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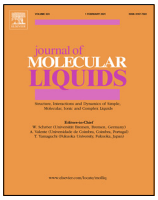

Physical properties of a new dipeptide ionic liquid in water and methanol at several temperatures: Correlation and prediction

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ABSTRACT

The physical properties of choline glycylglycinate (ChGlyGly) were experimentally determined at several temperatures. The empirical values of density, refractive index, speed of sound and dynamic viscosity for aqueous and methanolic mixtures of this ionic liquid were also ascertained at different temperatures. From these values, isentropic compressibility, molar volume, free volume, isobaric thermal expansivity and molar refraction have been calculated along with critical parameters (temperature, volume and pressure), acentric factor and boiling point. From a theoretical point of view, derived values of the neat ChGlyGly and the corresponding mixtures have been ascertained in the abovementioned temperature interval. Polynomial fittings turned to suitably describe the obtained data while Redlich-Kister has been used to fit to the derived magnitudes. To conclude, the density of the mixtures has been successfully predicted at several temperatures for the first time by means of different models.

1. Introduction

The search of new opportunities to use ionic liquids has motivated the scientific community to progress in the synthesis of new families of these solvents that can be labeled as “green”. This aspect can be tackled in the case of ionic liquids because they can be fine-tuned to create a plethora of combinations cation–anion to design the most convenient alternative [1]. This premise motivates the increase of research works where ammonium [2] and phosphonium [3] cations have been proposed to obtain more environmentally friendly ionic liquid families [4]. In this sense, the use of choline as cation has aroused a great interest to develop biocompatible compounds that could be employed in medicine [5], chemistry [6] or even as precursors of greener compounds like eutectic mixtures [7].

On the other hand, the use of amino acids as anions provides several interesting features such as their hydrogen bonding capacity and low viscosity that makes them unbeatable candidates to be paired with choline cation. Their potential was firstly investigated by Ohno and Fukumoto [8] and their competence as extractant agent in aqueous media was positively addressed. Other relevant features of these anions are their low-cost and commercial availability, which have increased their appeal as green and sustainable solvents [9]. In this case, these novel compounds are not available in the common commercial suppliers, so they have to be formulated at bench scale prior to achieve Ton scale. This handicap can be easily surpassed due to their simple preparation because the reaction is carried out by mixing choline hydroxide and the selected amino acid and vigorously stirred at mild conditions, obtaining water as product [10]. Thus, in this paper, ecotoxicological, biodegradability and bioeconomy issues, together with the requirement of more sustainable industrial processes were the pillars [11] over which a bet in choline amino acids has been performed.

For that matter, among the 20 kinds of natural amino acids mentioned by Ohno and Fukumoto previously, glycine is the preferred option due to its simplicity, economy and relevant role for human health. Thus, this aminoacid and the corresponding derivatives (dipeptides, polypeptides, proteins) may be considered as a new class of more biocompatible solvents with potential applications in biocatalysis. Therefore, the use of glycylglycinate as anion is presented as an alternative to achieve the abovementioned requirements [12]. Unfortunately, the structural data of this new ionic liquid are very scarce and the theoretical models are not able to predict the physicochemical values. In this scenario, thermodynamic properties have to be obtained for each new solvent through experimental characterization. So, ChGlyGly was characterized from 298.15 K to 343.15 K.

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In a second approach, we have focused on investigating ρ, n_D, u and η of this new ionic liquid: ChGlyGly (2-Hydroxyethyl, trimethylammonium glycylglycinate) mixed in aqueous and methanolic mixtures at temperatures comprised between 298.15 K and 323.15 K. These experimental data will help us to get further insights into the interactions, structural effects and future application at industrial scale, given the potential as a biocompatible solvent. Excess and derived properties (V^E, Δn_D, $\Delta\kappa_S$ and $\Delta\eta$) have been determined in the entire composition range and temperature. Redlich-Kister model was proposed to describe the derived data and these values were discussed in the light of the root mean square deviations.

The theoretical study of the measured experimental properties is a decisive approach in order to implement several predictive and correlative methods. The experimental data of the above physical properties are the basis for estimating several thermodynamic properties such as: molecular volume, V, molecular polarizability, $\alpha_{0,}$ isobaric thermal expansivity, α, molar refraction, R_m, free volume, f_m and critical parameters of ChGlyGly as a function of temperature.

Lastly, the density of the binary solutions (ChGlyGly with methanol/water) was estimated at several temperatures. In this case, different models have been satisfactorily used for prediction.

2. Experimental

2.1. Chemicals

ChGlyGly was prepared by the neutralization method in a previous paper of our group [13] and its structure is plotted in Fig. 1. The new ionic liquid was maintained under vacuum for 48 h at 313.15 K. Coulometric Karl-Fischer titration (Metrohm 899) was employed to ascertain the water content. Finally, the purity could be estimated to be more than 0.95 mass fraction. Milli Q quality water and methanol (Sigma-Aldrich, 0.99 mass fraction purity) were used to prepare the binary mixtures.

2.2. Apparatus and procedure

The binary samples used in the physicochemical characterization were prepared into stoppered bottles where known amounts of the pure components were added via syringe to the glass vials. The mass of the solvents was determined employing a Sartorius Cubis MSA balance (±10^{-5} g). The resulting combined expanded uncertainty of the experimental binary mixtures was ± 0.02 in mole fraction.

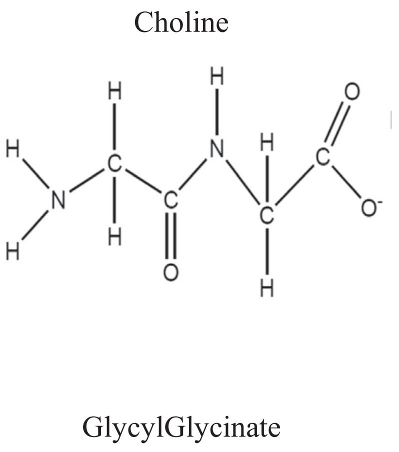

Fig. 1. Structure of ChGlyGly.

