Influence of temperature on thermodynamics for binary mixtures of short aliphatic protic ionic liquids

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Abstract: Two binary mixtures of protic ionic liquids comprising formate, acetate and propionate anions and 2-hydroxyethyl ammonium, bis(2-hydroxyethyl) ammonium and tris(2-hydroxyethyl) ammonium cations have been studied in terms of volumetric and acoustic properties as a function of temperature. The corresponding derived properties have been computed from the experimental data and fitted to temperature dependent Redlich–Kister and Redlich––Mayer equations; accurate results being obtained. Other properties such as intermolecular free length, acoustic impedance, geometrical volume, collision factor and isothermal coefficient of pressure excess molar enthalpy were computed due to their importance in the study of specific molecular interactions. The new experimental data were used to test the prediction capability of different models for density (Mchaweh–Nasrifar–Moshfeghian (MNM) model and the modified Heller temperature dependent equation (MHE)) and ultrasonic velocity (different empirical equations, collision factor theory (CFT) and free length theory (FLT)). The high non-ideality of these mixtures points to strong contractive behaviour at any temperature and composition. The obtained results indicate that ionic liquid interactions into mixture are stronger than in the ionic pure components for both mixtures at any studied condition. Despite the strong ion interaction, the tested models showed, at least, the qualitative prediction capability.

Keywords: derived properties; binary mixtures; theoretical models.

INTRODUCTION

In recent years, significant progress has been made in the study and application of room temperature ionic liquids.[1] These substances have received wide attention as environmentally-benign alternatives to the huge conventional organic solvents.[2,3] Despite their ionic nature, ionic liquids are "organic solvents" too and

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they exhibit a variety of amazing physicochemical properties which have not been achieved in conventional organic liquids, really useful for a wide range of industrial applications.[4–18] In general, ionic liquids are typically consisted of a collection of small inorganic anions and different derivations of a reduced group of bulky cations as imidazolium, pyridinium, quaternary ammonium, and phosphonium structures (so-called as aprotic ionic liquids). Against the strong electrostatic interaction among the different ions in liquid phase bulk environment, the steric hindrance effect of the large size of cations prevents ionic liquids from getting solidified at room temperature, as occurs in common inorganic salts. The coulombic interaction among ions is so strong, compared to intermolecular interaction between normal covalent molecules, that microscopic behaviour of ionic liquids is different from that of conventional liquids. Strong aggregates and chlatrate behaviour has been observed in this kind of compounds. The same behaviour has been observed for those ionic liquids so-called Brönsted-acidic ionic liquids (or protic ionic liquids) where steric hindrance potential has been distributed among anions and cations.[19–21] Of course, this kind of ionic compounds has also aroused the academic and industrial interest[22,23] due to the fact that they offer the same potential capabilities as those of aprotic nature and a collection of additional advantages, such as low cost of production, simple chemical synthesis and rapid biodegradability into natural environment.[24–31] According to the scarce experimental works related to ionic liquid yet, more research is necessary to understand the ionic internal organization and develop models for prediction and new processes simulation involving mixtures of ionic liquids.
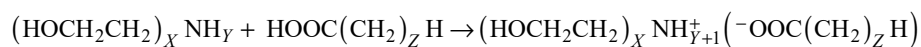
The present investigation deals with this topic, studying and analyzing the thermodynamic mixing trend of binary mixtures of three protic ionic liquids recently developed[32,33] (2-hydroxyethyl ammonium formate (2-HEAF), bis(2-hydroxyethyl) ammonium acetate (2-HDEAA) and tris(2-hydroxyethyl) ammonium propionate (2-HTEAPr)). The new experimental data (density and ultrasonic velocity) were used to compute the derived magnitudes (excess molar volumes and changes of isentropic compressibilities) and apparent molar values (apparent molar volumes and isentropic apparent molar compressibilities) which were correlated in terms of temperature dependent Redlich–Kister and RedlichMayer equations. Other derived properties such as intermolecular free length, acoustic impedance, geometrical volume, collision factor and isothermal coefficient of pressure excess molar enthalpy were computed due to their importance in the study of specific molecular interactions. The experimental volumetric and acoustic data were used to test the prediction capability of different models for density (Mchaweh–NasrifarMoshfeghian (MNM) model and the modified Heller temperature dependent equation (MHE)) and ultrasonic velocity (different empirical equations, free length theory (FLT) and collision factor theory (CFT)). The obtained results indicate that ionic liquid interactions in mixtures are stronger

than in each pure ionic component for both mixtures. This trend is reinforced by rising temperatures due to kinetic effects and a better accommodation of the aliphatic residues. The high non-ideality of these mixtures point to a stronger contractive behaviour with minima at equimolar compositions of each protic ionic liquid mixtures. As observed, despite the high non-ideality of these mixtures, the tested models got, at least, qualitative good results.

EXPERIMENTAL

Preparation of the protic ionic liquids

The amine compounds (monoethanolamine, diethanolamine or triethanolamine, Merck Synthesis, purity min. 99 %) were placed in a threenecked flask all-made-in-glass equipped with a reflux condenser, a PT-100 temperature sensor for controlling temperature and a dropping funnel. The flask was mounted in a thermal bath. A slight heating and strong agitation were necessary to increase miscibility between reactants and then, allow titration processes. The organic acid (formic, acetic or propionic acids, Merck Synthesis, purity min. 99 %) was added dropwise to the flask under stirring with a magnetic bar. Stirring was continued for 24 h at laboratory temperature to obtain a final viscous liquid. Lower viscosity was observed in the final product by decreasing molar mass of reactants. No solid crystals were observed when the liquid sample was stored after purification at freeze temperature for a few months. The reaction is an acid–base neutralization creating a formate, acetate or propionate salt of mono, di- or tri-ethanolamine, that in a general form should be expressed as follows:

$$\left(\mathrm{HOCH_2CH_2}\right)_X \mathrm{NH}_Y + \mathrm{HOOC}\left(\mathrm{CH_2}\right)_Z \mathrm{H} \rightarrow \left(\mathrm{HOCH_2CH_2}\right)_X \mathrm{NH}_{Y+1}^{+}\left(^{-}\mathrm{OOC}\left(\mathrm{CH_2}\right)_Z \mathrm{H}\right)$$

where X is the number of ethanol substitutions into the amine compound, Y the protons ($X + Y = 3$) and Z the length of acid chain. For example, when $X = 1$, $Y = 2$ and $Z = 0$ this equation shows the chemical reaction for the reactants monoethanolamine + formic acid, and 2-hydroxyethyl ammonium formate (2-HEAF) as neutralization product.

