

In these equations, ρ and n_D are the density and refractive index of the binary mixture, ρ_i and n_{Di} are the density and refractive index of ChGly, water or methanol, κ_S is the isentropic compressibility of the mixture, $\kappa_{S,i}$ is the isentropic compressibility of the pure components and η is the dynamic viscosity of the mixture and η_i^o represents the viscosity for each pure component.

The excess and derived quantities of the binary mixtures were fitted to a Redlich-Kister type equation [26]:

$$\Delta Q = x_1 \cdot (1 - x_1) \sum_{i=0}^{m} A_i \cdot (2x_1 - 1)^i \tag{13}$$

where ΔQ is defined as the excess or derived property, x is the mole fraction and A_i is the fitting parameter. Applying the SOLVER function in Microsoft EXCEL, the degree of polynomial expression was optimized. The correlation parameters are listed in Tables 3 and 4 together with the standard deviations. These standard deviations were calculated by applying previous Eq. (2). The derived and calculated data of the binary mixtures are shown in Figs. 5–8.

In Fig. 5, V_m^E values for the binary mixtures ChGly with water (above) or methanol (bottom) as a function of the mole fraction and the selected temperatures are recorded. In this case, these values are negative at all concentrations with the minimum between −0.6 and −0.7 (mol cm^{-3}) for ChGly (1) + H_2O (2) and −1.5 and −1.6 (mol cm^{-3}) for ChGly (1) + CH_3OH (2). Thus, the negative values could be associated to attractive forces between the liquid components and, more specifically, the proved hydrogen bonding capacity of water or methanol to interact with ChGly which can be translated into an easy accommodation of the small molecules in the interstitial sites of ChGly. The influence of temperature in these interactions is higher when methanol is employed as solvent. Temperature increase boosts kinetic energy of the molecules, which favours the breaking of the intermolecular forces. This fact is translated into an excess property reduction at elevated temperatures [25,27].

On the contrary, in Fig. 6, Δn_D values for the studied binary mixtures are positive at the whole composition range and temperatures. This expansive values are commonly associated to weaker interaction forces between the molecules, and more specifically occurs when one of the components is polar and the other one weakly polar. This effect causes differences in the Δn_D of the selected binary, where a decrease of the intermolecular forces in the case of water and is associated to a lower steric volumes and higher refraction values [28].

In Fig. 7, $\Delta\kappa_S$ data are plotted and these values are negative for the binary mixtures across the composition range. This negative trend indicates that the mixture is less compressible than the corresponding ideal one. This fact is more evident for the alcoholic mixture than for the aqueous one, as the existence of stronger interactions between methanol and ChGly is translated into larger negative values. It is necessary to notice the influence of the temperature in this derived property. In this case, the stronger interactions between methanol and ChGly are recorded at 323.15 K. Contrarily to this, the higher $\Delta\kappa_S$ values fo ChGly and water occur at 298.15 K. On this occasion, a more compact structure is formed at low temperatures between water and ChGly, which explains the minimum observed for these values. At greater temperatures, the disruption of the interactions between the molecules is reflected in higher $\Delta\kappa_S$ values, indicating a more remarkable ideal behavior [29].

$\Delta\eta$ values plotted in Fig. 8 are negative over the entire composition range from 298.15 to 323.15 K. These data increase when temperature is increased for the binary mixtures, however more negative values are observed for methanol and ChGly mixture. These deviations from the ideality of the alcoholic mixture could be explained in terms of the strong molecular interactions and the compact structure formed by the inclusion of methanol into the cavities of ChGly [30].

3.6. Models to estimate the density of the binary mixtures at all the temperatures

The density of the selected binary mixtures ChGly with water or/and methanol has been estimated at all the temperatures by