2.2.1. Experimental densities and speeds of sound determination

Anton Paar DSA-5000 M was chosen to experimentally determine the density and speed of sound of ChGlyGly and ChGlyGly + H_2O and ChGlyGly + CH_3OH in the selected temperature range. This device has been daily calibrated with ambient air and Millipore quality water for the sake of data reliability. The main advantage of this densimeter is the automatic viscosity correction of the experimental density and speed of sound values. This procedure gets the combined expanded uncertainties for density of $5\cdot10^{-4}$ g·cm^{-3} and speed of sound of 0.5 m·s^{-1}, with a level of confidence = 0.95 and k = 2.

2.2.2. Experimental refractive indices determination

Refractometer (ABBEMAT-W*R*) was selected to experimentally determine the refractive indices. The quality of the experimental data depends on a previous calibration with Millipore water and the resulting uncertainty was $4\cdot10^{-5}$.

2.2.3. Experimental dynamic viscosities determination

Viscometer (Anton Paar Lovis 2000 M) was utilized to determine the dynamic viscosities. In this research work, it was essential to use two capillaries: one of them with a diameter of 1.59 mm for the samples with dynamic viscosity values between 0.3 and 90 mPa·s and another one with a diameter of 2.5 mm for dynamic viscosity data ranging from 12 to 10000 mPa·s. A previous calibration step with standards N-50 and N-80 guarantees Uc(η) = 0.20 mPa·s for experimental dynamic viscosities lower than 1 mPa·s; Uc(η) = 0.60 mPa·s for dynamic viscosities ranging from 1 to 10 mPa·s and Uc(η) = 0.80 mPa·s for dynamic viscosities from 11 mPa·s to 50 mPa·s. These results were obtained with a level of confidence of 0.95 and k of 2 associated with measurement of dynamic viscosities. The experimental procedure was made at several temperatures and the precision in this data was 0.01 K.

3. Results and discussion

3.1. Determination of physical properties of ChGlyGly and correlation

The experimental values of ChGlyGly density (ρ) were carried out from 298.15 K to 343.15 K and they are summarized in Table S1. The linearity of density with temperature can be highlighted. This behaviour is in accordance with the previous experimental data collected in literature [14]. The influence of different amino acids as anion in the density is demonstrated. Thus, the values of ρ are different when only methyl groups are present (alanine), or when different functional groups such as ethyl alcohol (proline) or carbonyl joined to a pyrrolidine (serine) are included in the amino acid. These different sizes and structures favour the presence of polar domains, which is translated into uncomfortable arrangements of the network and higher density values. In this particular case, it is significant that the values of amino acid-based ionic liquids (ChGly) density are similar to those obtained when the cation is changed by C_2MIM [15,16]. However, in this work it is possible to corroborate the influence of the anion in the values of the density when the dipeptide GlyGly is used as anion. This new ionic liquid exhibits higher values of the above extensive property than those obtained for Gly. This behaviour is extensively reflected in the literature for ionic liquids when the anion is modified [17].

In Table S1 are listed for the first time the u of ChGlyGly from 298.15 K to 343.15 K. These data are scarce due to the novelty of the synthesized biocompatible ionic liquid so it is important to get more knowledge through properties like the isentropic compressibility. An analysis of the data indicates that this property is linearly decreased when the temperature is increased.

n_D of ChGlyGly from 298.15 K to 343.15 K are compiled in Table S1. These data suggest that this optical property follows a linear trend analogous to that described for density, since temperature increase is translated into a refractive index reduction. On the other hand, this optical property is not greatly affected by GlyGly dipeptide, diverging to the tendency recorded for density. Similar trends were concluded for imidazolium-based ionic liquids paired with glycinate anion [15].

In the context of a proper physicochemical characterization, η is one of the most crucial properties to get a further insight into the intermolecular interaction. This relevance has made us to assess how temperature affects viscosity. The analysis of the values indicates that the dynamic viscosity is reduced exponentially at higher temperatures. Thus, recent literature [14,18] reveals that the size of the amino acid and the intermolecular forces like van der Waals and/or hydrogen bonding are decisive factors to modify this transport property. The values of dynamic viscosity at 298.15 K follow this series: ChSer [14] > ChPro [14] > ChGlyGly (this work) > ChAla [14] > ChGly [14]. In this case, the influence of methyl, dipeptide, pyrrolidine or hydroxyethyl group in the anion is corroborated.

The experimental ρ, n_D and u values have been correlated with the following polynomial equation:

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

where Q corresponds to the above mentioned physical properties, m is the degree of the polynomial expression and A_i is the resulting fitting parameter. The derived values and the root mean deviations (RMD) are listed in Table 1. Eq (2) describes the deviation equation used in this work:

$$\mathrm{RMD} = \left(\sum_{i}^{\mathrm{N}} \left(p_{\mathrm{exp}} - p_{\mathrm{pred}}\right)^2 / \mathrm{N}\right)^{0.5} \tag{2}$$

p was considered as the experimental and theoretical values, while N was the number of data. In this particular case, the lowest σ values indicate that the proposed equation is appropriate to correlate the experimental data for ρ, n_D and u.

The experimental η values listed in Table S1 indicate that this transport property is a non-linear function of temperature and decreases exponentially with it. This behaviour could be reasonably described by the following equations.

Litovitz equation [19,20] was firstly used to fit the experimental data of ChGlyGly;

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

η_L and B_L are the correlation parameters, which are compiled in Table 2. The appropriateness of this two-parameter equation to correlate this property is corroborated by *RMD* values.