Spectroscopy test

^{1}H-NMR and FT-IR spectra were performed in order to characterize the synthesis products and to confirm their structure. The ^{1}H-NMR spectra were measured on a Bruker Ascend Ultrashield[TM] Plus-EDS 600 MHz spectrometer, using DMSO-d_6 as solvent with TMS as internal standard. The expected signals of these ionic compounds were identified attending to the characteristic molecular groups ($\mathrm{CH_3}$–$\mathrm{COO^-}$, $\mathrm{CH_2}$–N and –O–$\mathrm{CH_2}$).

FT-IR spectra were taken by a Jasco FT/IR 680 plus model IR spectrometer, using a NaCl disk. The broad band in the 3500–2400 cm^{-1} range exhibits typical ammonium structure for all the neutralization products. The OH stretching vibration is embedded in this band. The broad band centered at 1600 cm^{-1} is a combined band of the carbonyl stretching and N–H plane bending vibrations, as well as two characteristic band are showed 3500–2400 cm^{-1} for $\mathrm{NH_3^+}$ + $\mathrm{OH^-}$ and other wide band at 1600 cm^{-1} for $\mathrm{COO^-}$ + N–H plane bend 2-HDEAA.

For example, Figs. 1 and 2 gather the corresponding spectra for the protic ionic liquid 2-HDEAA.

Physical properties of the device

During the course of the experiments, the purity of the protic ionic liquids was monitored by different physical properties measurements after reaction and as a function of time. The protic ionic liquids (2-hydroxyethyl ammonium formate (2-HEAF), bis(2-hydroxy) ethylam-

monium acetate (2-HDEAA) and Tris(2-hydroxyethyl) ammonium propionate (2-HTEAPr)) were stored in sun light protected form, constant humidity, nitrogen atmosphere and ambient temperature. Usual manipulation and purification in our experimental procedure was applied.[21] The molecular mass (MM), experimental and open literature physichochemical data at standard condition for the studied protic ionic liquids (PIL) are shown in Table I.
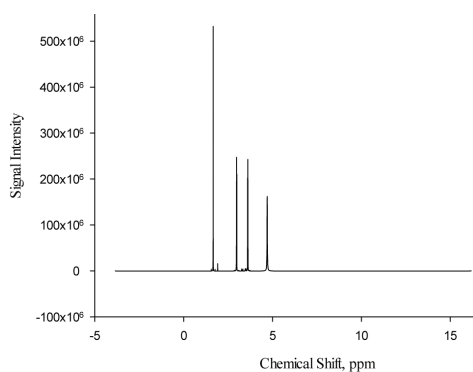

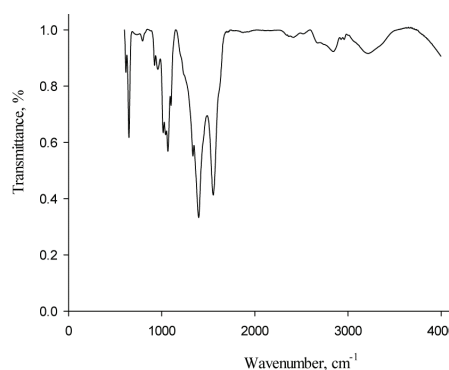Fig. 1. NMR spectra for bis(2-hydroxyethyl) ammonium acetate (2-HDEAA).

Fig. 2. FT-IR spectra for bis(2-hydroxyethyl) ammonium acetate (2-HDEAA).

The deviations of experimental from literature data are lower than 1.4 and 4.2 % for density and ultrasonic velocity, respectively.

TABLE I. Comparison of experimental with literature data for pure compounds at 298.15 K and other relevant informations. Standard uncertainties, u, are $u(\rho) = 0.005$ % and $u(u) =$ $= 0.05\%$ (level of confidence = 95 %)

PIL	MM / g mol^{-1}	ρ / g cm^{-3} (exp.)	ρ / g cm^{-3} (lit.)	u / m s^{-1} (exp.)	u / m s^{-1} (lit.)
2-HEAF	107.110	1.1929	1.204[35] 1.176489[32]	1782.87	1709.00[32]
2-HDEAA	165.190	1.1675	1.167483[33] 1.170200[36]	1863.35	1863.35[33]
2-HTEAPr	223.269	1.1420	Na	1663.73	Na

The densities and ultrasonic velocities of pure ionic components were measured with an Anton Paar DSA-5000 vibrational tube densimeter and sound analyzer. The uncertainties (combined expanded uncertainty at the 95 % confidence level with a coverage factor of $k = 2$) of the density and ultrasonic velocities measurements are 0.01 and 0.10 %, with repeatabilities of 0.001 g·cm^{-3} and 0.10 m·s^{-1}, respectively. Apparatus calibration was performed periodically in accordance with vendor instructions using a double reference using Millipore quality water and ambient air at each temperature. Accuracy in the temperature of measurement was better than $\pm 10^{-2}$ K by means of a temperature control device that apply the Peltier principle to maintain isothermal conditions during the measurements into the density and ultrasonic velocity cells.

Stability at room temperature

For any of these short aliphatic protic ionic liquid the potential exists to undergo a condensation reaction to form an amide compound. Therefore, an adequate control of temperature

is essential throughout the chemical reaction of salt formation, as well as, their storage under stable conditions, otherwise heat rise may produce the dehydration of the protic ionic liquid to give the corresponding amide as in the case for nylon salts (salts of diamines with dicarboxy acids). As observed in our laboratory during ionic liquid synthesis, dehydration begins around 423 K, for those lightest ionic liquids of this family (short chain anion as 2-HEAF).

There was no detectable decomposition when these ionic liquids are left for over 12 months at laboratory temperature, sun protect condition and inert atmosphere. Less than 1 % amide was detected after this range of time. It appears evident that the probability of amide formation is low for this kind of structures, if synthesis reaction, purification process and storage was carried out as recommended. The water content in the studied protic ionic liquids was not measured because the room humidity was not completely controlled during experimental work. In addition, the comparisons with standard samples of the different protic ionic liquids recently dried and other ones exposed during 24 h at ambient humidity, showed almost null differences on the density or ultrasonic velocity.