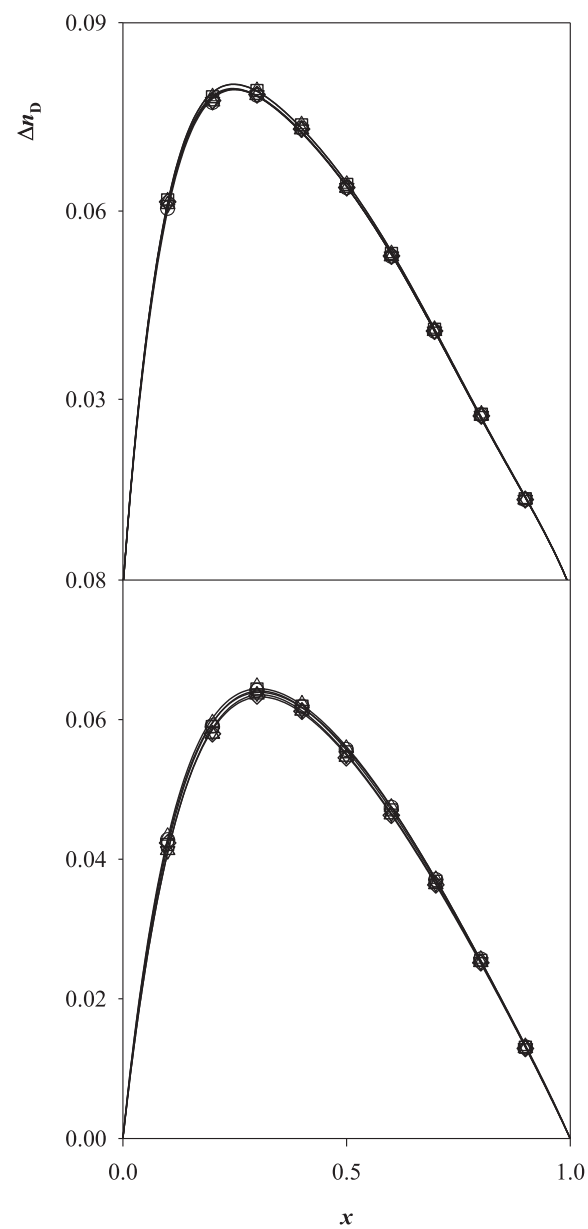


Fig. 6. Changes of refractive index on mixing (Δn_D) of the binary mixture: (top) ChGly (1) + H_2O (2) and (bottom) ChGly (1) + CH_3OH (2) at: (○) 298.15 K, (Δ) 303.15 K, (□) 308.15 K, (▽) 313.15 K, (☆) 318.15 K and (◆) 323.15 K.

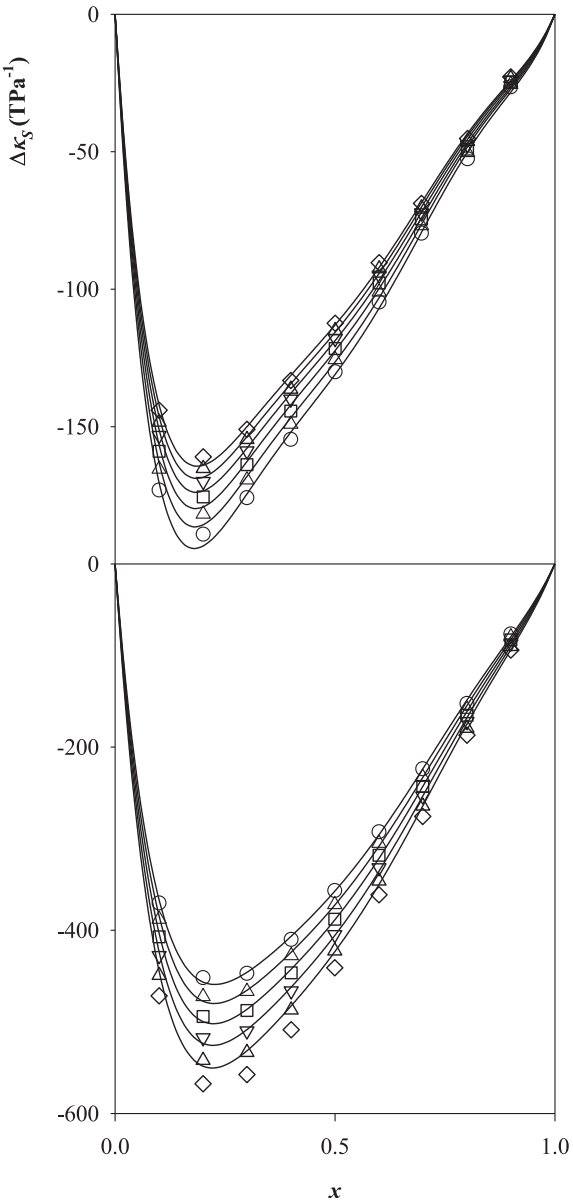


Fig. 7. Deviations in isentropic compressibility (Δk_S) of the binary mixture: (top) ChGly (1) + H_2O (2) and (bottom) ChGly (1) + CH_3OH (2) at: (○) 298.15 K, (Δ) 303.15 K, (□) 308.15 K, (▽) 313.15 K, (☆) 318.15 K and (◆) 323.15 K.