In the same line, other equations were proposed in order to investigate the relationship between the temperature and the dynamic viscosity [21–24]. The following expressions with three fitting coefficients have been used to correlate the dynamic viscosity data and temperature.

Table 1
Fitting parameters (A_i) and RMD values from Eq. (1).

Physical properties	A_0	A_1	RMD
$\rho/(\mathrm{g{\cdot}cm^{-3}})$	1.3826	−0.0006	0.0002
n_D	1.5831	−0.0002	0.0002
$u/(\mathrm{m{\cdot}s^{-1}})$	3064.2	−3.140	6.56

$$\eta = A_\eta exp\left(\frac{k_\eta}{T - T_{o\eta}}\right) \tag{4}$$

$$\eta = \eta_o exp\left[\left(\frac{A}{T}\right)^B\right] \tag{5}$$

$$\eta = \eta_0 exp\left[\left(\frac{A}{T}\right) exp\left(\frac{B}{T}\right)\right] \tag{6}$$

In this study, Vogel-Fulcher-Tammann (VFT) equation based on an Arrhenius-type law (Eq. (4)) was proposed and the adjustable parameters A_η, k_η and $T_{0\eta}$ were determined. An expression Eq (5) based on an atomic hopping approach was applied (Avramov-Milchev (AM). Finally, a physically realistic model (Eq (6)) derived from Gibbs-Adam and the constraint theories was addressed. This expression is similar to the empirical equation previously proposed by Waterton, lastly reformulated by Smedskjaer as MYEGA. In Table 2, the fitting parameters and the RMD data were collected. The analysis of the obtained results indicates that the dynamic viscosity of ChGlyGly is better described by non-Arrhenius type models, being AM and MYEGA equations the ones leading to the lowest deviations.

Recently, some authors have considered fluidity (η^{-1}) instead of viscosity due to the former is lower dependent of the temperature. This statement made us to bet in Eq (7) to analyze this effect.

$$(1/\eta)^{\varphi} = a + bT \tag{7}$$

a, b and ϕ are the fitting parameter. These values are listed in Table 2. In this context, the fitting parameters using ϕ = 0.3 were calculated. This value was recommended by Bourab and col. [21] when ionic liquids are used. The same parameters were calculated considering ϕ as a variable. The analysis of the RMD data unveils that similar values have been obtained.

3.2. Calculation of derived thermodynamic magnitudes of ChGlyGly

The derived magnitudes: isobaric thermal expansivity, α, and molar volume, V_m, were calculated using the previous density data. These theoretical values are the key proposed by the authors to clarify the thermodynamic behaviour of the new aminoacid-based ionic liquid that use a dipeptide as anion. These values were calculated as follows,

$$\alpha = \frac{-1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \tag{8}$$

$$V_m = \frac{M}{\rho} \tag{9}$$

M is the molar weight of ChGlyGly.

In Table 3 the isobaric thermal expansivity, α, and molar volume V_m, for each temperature are summarized. The isobaric thermal expansivity values constantly increase with temperature. In this case, the values obtained for ChGlyGly are in a similar order of magnitude than those obtained for other common ionic liquids families (e.g. imidazolium, pyridinium, phosphonium and cholinium), pairing amino acids as anions [15,18]. On the other hand, the molar volume, V_m, is greatly influenced by the temperature, although the scarcity of literature data hinders a proper analysis of the influence of the GlyGly anion in a cholinium-based ionic liquid. In reference [18], the V_m of choline cation and glycinate anion is 154.23 $\mathrm{cm^3{\cdot}mol^{-1}}$ at 298.15 K, resulting from summing both ions. In this case, the differences with the molar volume for ChGlyGly obtained in this work (195.3 $\mathrm{cm^3{\cdot}mol^{-1}}$ at 298.15 K) could be attributed to the presence of an extra glycine group.

Table 2
Fitting parameters and RMD values to fit dynamic viscosities of ChGlyGly at several temperatures.

Equation	Parameters					RMD
Litovitz	η_L = 0.2393 ((mPa·s)	B_L = 2.7·10^8 (K^3)				16.0
VFT			A_η = 0.0392 ((mPa·s)	k_η = 1353.5 (mPa·s·K)	$T_{0\eta}$ = 184.53 (K)	4.79
AM			η_0 = 1.6038 ((mPa·s)	A = 520.0 (K)	B = 3.783	3.68
MYEGA			η_0 = 0.3472 ((mPa·s)	A = 140.8 (K)	B = 653.3 (K)	3.78
$(1/\eta)^\phi$	a = -0.8502	b = 0.0031	ϕ = 0.28			0.002
$(1/\eta)^{0.3}$	a = -0.7362	b = 0.0027				0.003

Table 3
Derived thermodynamic magnitudes of ChGlyGly.

T/K	α·10^4/(K^{-1})	V_m/(cm^3·mol^{-1})	R_m/(cm^3·mol^{-1})	α_0/(Å^3)	f_m/(cm^3·mol^{-1})
298.15	4.83	195.3	45.13	23.04	137.2
303.15	4.85	195.8	45.15	23.07	137.6
308.15	4.86	196.3	45.16	23.08	138.1
313.15	4.87	196.8	45.17	23.09	138.5
318.15	4.88	197.3	45.19	23.10	139.0
323.15	4.89	197.7	45.20	23.11	139.5
328.15	4.91	198.2	45.22	23.11	139.9
333.15	4.92	198.7	45.23	23.12	140.4
338.15	4.93	199.2	45.24	23.13	140.8
343.15	4.94	199.7	45.25	23.14	141.3