RESULTS AND DISCUSSION

Physical properties correlation

For compact and smooth representation, the density and ultrasonic velocity of the ionic mixtures were correlated as a function of composition in accordance to the Eq. (1):

$$P = \sum_{i=0}^{N} A_i x^i \tag{1}$$

where A_i is a polynomial temperature dependence function as follows:

$$A_i = \sum_{j=0}^{M} B_{ij} T^j \tag{2}$$

and where P is density (g cm^{-3}) or ultrasonic velocity (m s^{-1}), x is the mole fraction of the solvent (2-HDEAA or 2-HTEAPr) and B_{ij} final fitting parameters. N and M stand for the extension of the mathematical series which were optimized by means of the Bevington test. Densities and ultrasonic velocity are given in the Supplementary Material to this paper (Table S-I) for the two studied mixtures. The fitting parameters were obtained by the unweighted least squared method applying a fitting Marquardt algorithm. The root mean square deviations were computed using Eq. (3), where z is the value of the property, and n_{DAT} is the number of experimental data:

$$\sigma = \left[\frac{\displaystyle\sum_{i=1}^{n_{DAT}} \left(z_{exp} - z_{pred} \right)^2}{n_{DAT}} \right]^{1/2} \tag{3}$$

The fitting parameters and the corresponding deviations are gathered in Table S-II of the Supplementary material.

In Figs. 3 and 4, the temperature trend of density, ultrasonic velocity and isentropic compressibility (computed by the Newton-Laplace equation) are gathered. These figures show the high increment of density as a function of
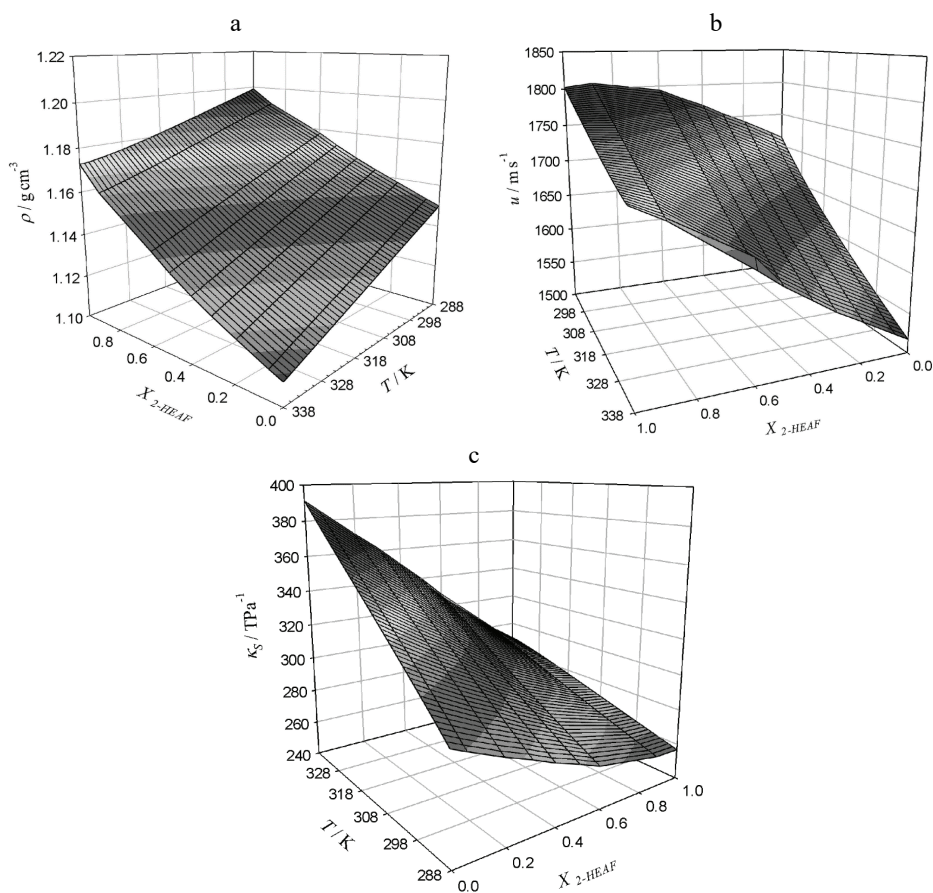

Fig. 3. a – Surface of density; b – surface of ultrasonic velocity; and c – surface of isentropic compressibility for 2-hydroxy ethyl ammonium formate (2-HEAF) + tris(2-hydroxyethyl) ammonium propionate (2-HTEAPr) mixture in the range of temperatures 288.15–338.15 K.