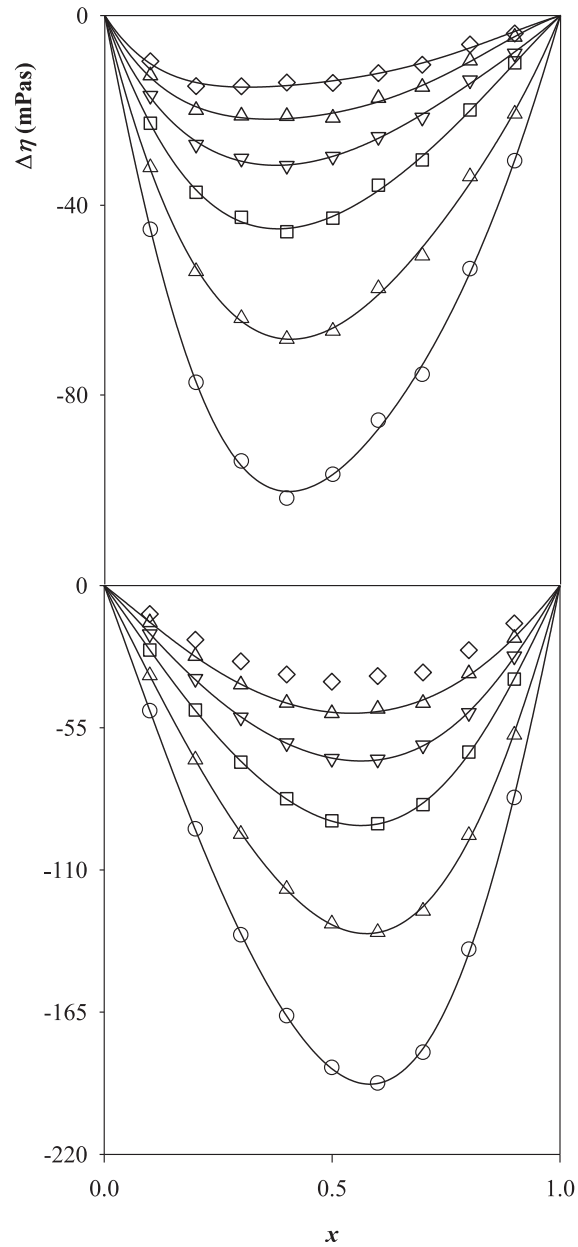


Fig. 8. Viscosity deviations ($\Delta\eta$) of the binary mixture: (top) ChGly (1) + H_2O (2) and (bottom) ChGly (1) + CH_3OH (2) at: (○) 298.15 K, (Δ) 303.15 K, (□) 308.15 K, (▽) 313.15 K, (☆) 318.15 K and (◆) 323.15 K.

using the following expression assuming the Lorentz-Lorenz approximation [30,31]:

$$\rho = \frac{\left(\frac{n_D^2-1}{n_D^2+2}\right)\cdot(x_1M_1+x_2M_2)}{\left(\frac{n_{D,1}^2-1}{n_{D,1}^2+2}\right)\cdot\frac{M_1}{\rho_1}+\left(\frac{n_{D,2}^2-1}{n_{D,2}^2+2}\right)\cdot\frac{M_2}{\rho_2}} \tag{14}$$

where ρ and n_D are the density and refractive index of the mixture, $n_{D,1}$ and $n_{D,2}$ are the refractive index of ChGly, water and methanol, ρ_1 and ρ_2 are the density of ChGly, water and methanol, and M_1 and M_2 are the molar mass of the pure components in the binary mixture.

The main advantage of this method is supported by the fact that the density of a mixture can be simply obtained from the density and refractive index of the pure components. Furthermore, the easiness to predict the densities, even in the absence of their surface tension data often required in Parachor models, stresses the viability of this approach. The appropriateness of the proposed equation to predict the density of the binary mixtures at the selected temperatures has been ascertained by calculating the root mean square deviation (Eq. (2)) which are listed in Table 5.