The interaction among molecules such as ionic liquids could be elucidated bearing in mind the relationship between light and mass [25]. One of the most known approaches used to this end is the Lorentz-Lorenz expression that consider the refractive index and the electronic polarizability, α_0, resulting in the molar refraction R_m and free volume f_m:

$$R_m = \left[\frac{n_D^2 - 1}{n_D^2 + 2}\right]\left(\frac{M}{\rho}\right) = \frac{4\pi N_A}{3}\alpha_0 \tag{10}$$

$$f_m = V_m - R_m \tag{11}$$

The derived magnitudes R_m, α_0, and f_m were inferred from the experimental density and refractive index of ChGlyGly at several temperatures and are collected in Table 3. The derived magnitudes are slightly affected by the temperature in the selected range, which is agreement with previous results obtained for amino acid-based ionic liquids [15,18]. R_m and f_m data for ChGlyGly are lower than those obtained for phosphonium-based ionic liquids [18,25]. This fact could be associated with the formation of an extensive hydrogen bond network in ammonium-based ionic liquids. However, given that these equations consider a spherical geometry of the molecules and ionic liquids are not isotropic, more in depth studies including molecular simulation should be carried out to get a more realistic calculation.

Finally, the critical parameters of ChGlyGly have been determined due to their relevance when designing and simulating biotechnological and chemical plants. The main drawback associated to the experimental determination of these values is to use high temperatures. To solve this problem, a modified Lydersen-Joback-Reid method [26–29] was selected to estimate values of critical properties, the acentric factor (w) and normal boiling temperature (T_b) for ChGlyGly. This method is advantageous as it just requires the knowledge of the structure of the molecule and the molecular mass. The estimation of critical properties, acentric factor and normal boiling temperature can be easily inferred from through the corresponding equations included in the paper by Valderrama and Robles [29], considering the individual contributions of each group to critical temperature, critical pressure, critical volume and normal boiling temperature. The values of the obtained derived magnitudes are shown in Table S2. However, although it is expected that the ionic liquid is degraded at values lower than those included in this table, future thermogravimetric and differential scanning calorimetry analysis are required to confirm this hypothesis.

3.3. Physical properties of ChGlyGly + methanol and ChGlyGly + water

The experimental data (ρ, n_D, u and η) of the methanolic and aqueous mixtures of ChGlyGly have been determined for the first time and the influence of water and methanol when they are mixed with ChClyGly has been analyzed. These data are compiled in Tables S3 and S4 and they are also plotted in Figs. 2 to 5.

In Fig. 2, the experimental ρ of the binary mixture of ChGlyGly with water/methanol is plotted vs the temperature. An analysis of these data indicate that this property increases with the mole fraction. However, when the temperature is greater these data are lower no matter the polar solvent. If the presence of solvent is discussed, it is necessary to assess that water prompts the interplays

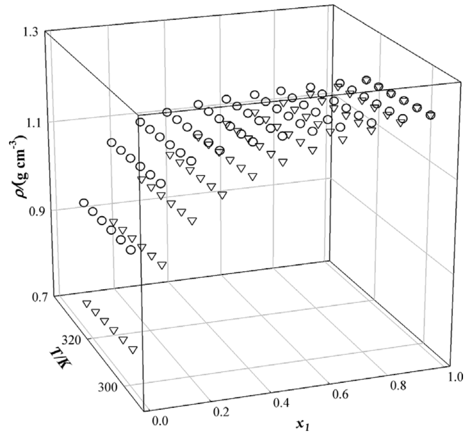

Fig. 2. Densities of the mixture: (○) ChGlyGly (1) + H_2O (2) and (▽) ChGlyGly (1) + CH_3OH (2).

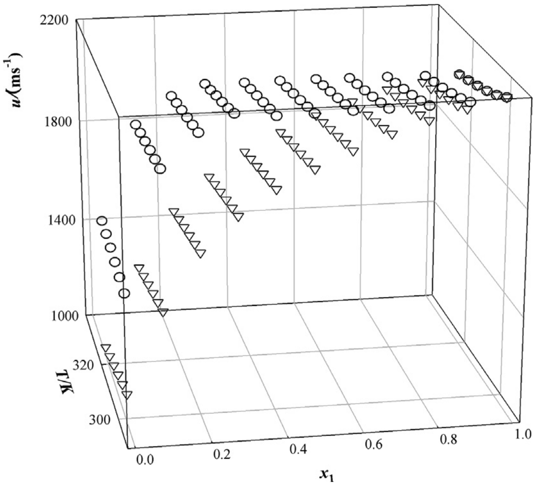

Fig. 3. Speeds of sound of the mixture: (○) ChGlyGly (1) + H_2O (2) and (▽) ChGlyGly (1) + CH_3OH (2).

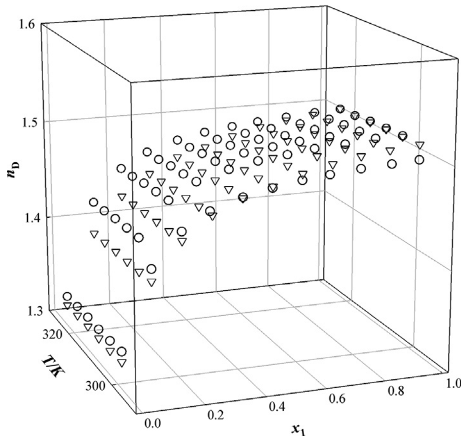

Fig. 4. Refractive indices of the mixture: (○) ChGlyGly (1) + H_2O (2) and (▽) ChGlyGly (1) + CH_3OH (2).