2-HEAF or 2-HDEAA composition into both figures and the almost linear influence of temperature on density values (Figs. 3a and 4a). In Fig. 3b the curious effect at high concentrations and high temperatures in terms of ultrasonic velocity for the 2-HEAF + 2-HTEAPr mixture should be observed. This magnitude shows a maximum at high concentration of 2-HEAF which could be explained as an increase in the packing efficiency of the ions of the proprionate salt into 2-HEAF at high temperatures. Figs. 3c and 4c show the effect of these two magnitudes in terms of the isentropic compressibility, where the strong diminution of this property for lower temperatures and rising concentrations of the lightest ionic component into the mixture (2-HEAF into Fig. 3c and 2-HDEAA into Fig. 4c, respectively) should be observed.
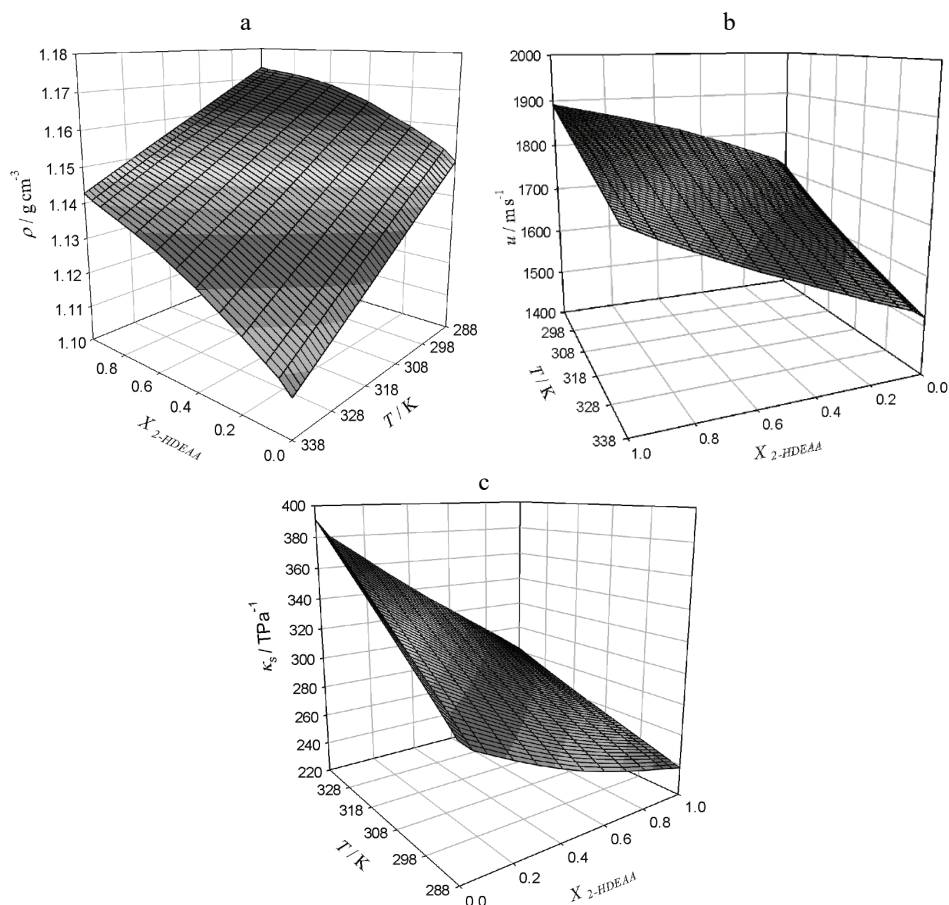

Fig. 4. a – Surface of density; b – surface of ultrasonic velocity; and c – surface of isentropic compressibility for bis(2-hydroxyethyl) ammonium acetate (2-HDEAA)) + tris(2-hydroxyethyl) ammonium propionate (2-HTEAPr) mixture in the range of temperatures of 288.15–338.15 K.

Derived properties correlation

The excess molar volumes and changes of isentropic compressibilities on mixing (attending to Laplace equation) values are presented in the Table S-I of the Supplementary material and were computed from the Eqs. (4) and (5):

$$V^{\mathrm{E}} = \sum_{i=1}^{n} x_i M_i \left(\rho^{-1} - \rho_i^{-1} \right) \tag{4}$$

$$\delta \kappa_{\mathrm{S}} = \frac{1}{\rho u^2} - \sum_{i=1}^{n} \frac{x_i}{\rho_i u_i^2} \tag{5}$$

In these equations, ρ is the density and κ_{S} the isentropic compressibility on mixing. The ρ_i and $\kappa_{\mathrm{S}i}$ symbols are the properties of pure chemicals at the same temperature and n is the number of components in the mixture. A modified Redlich-Kister type equation was used to correlate the derived properties of the binary mixtures of protic ionic liquids, by using the unweighted least squares method fitting parameters which were obtained by the unweighted least squared method applying a fitting Marquardt algorithm, all experimental points weighting equally. The fitting equation can be expressed as:

$$\delta Q_{ij} = x_i x_j \sum_{p=0}^{m} C_p (x_i - x_j)^p \tag{6}$$

$$C_p = \sum_{i=0}^{2} C_{pi} T^i \tag{7}$$

where δQ is $V^{E}/$ cm^3·mol^{-1}, or $\delta \kappa_{\mathrm{S}}$ / TPa^{-1}, respectively. The degree of this equation (*m* parameter) was optimized by applying the *F*-test. Each C_p parameter was extended as quadratic polynomic dependent function of temperature (Eq. (7)). The C_{pi} fitting parameters are gathered in Table S-III of the Supplementary material, with the corresponding root mean square deviations (Eq. (3)). No previously data of these mixtures was found in open literature. Figs. 5 and 6 show the derived magnitudes as a function of temperature for both mixtures.

The physical properties and the derived magnitudes are given in Table S-I. These mixtures show an analogous trend in terms of temperature and solvent composition. Strong minima of excess molar volumes and changes of isentropic compressibilities at equimolar composition are observed in both mixtures.

Apparent molar magnitudes

The apparent molar volumes (ϕ_V, cm^3 mol^{-1}) of 2-HEAF or 2-HDEAA into 2-HTEAPr solvent are calculated from the volumetric experimental values by the following equation:

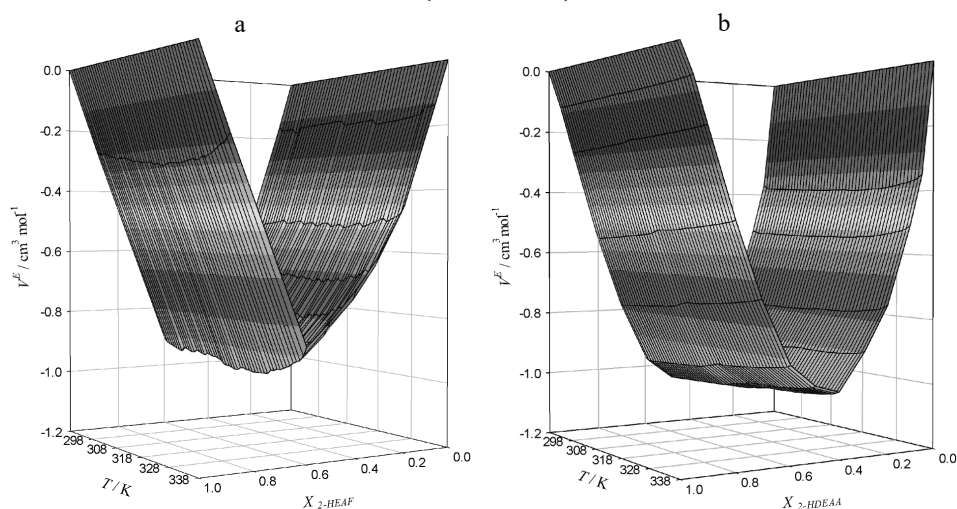$$\phi_V = 1000\left(\frac{\rho_{SOLV} - \rho}{m\rho\rho_{SOLV}}\right) + \frac{M_{IL}}{\rho} \qquad (8)$$