In parallel, a study of the reliability of several models (Riedel, Narsimham, Bradford-Thodos, Yen-Woods, Rackett, Spencer-Danner and Hankinson-Thomson (COSTALD)) was approached to predict the density of the ChGly based binary mixtures under study [7] in the selected temperature range and the deviations are shown in Table 5. Nevertheless, these models are based on critical properties, acentric factors and normal boiling temperatures that have been calculated for ChGly by the modified Lydersen-Joback-Reid method [32–34] and have been compiled in Table S5.

The appropriateness of the proposed equations to predict the density of the mixtures is corroborated by several papers [35–37] and their application are extensive in many research works. In this

Table 5
Standard deviations, σ to estimate the density of the binary mixtures at several temperatures.

Equations	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
ChGly (1) + H_2O (2)						
Lorentz-Lorenz approximation	0.0034	0.0026	0.0024	0.0027	0.0025	0.0023
Riedel	0.0468	0.0475	0.0483	0.0491	0.0499	0.0508
Yen-Woods	0.1099	0.1107	0.1116	0.1124	0.1134	0.1143
Narsimham	1.1275	1.1229	1.1182	1.1135	1.1087	1.1039
Bradford-Thodos	0.0963	0.0973	0.0983	0.0993	0.1004	0.1014
Rackett	0.0339	0.0340	0.0341	0.0344	0.0348	0.0354
Spencer-Danner	0.2154	0.2137	0.2119	0.2102	0.2084	0.2066
Hankinson-Thomson	0.2261	0.2223	0.2184	0.2146	0.2106	0.2067
ChGly (1) + CH_3OH 1 (2)						
Lorentz-Lorenz approximation	0.0017	0.0019	0.0013	0.0011	0.0011	0.0009
Riedel	0.0453	0.0460	0.0469	0.0478	0.0488	0.0498
Yen-Woods	0.1058	0.1067	0.1077	0.1087	0.1097	0.1108
Narsimham	0.2439	0.2419	0.2398	0.2377	0.2355	0.2333
Bradford-Thodos	0.0909	0.0920	0.0931	0.0942	0.0954	0.0967
Rackett	0.0419	0.0412	0.0406	0.0401	0.0396	0.0392
Spencer-Danner	0.2320	0.2296	0.2271	0.2246	0.2221	0.2196
Hankinson-Thomson	0.4348	0.4298	0.4247	0.4196	0.4144	0.4092

study, the most interesting equation able to estimate this physical property is the simplest (Eq. (14)) one, no matter the temperature of operation. On the other hand, among the equations affected by the mixing rules and critical properties, Racket and Riedel ones are the most adequate to characterize the density of the mixture at different temperatures for the binary mixtures involving water and methanol as solvents with ionic liquids.

4. Conclusions

The influence of temperature in the physical properties of the biocompatible ionic liquid (ChGly) has been addressed. Several decisive derived properties of this ionic liquid have been determined to increase the pure data bank of this novel compounds. A systematic study was carried out to determine the influence of polar solvents (water and methanol) on the physical properties of ChGly at several temperatures. From these experimental data (ρ, n_D, u, and η), their corresponding derived properties (V_m^E, Δn_D, $\Delta\kappa_S$, 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 the binary mixtures. In general, a contractive tendency for all the binary mixtures is detected, except for changes of refractive index on mixing. In this case, the packing effect in the binary systems containing ChGly and methanol at moderate temperatures is lowered, probably due to the molecular size.

Finally, a theoretical study of these magnitudes have been carried out. First of all, Redlich Kister equation has been proposed to properly correlate the abovementioned magnitudes. Lorentz-Lorenz approximation equation and Riedel, Narsimham, Bradford-Thodos, Yen-Woods, Rackett, Spencer-Danner and Hankinson-Thomson (COSTALD) models have been suggested to easily estimate the density of the binary mixtures at several temperatures. In this work, Lorentz-Lorenz approximation appears to be the most suitable predictive equation.

CRediT authorship contribution statement

María S. Álvarez: Conceptualization, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Nuria Mouronte:** . **María A. Longo:** Validation. **Francisco J. Deive:** Validation. **Ana Rodríguez:** Conceptualization, Formal analysis, Writing – original draft.

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.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2022.120022.

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