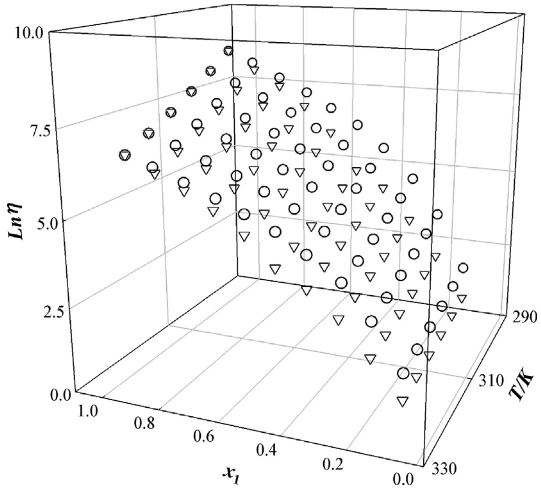

Fig. 5. Ln η of the mixture: (○) ChGlyGly (1) + H_2O (2) and (▽) ChGlyGly (1) + CH_3OH (2).

with the polar domain of ChGlyGly causing a higher packing of the molecules, and a subsequent increase of density values. A plausible explanation to this fact could be sustained in the divergences regarding intermolecular forces (hydrogen bonds) between water or methanol and ChGlyGly. A past research work of the group [16] involving ChGly indicates that aqueous solutions of this ionic liquid favour aggregates formation. Then, the volumetric properties will be greatly affected by these interactions. However, this effect diminishes at mole fraction greater than 0.8 for ChGlyGly due to the fact that the presence of the ionic liquid controls the interactions. Additionally, the fact that methanol bears much lower density than water involves a general decrease in densities values of methanolic mixtures, so both intermolecular forces and molecule packing have to be considered to explain the observed trend in density data.

This pattern is observed in the case of the u of ChGlyGly + water and ChGlyGly + methanol at several temperatures (Fig. 3). In this case, the compression and decompression effects are able to regulate the degree of packing of the molecules.

The optical effect in a media is quantified by the n_D values. These experimental binary data of ChGlyGly with water/methanol are plotted in Fig. 4 at several temperatures. In this case, the light propagation is not affected by the interactions between the solvents and ChGlyGly, which means that the obtained values are independent no matter the polar solvent selected. The analysis of literature [30] allows checking that the study of several ionic liquids with the same solvent (water) involve refractive index variations in a similar way.

Finally, Ln η data are plotted as a function of the mole fraction and temperature in Fig. 5 instead of the viscosity for the sake of the clarity of the visualization. The analysis of these data indicates that dispersive forces, hydrogen bonding, and columbic interactions are decisive in this transport property [25]. Thus, the polar interactions between the solvent (water or methanol) and ionic liquid are behind the flow resistance and then the experimental η values of the aqueous and methanolic mixtures are higher at higher ionic liquid concentrations. This effect is reduced at elevated temperatures and the experimental η values of the binary mixtures are lower.

3.4. Derived properties and correlation of ChGlyGly + methanol and ChGlyGly + water.

V^E, excess molar volumes, Δn_D, changes of refractive index on mixing, $\Delta\kappa_S$, deviations in isentropic compressibility and $\Delta\eta$, viscosity deviations at several temperatures were inferred from the previously obtained physical properties, as follows:

$$V^E = \sum_{i=1}^{N} x_i M_i \left(\rho^{-1} - \rho_i^{\circ\,-1}\right) \tag{12}$$

$$\Delta n_D = n_D - \sum_{i=1}^{N} x_i n_{Di}^{\circ} \tag{13}$$

$$\Delta\kappa_S = \kappa_S - \sum_{i=1}^{N} x_i \kappa_{S,i} \tag{14}$$

$$\Delta\eta = \eta - \sum_{i\,=\,1}^{N} \left(\eta_i^o \cdot x_i\right) \tag{15}$$

ρ, n_D, ρ_i° and n_{Di}° are the physical properties, κ_S and $\kappa_{S,i}$ (calculated through Laplace equation: $\kappa_S = \rho^{-1} \cdot u^{-2}$) are the isentropic compressibility and η and η_i^o are the dynamic viscosity (both for individual components and mixtures). The subscript i defines the pure component (ChGlyGly, methanol or water) in the binary mixture.

Redlich-Kister expression was proposed to correlate the excess and derived magnitudes of the binary mixtures [31]:

$$\Delta Q = x_1 \cdot (1 - x_1) \sum_{i=0}^{m} A_i \cdot (2x_1 - 1)^i \tag{16}$$

ΔQ corresponds with V^E, Δn_D, $\Delta\kappa_S$ and $\Delta\eta$, and A_i is the fitting parameter. These values are listed in Tables S5 and S6, where the RMD values are also included. The derived and correlated data of ChGlyGly with water/methanol are plotted in Figs. 6 to 9.

Fig. 6 depicts the V^E values for the binary mixtures for different mole fractions and temperatures. The values of the excess magnitudes are very small, which involves a low deviation from the ideality (lower than 2 % of the total molar volume for all the mixtures). The negative data are recorded for all concentrations and temperatures, with the minimum about -0.7 (mol•cm^{-3}) for ChGlyGly + H_2O and -2.1 (mol•cm^{-3}) for ChGlyGly + CH_3OH. The interactions between ionic liquid and water or/methanol are complex and involve many possibilities including cation–anion interplays with solvents, H-bonding and packing effects, being the interaction between ChGlyGly and hydrogen from water or methanol the one explaining the observed negative values. Thus, the hydrogen bonding network established between the solvent (methanol or water) and the polar block of ChGlyGly leads to an easier inclusion of the small water or methanol molecules in the interstitial spots of the ionic liquid. In the case of temperature, higher values favor the breaking of the intermolecular bonds due to the greater molecules speed, causing an excess property reduction [32,33]. This effect is more evident in the case of methanol acting as solvent, a behavior coincident with what has been previously reported for other mixtures containing ammonium-based ionic liquids and water/ethanol [34].