Fig. 5. Surfaces of excess molar volumes (cm³mol⁻¹) of: a – 2-hydroxyethylammonium formate (2-HEAF) + tris(2-hydroxyethyl)ammonium propionate (2-HTEAPr) mixture and b – bis(2-hydroxyethyl)ammonium acetate (2-HDEAA) + tris(2-hydroxyethyl)ammonium propionate (2-HTEAPr) mixture in the range of temperatures 288.15–338.15 K.
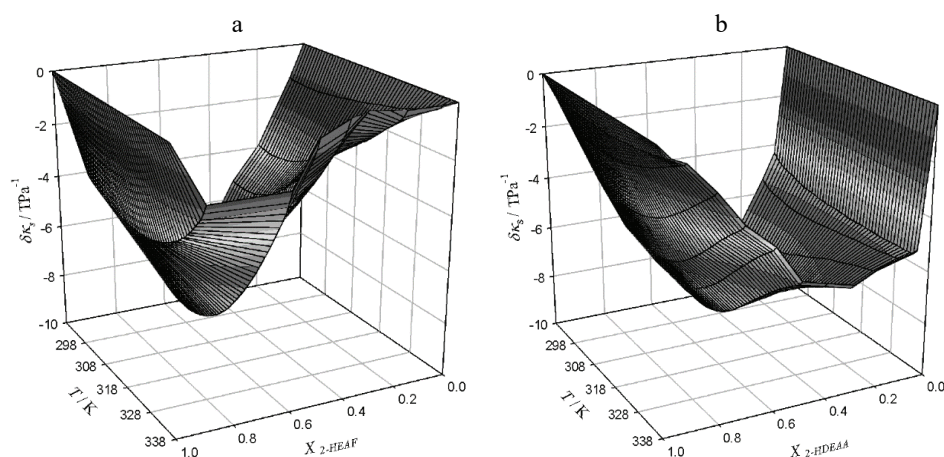

Fig. 6. Surface of changes of isentropic compressibility of: a – 2-hydroxyethylammonium formate (2-HEAF) + tris(2-hydroxyethyl)ammonium propionate (2-HTEAPr) mixture and b – bis(2-hydroxyethyl)ammonium acetate (2-HDEAA) + tris(2-hydroxyethyl)ammonium propionate (2-HTEAPr) mixture in the range of temperatures 288.15–338.15 K.

where ρ is the density of solution, ρ_{SOLV} is the density of the solvent at the same temperature (2-HTEAPr), m is the molality of the solution and M_{IL} is the molar

mass of the solute (2-HEAF or 2-HDEAA protic ionic liquid). The isentropic apparent molar compressibilities ($\kappa_{\varphi S}$, cm^3 mol^{-1} TPa^{-1}) are calculated from density and ultrasonic velocities using the following equation:

$$K_{\varphi S} = 1000\left(\frac{\kappa_S - \kappa_{SSOLV}}{m\rho}\right) + \kappa_S \varphi_V \tag{9}$$

where κ_S is the isentropic compressibility of solution, κ_{SSOLV} is the isentropic compressibility of the ionic solvent at the same temperature, and the other symbols express the same meaning as above. The apparent magnitudes were also correlated by a modified Redlich–Mayer equation where the fitting parameters show a temperature dependence as follows:

$$\Phi_V = \Phi_V^0 + \sum_{i=0}^{N} J_V m^{(i+1/2)} \tag{10}$$

$$\kappa_{\Phi S} = \kappa_{\Phi S}^0 + \sum_{i=0}^{M} K_\kappa m^{(i+1/2)} \tag{11}$$

where J_V, K_κ and Φ_V^0 and $\kappa_{\Phi S}^0$ are fitting temperature dependent parameters (Table S-IV), which were computed, as explained earlier. These values are gathered in Figs. 7 and 8. From these expressions, the limiting values for apparent molar volumes (with superscript zero) show a decreasing linear tendency for rising temperature for both mixtures (Fig. 9). At infinite dilution, each solute ion (2-HEAF or 2-HDEAA) is surrounded only by the corresponding counter ion of the solvent (2-HTEAPr), being infinitely distant with the other solute ions. It follows that the apparent molar volume at infinite dilution is unaffected by the interaction among solute ions and then it is a pure measurement of ion + solvent ions interaction. Fig. 9 shows that the limiting apparent molar volumes for 2-HEAF mixture at different temperatures are slightly lower than the corresponding values for 2-HDEAA mixture, showing both mixtures an analogous temperature trend.

The parameters derived from the experimental measured data were intermolecular free length (L_f), van der Waals constant (b), molecular radius (r), geometrical volume (B), molar surface area (Y), available volume (V_a), volume at absolute zero (V_0), collision factor (S) and specific acoustic impedance (Z).

For simplification, only the values of specific acoustic impedance, intermolecular free length, geometrical volume and collision factor and are enclosed in Table S-I. The other parameters are gathered in Table S-V for the pure solvents at 288.15, 298.15 and 338.15 K.

The isothermal coefficient of pressure excess molar enthalpy can be derived accurately from volumetric measurements by application of the following expression:

$$\left(\frac{\partial H^{\mathrm{E}}}{\partial p}\right)_{T,x} = V^{\mathrm{E}} - T\left(\frac{\partial V^{\mathrm{E}}}{\partial T}\right)_{p,x} \tag{12}$$
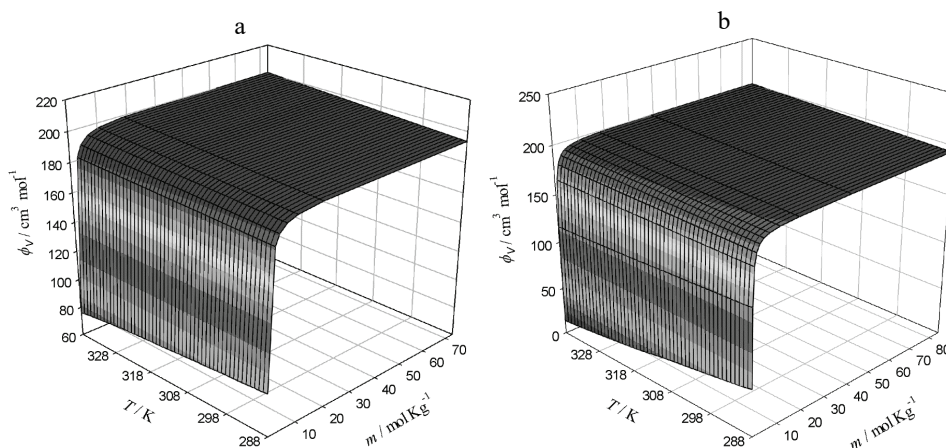