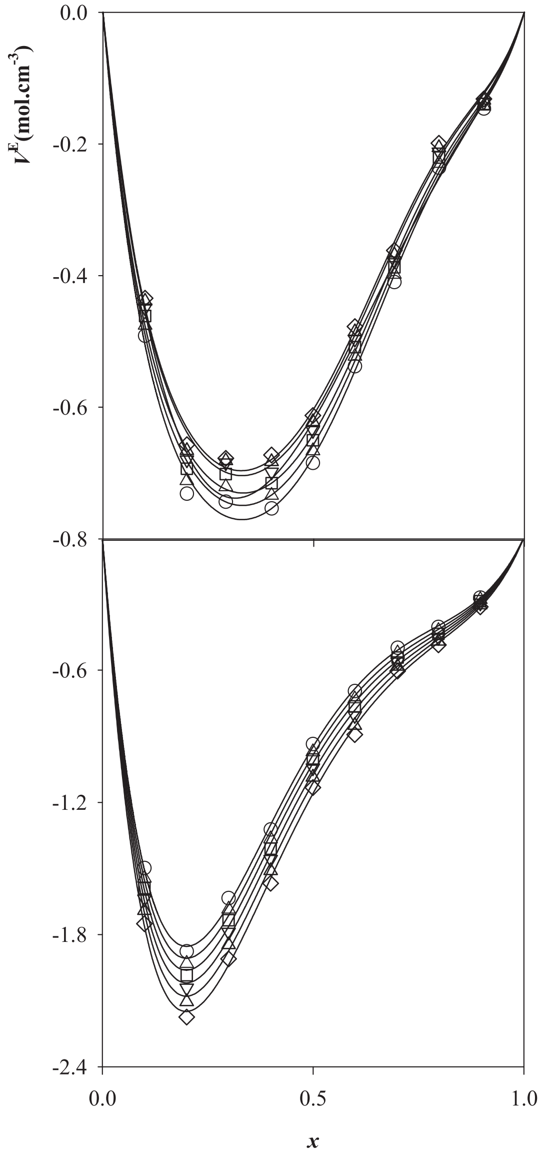

Fig. 6. V^E of the mixture: (top) ChGlyGly (1) + H_2O (2) and (bottom) ChGlyGly (1) + CH_3OH (2) at: (○) 298.15 K, (△) 303.15 K, (□) 308.15 K, (▽) 313.15 K, (*) 318.15 K and (◇) 323.15 K.

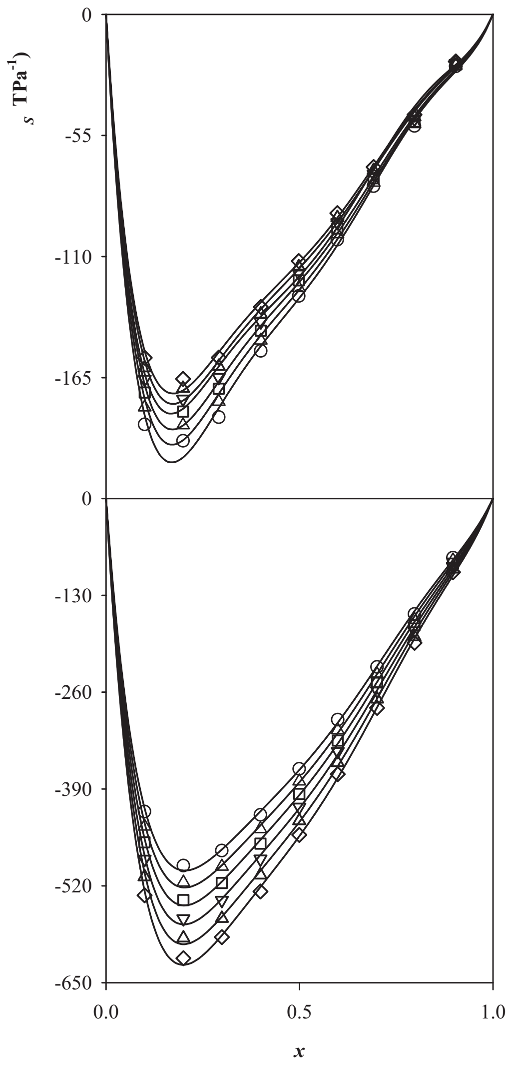

Fig. 7. $\Delta\kappa_S$ of the mixture: (top) ChGlyGly (1) + H_2O (2) and (bottom) ChGlyGly (1) + CH_3OH (2) at: (○) 298.15 K, (△) 303.15 K, (□) 308.15 K, (▽) 313.15 K, (*) 318.15 K and (◇)323.15 K.

$\Delta\kappa_S$ data are negative across the composition range no matter the temperature. This trend is plotted in Fig. 7 and allows to conclude a lower compressible character of the mixture regarding the ideal one. This behavior is more evident in the presence of methanol, where the greater interaction forces between the alcohol and ChGlyGly leads to lower values. In the same line, a divergent behaviour is recorded for temperature: i) the stronger interplays between ChGlyGly and methanol take place at 323.15 K and ii) the greater $\Delta\kappa_S$ values for ChGlyGly and water are recorded at lower temperature (298.15 K).

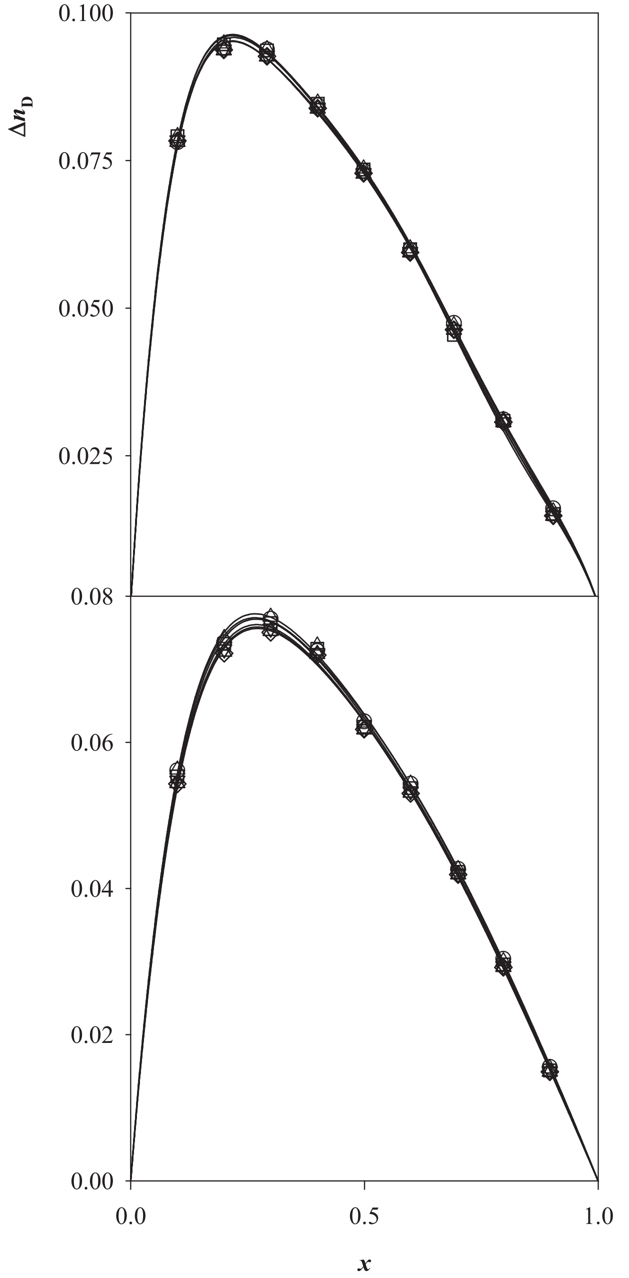

Fig. 8. Δn_D of the mixture: (top) ChGlyGly (1) + H_2O (2) and (bottom) ChGlyGly (1) + CH_3OH (2) at: (○) 298.15 K, (Δ) 303.15 K, (□) 308.15 K, (∇) 313.15 K, (*) 318.15 K and (◇)323.15 K.

A possible explanation at this inversion could lie in the fact that a more compact structure composed by water and ChGlyCly could be formed at room temperatures, which would explain the minimum values. Nonetheless, when the temperature increases, the interactive forces are weaker, which is reflected in higher $\Delta\kappa_S$ values [35].

Δn_D values are positive no matter the composition over the selected temperatures for the proposed binary mixtures. These derived data are plotted in Fig. 8. These differences in the Δn_D are related to the reduction of the intermolecular forces and could be explained by: i) higher refraction values and ii) lower steric volumes [36].

$\Delta\eta$ values are plotted in Fig. 9 and are negative at all compositions in the selected temperatures. In general, these derived magnitudes are higher at greater temperatures. Nonetheless, the polarity of the solvent plays a relevant role as it can be seen in the figure, where the lowest values are recorded for methanolic solutions. The maximum interaction forces and the dense structure derived from the alcohol accommodation into the interstitial sites of dipeptide-based ionic liquid could be hypothesized to explain the ideality deviations [37].

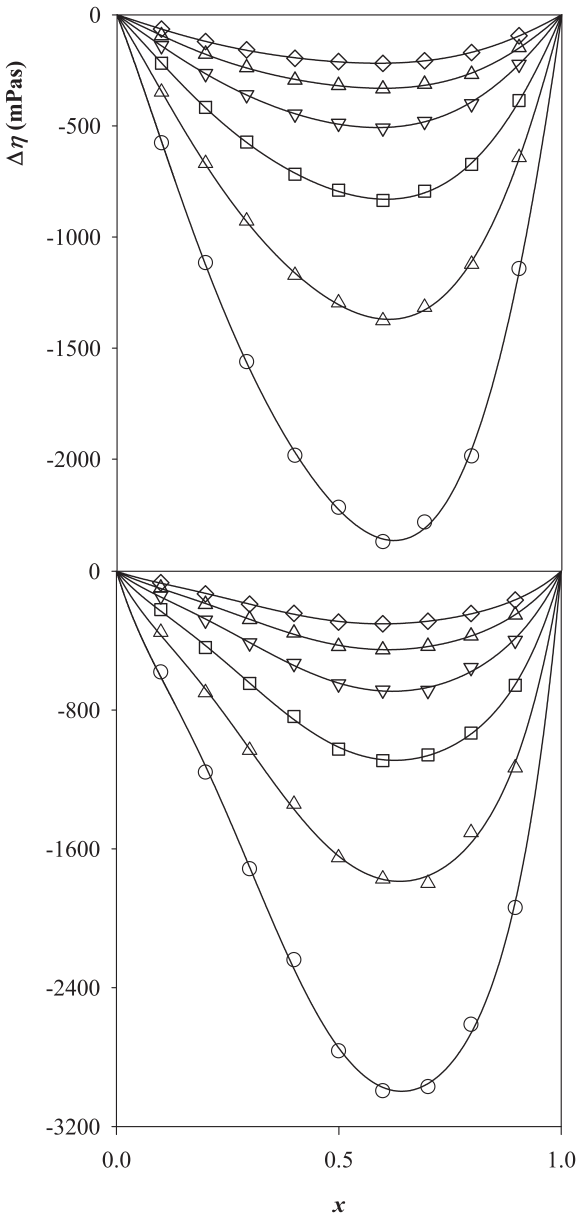

Fig. 9. $\Delta\eta$ of the mixture: (top) ChGlyGly (1) + H_2O (2) and (bottom) ChGlyGly (1) + CH_3OH (2) at: (○) 298.15 K, (Δ) 303.15 K, (□) 308.15 K, (∇) 313.15 K, (*) 318.15 K and (◇)323.15 K.