Fig. 7. Curves of apparent molar volumes of: a – tris(2-hydroxyethyl)ammonium propionate (2-HTEAPr) and its solution with 2-hydroxyethylammonium formate (2-HEAF) and b – tris(2-hydroxyethyl)ammonium propionate (2-HTEAPr) and its solution with bis(2-hydroxyethyl)ammonium acetate (2-HDEAA) in the range of temperatures 288.15–338.15 K.
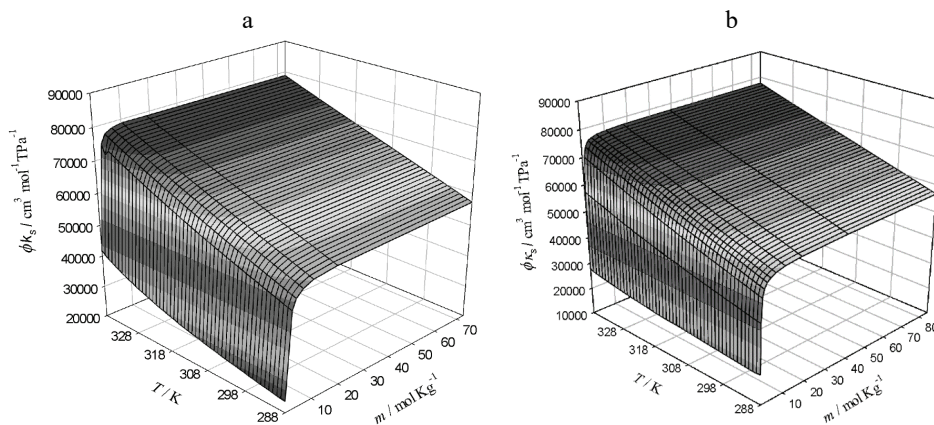

Fig. 8. Curve of apparent molar isentropic compressibility of: a – tris(2-hydroxyethyl)-ammonium propionate (2-HTEAPr) and its solution with 2-hydroxyethylammonium formate (2-HEAF) and b – tris(2-hydroxy ethyl) ammonium propionate (2-HTEAPr) and its solution with bis(2-hydroxy ethyl)ammonium acetate (2-HDEAA) in the range of temperatures 288.15–338.15 K.

This magnitude stands for the dependence of excess molar enthalpy of mixing on pressure at fixed composition and temperature. This magnitude shows negative values for all mixtures. The mixture 2-HDEAA + 2-HTEAPr shows the

most negative values for the isothermal coefficient. The influence of decreasing temperature produces lower negative values for both systems, as observed in Fig. 10.
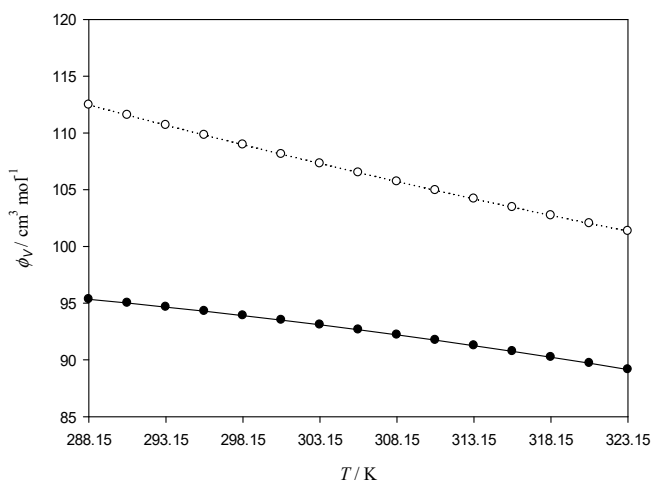

Fig. 9. Curves of apparent molar volumes at infinite dilution (cm^3 mol^{-1}) of tris(2-hydroxy-ethyl)ammonium propionate (2-HTEAPr) and its solutions with: ●) 2-hydroxyethylammo-nium formate (2-HEAF) and ○) bis(2-hydroxyethyl)ammonium acetate (2-HDEAA) at 298.15 K.
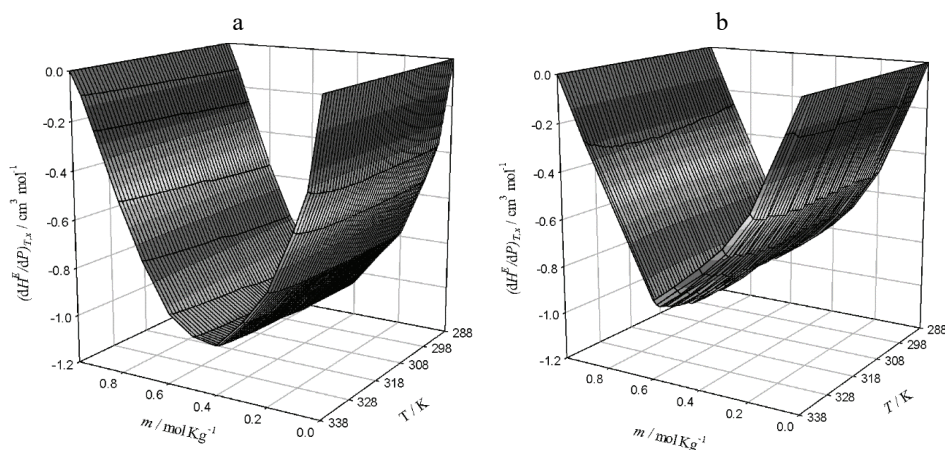

Fig. 10. Curve of isothermal coefficient of pressure excess molar enthalpy of:
a – tris(2-hydroxyethyl)ammonium propionate (2-HTEAPr) and its solution with 2-hydroxy-ethylammonium formate (2-HEAF) and b – tris(2-hydroxyethyl)ammonium propionate (2-HTEAPr) and its solution with bis(2-hydroxyethyl) ammonium acetate (2-HDEAA) in the range of temperatures 288.15–338.15 K.

Density prediction

The modern industrial chemical processes involve the use of computer aided procedures increasingly. Despite the successful developing of several procedures of density estimation for pure compounds or mixtures, only a few of them may be of real application for chemicals of non-ideal trend or high molar mass.[37] An additional challenge is the describing of the ion interaction and the dispersive effects into ionic liquid mixtures, due to the importance of the steric hindrance among their structures. The rare studies involving binary or higher complex mixtures of this kind of compounds makes the theoretical model development difficult, as well as a complete understanding of the ion interaction into these mixtures.

In this work, experimental data for the density of the mixtures were compared with values determined by the Mchaweh-Nasrifar–Moshfeghian model (MNM model) and the modified Heller temperature dependent equation were used for density prediction.

A simplification for the Nasrifar–Moshfeghian liquid density correlation (NM correlation) was applied, replacing the Mathias and Copeman temperature-dependent term with the original Soave–Redlich–Kwong equation of state (SRK EOS) temperature-dependent term. This replacement has overcome the limitations in use for the original model, which were due to the Mathias and Copeman vapor pressure dependent parameters.[38] The Nasrifar–Moshfeghian model (NM)[39] requires three parameters for each compound, that are not readily available for all compounds. In the absence of these three parameters, the NM correlation fails to predict the density of pure compounds and their mixtures. The modification of this model, MNM model, overcomes this barrier by replacing the predictive Soave–Redlich–Kwong (PSRK) parameter α with the original SRK term (α_{SRK}). The parameter α_{SRK} is defined in terms of reduced temperature (T_R):

$$\alpha_{SRK} = \left[1 + \dot{m}\left(1 - \sqrt{T_R}\right)\right]^2 \qquad (13)$$

where $\dot{m}$ is given by the following relation:

$$\dot{m} = 0.480 + 1.574\omega - 0.176\omega^2 \qquad (14)$$

where ω is the acentric factor of the mixture, calculated as follows:

$$\omega = \sum_{i=1}^{N} x_i \omega_i \qquad (15)$$

The temperature dependent term τ_{mix} is computed using the following equation:

$$\tau_{mix} = 1 - \frac{T_R}{\alpha_{SRK}} \tag{16}$$

The reduced temperature of the mixtures is defined as:

$$T_R = \frac{T}{\displaystyle\sum_{i=1}^{N} x_i T_{Ci}} \tag{17}$$

where T is the studied temperature and T_C is the critical temperature foe each component into mixture.

The critical density (ρ_C) of the mixture is calculated as follows:

$$\rho_C = \left[\sum_{i=1}^{N} x_i \rho_{Ci}^{-3/4} \right]^{-4/3} \tag{18}$$

where x_i is the molar fraction and ρ_{Ci} is the critical density of each compound into mixture. The reference density of the mixture (ρ_0) is calculated using the following term:

$$\rho_0 = 1 + 1.1688 \left(1 - \tau_{mix}\right)^{1/3} + 1.8177 \left(1 - \tau_{mix}\right)^{2/3} - \\ -2.6581 \left(1 - \tau_{mix}\right)^{3/3} + 2.1613 \left(1 - \tau_{mix}\right)^{4/3} \tag{19}$$

The revised MNM model, after replacement, has the following general equation for the solution density:

$$\rho = \rho_C \rho_0 \tag{20}$$

The critical properties and acentric factors required of the studied protic ionic liquids were estimated by a group contribution method based on the well--known concepts of Lydersen and Joback Reid, proposed by Valderrama and Robles[40] (Table II).

TABLE II. Estimated critical values[40] for the compounds enclosed into binary mixtures

Compound	p_c / bar	T_c / K	Z_c	ω
2-HEAF	54.049	683.2	0.377	0.898
2-HDEAA	31.830	829.3	0.291	1.404
2-HTEAPr	26.098	970.1	0.289	1.712

This model gathers underestimated values for both mixtures, showing the highest deviations at high solvent compositions. The temperature is a secondary factor and slightly affects the final prediction.

The modified Heller temperature dependent equation[41] was modified to estimate the volumetric trend of these mixtures as a function or temperature, as follows:

$$\rho = \sum_{i=1}^{N} \left(\frac{w_i}{\sum_{i=0}^{N} \sum_{j=0}^{M} D_{ij} T^j} \right)^{-1}$$

(21)

where i stands for the solute protic ionic liquid (2-HEAF or 2-HDEAA) or the corresponding solvent (2-HTEAPr) into the binary mixture and w_i stands for the mass fraction. Attending to the measured data, the estimation of density was made as function of temperature, so, disposable data at different temperatures for protic ionic liquid and solvents are necessary. The experimental density data of solvents were applied by means a polynomial[32] and for each protic ionic liquid solute, earlier collections of data published by the authors.[33] The deviation of these density estimation methods with respect to experimental data has been gathered into Table III. Comparatively, MHE offers much better results in terms of deviation than MNM for these mixtures, offering lower deviations for the lowest studied temperatures.

TABLE III. Root mean square deviations (σ, Eq. (3)) of the experimental and estimated results for density (g·cm^{-3}) by MNM model and Heller equation at 288.15, 298.15 and 338.15 K

Temperature, K	MNM model (Eq. (20))	Heller Equation (Eq. (21))
2-HEAF + 2-HTEAPr		
288.15	0.0462	0.0037
298.15	0.0610	0.0043
338.15	0.0649	0.0042
2-HDEAA + 2-HTEAPr		
288.15	0.0717	0.0041
298.15	0.0902	0.0046
338.15	0.0949	0.0047

Ultrasonic velocity prediction

In the last few years an increasing interest for the application of low and high frequency ultrasound techniques for thermodynamic applications has appeared.[42] Without doubt it is caused by the multiple use that these measurements may have as heat capacity, compressibility studies or simple and accurate concentration measurements. Ultrasonic velocity has been systematically measured in the last years, but this kind of data is scarce yet. Predictive procedures are then of primary interest, the same problems that were observed for density

being found. In this work, the experimental data for the ultrasonic velocity of the mixtures were compared with values determined by the Collision Factor Theory (CFT)[43] (Eq. (22)), the free length theory (FLT)[44] (Eqs. (23) and (24)) and the following mixing rules: Danusso[45] (Eq. (S-1)), Nomoto[46] (Eq. (S-2)), Junjie[47] (Eq. (S-3)) and Impedance model[48] (Eq. (S-4)) given in Supplementary material.