3.5. Density estimation of ChGlyGly + water and ChGlyGly + methanol

Lorentz-Lorenz approximation (LLA) has been chosen to predict the density of ChGlyGly + water and ChGlyGly + methanol at several temperatures [38]:

$$\rho = \frac{\left(\frac{n_D^2-1}{n_D^2+2}\right)\cdot(x_1M_1+x_2M_2)}{\left(\frac{n_{D1}^2-1}{n_{D1}^2+2}\right)\cdot\frac{M_1}{\rho_1}+\left(\frac{n_{D2}^2-1}{n_{D2}^2+2}\right)\cdot\frac{M_2}{\rho_2}} \quad (17)$$

Table 4
RMD values for density estimation at several temperatures.

	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
ChGlyGly (1) + H_2O (2)						
LLA	0.002	0.001	0.002	0.002	0.002	0.001
Riedel	0.079	0.080	0.081	0.081	0.082	0.083
Yen-Woods	0.171	0.171	0.171	0.171	0.171	0.171
Rackett	0.087	0.084	0.084	0.084	0.084	0.085
MH	0.145	0.143	0.141	0.138	0.136	0.134
VSD	0.217	0.216	0.215	0.215	0.214	0.213
VSY	0.159	0.160	0.161	0.161	0.162	0.162
LGM	0.103	0.102	0.101	0.100	0.099	0.098
ChGlyGly (1) + CH_3OH (2)						
LLA	0.003	0.003	0.002	0.002	0.002	0.002
Riedel	0.062	0.063	0.063	0.064	0.065	0.066
Yen-Woods	0.151	0.151	0.151	0.152	0.152	0.152
Rackett	0.076	0.068	0.068	0.068	0.068	0.068
MH	0.188	0.187	0.186	0.185	0.184	0.183
VSD	0.114	0.114	0.114	0.115	0.115	0.115
VSY	0.100	0.100	0.101	0.102	0.103	0.104
LGM	0.109	0.110	0.111	0.112	0.113	0.114

where ρ, ρ_1 and ρ_2 are the density of the mixture and the pure components. n_D, n_{D1}, and n_{D2} are the refractive index of the mixture and ChGlyGly, water, and methanol. M_1 and M_2 are the mass molar of the pure components. The selection of this expression to estimate the physical property is basically founded on its simplicity, because only the density and refractive index of the pure components and the mixture is required. The appropriateness of this expression for density prediction of the binary mixtures has been discussed in the light of the RMD calculated in accordance with Eq. (2) and the values are compiled in Table 4.

Considering the suitable results, the different models of Riedel, Yen-Woods, Racket and MH (Mchaweh et al Model) were applied to in this study, using the mixing rules proposed by well-known authors [39–43]. Likewise, the VSD (Valderrama and Abu-Sharkh SD Model), VSY (Valderrama and Abu-Sharkh SY Model) and LGM (Linear Generalized Model) equations [44,45] were used taking into account the mixing rules proposed by Poling and Prausnitz [43], which allow expressing the parameters of said equations from the individual contributions of the different components that include these mixtures. In these expressions, several critical properties (V_c, T_c, P_c), acentric factors (w), and normal boiling temperatures (T_b), that have previously been determined for the ChGlyGly and that are shown in Table S2, are required. Despite the possible limitations of the critical parameters calculation that demand a future in depth characterization including thermogravimetric studies, this information is useful to elucidate the viability of different prediction methods for avoiding time consuming laboratory determination of physical properties.

The differences obtained for density prediction of aqueous and methanolic mixtures of ChGlyGly at the studied temperatures are shown in Table 4 in terms of RMS values. The most outstanding benefit of these models lies in the fact that these expressions can be extended from pure components to mixtures by using different mixing rules. Although the comparison of the results suggests the pertinence of the simplest equation (Eq. (17)) to estimate this physical property for the all the temperatures, it should be noted that this equation demands the experimental determination of refractive indices, so the usefulness of generalised models affected by the critical parameters and mixing rules is out of doubt. Among these equations, Riedel one is the most appropriate one to describe the density of the aqueous and alcoholic mixtures.

4. Conclusions

The effect of temperature (298.15 to 343.15) K in the ρ, n_D, u and η of an amino acid-based ionic liquid (ChGlyGly) were discussed and their derived properties have been determined. After this, the physical properties of ChGlyGly at several temperatures in the presence of polar solvents (methanol/water) were carried out and the derived properties (V^E, Δn_D, $\Delta\kappa_S$, and $\Delta\eta$) were calculated from (298.15 to 323.15) K. These theoretical values are valuable tools to give hints on the molecular interactions between solute and solvent. In general terms, negative values of the derived properties of ChGlyGly + water and ChGlyGly + methanol were detected, except for Δn_D. This fact could be attributed to the strong interactions of ChGlyGly and methanol at moderate temperatures.

In parallel, the abovementioned magnitudes were properly correlated by Redlich-Kister equation. LLA equation and Riedel, Yen-Woods, Rackett, VSD, VSY, MH and LGM generalised models were used for density prediction of ChGlyGly + water and ChGlyGly + methanol in the selected temperature interval. Finally, although LLA turned out to be the most suitable predictive equation, the interest of Riedel model was concluded to predict density from critical parameters.

CRediT authorship contribution statement

María S. Álvarez: Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Miguel Rivas:** Software, Formal analysis, Validation, Writing – review & editing. **Francisco J. Deive:** Conceptualization, Validation, Writing – review & editing, Funding acquisition. **Ana Rodríguez:** Conceptualization, Supervision, Formal analysis, Writing – original draft, Writing – review & editing.

Data availability

No data was used for the research described in the article.

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.2023.121435.

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