The collision factor theory model is dependent on the collision factors among molecules as a function of temperature into mixture, and is expressed as follows:

$$u = \frac{u_\infty \sum x_i S_i \sum x_i B_i}{V_{mix}} \tag{22}$$

where u_∞ is 1600 m/s, S is the collision factor, V_{mix} is molar volume of mixture and B is the characteristic molar volumes of each compound into mixture, calculated by the group contribution method of Bondi.[49] The appropriate relations for these calculations and its theoretical basis were described in the literature indicated above. The collision factors (S) of the pure solvents used in the CFT calculations were estimated by using the experimental ultrasonic velocities and the molar volumes enclosed in this paper.

The free length theory estimates the ultrasonic velocities of a mixture attending to the free displacement of molecules as a main function of temperature:

$$u = \frac{K}{L_{mix} \rho_{mix}^{1/2}} \tag{23}$$

where K is the Jacobson temperature dependent constant and is equal to $K =$ $= (93.875 + 0.375T) \times 10^{-8}$, where T is absolute temperature, and L_{mix} is described below:

$$L_{mix} = 2\left(\frac{V - \sum x_i V_i}{\sum x_i Y_i}\right) \tag{24}$$

where V represent the volume at absolute zero of each pure component and Y is the surface area per mole.

The deviations of these procedures for the studied mixtures are gathered in Table IV. As observed, for all methods the lowest deviations are obtained for the 2-HDEAA + 2-HTEAPr mixture. In general, the empirical equations offers better results in terms of deviation in comparison with CFT and FLT models in the studied temperature range.

TABLE IV. Root mean square deviations (σ) (Eq. (3)) of the experimental and estimated results for ultrasonic velocities, m·s^{-1}, by different models (Eqs. (21)–(26)) at 288.15, 298.15 and 338.15 K

T / K	CFT	FLT	Danusso	Nomoto	Junjie	Impedance model
2-HEAF + 2-HTEAPr						
288.15	29.37	203.98	36.35	27.89	29.44	16.28
298.15	30.55	186.50	39.52	30.24	32.66	14.61

TABLE IV. Continued

T / K	CFT	FLT	Danusso	Nomoto	Junjie	Impedance model
2-HEAF + 2-HTEAPr						
338.15	43.01	209.53	35.02	23.40	29.56	6.28
2-HDEAA + 2-HTEAPr						
288.15	9.26	200.95	2.67	7.24	3.61	11.95
298.15	7.74	169.63	6.09	11.27	6.60	9.88
338.15	4.85	142.92	22.53	28.32	20.67	5.45

CONCLUSIONS

Physicochemical data of protic ionic liquids are important for both the design of innovative and cleaner industrial processes and for the understanding of the ionic interactions in such kind of compounds. In the present paper, we have presented the experimental data of densities and ultrasonic velocity as a function of temperature of the binary mixtures (2-hydroxyethylammonium formate (2--HEAF) or bis(2-hydroxyiethyl)ammonium acetate (2-HDEAA) + tris(2-hydroxyethyl)ammonium propionate (2-HTEAPr)), showing strong contractive behaviour at equimolar compositions.

No information on these mixtures is gathered in open literature to the best of our knowledge. From these results, it was found:

1. The increase of temperature diminish the interaction among ions, lower values of density, and ultrasonic velocity (and then increasing values of isentropic compressibility) have been observed.

2. The organic residual chains, in both ions forming both ionic liquid, have strong effects on the physicochemical properties. The steric hindrance is a key factor for the arrangement into a liquid state. The ions enclosed are of two types, the linear anion (formate, acetate or propionate) and the linear (mono) or plane//globular (di- or trisubstitution) cation. The factors studied here are the chain length of the anion and the substitution into the cation (bulk degree), respectively. The influence of anion residue is higher in terms of steric hindrance, due to its longer structure, producing a higher disturbance of the ion package. This fact may be observed in terms of higher values of densities and ultrasonic velocities for those salts of higher substitution.

3. Due to the innovative character of those compounds, there are few disposable data in open literature about the mixing properties of protic ionic liquids. The state of the art is worse in terms of estimation models that play a key role for future design and simulation. The tested models show, at least, the qualitative capability of estimation. The empirical models (MHE for density and Danusso, Nomoto, Junjie and Impedance model for ultrasonic velocity) at low temperature showed the best results.

4. As explained above, the low cost, simplicity of synthesis, biodegradation at environmental conditions and potential applications of these liquid salts offer a promising future, due to the possibility of designing green chemical processes. The better knowledge of mixing ionic liquid thermodynamics is necessary for this aim, in order to obtain the accurate design and simulation of industrial applications.

SUPPLEMENTARY MATERIAL

The areas evaluated in the tests and some of the test questions are available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

ИЗВОД

УТИЦАЈ ТЕМПЕРАТУРЕ НА ТЕРМОДИНАМИЧКА СТОЈСТВА БИНАРНИХ СМЕША ПРОТИЧНИХ ЈОНСКИХ ТЕЧНОСТИ КРАТКОГ ЛАНЦА

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У раду је испитиван утицај температуре на волуметријска и акустична својства две бинарне смеше протичних јонских течности које садрже анјоне формата, ацетата и пропионата и катјоне 2-хидроксиетиламонијум, бис(2-хидроксиетил)амонијум и трис(2-хидроксиетил)амонијум. Коришћењем добијених експерименталних података израчунате су изведене величине, а затим су фитоване Redlich–Kister и Redlich–Mayer једначинама у функцији од температуре. Остала својства, као што су интермолекулска слободна дужина, акустична импеданса, геометријска запремина, фактор судара и изотермски коефицијент притиска допунске моларне енталпије, израчуната су због свог значаја у изучавању специфичних молекулских интеракција. Нови експериментални подаци су коришћени у циљу тестирања способности предсказивања различитих модела за густину (Mchaweh-Nasrifar–Moshfeghian (MNM) модел и модификована Heller једначина температурне зависности (MHE)) и брзину звука (различите емпиријске једначине, теорија фактора судара, тј. Collision Factor Theory (CFT) и теорија слободне дужине, тј. Free Length Theory (FLT)). Изражена неидеалност код ових смеша јавља се услед снажних

контракција на свим температурама и при свим саставима смеша. Добијени резултати указују на јаче интеракције између различитих компонената у смеши у односу на интеракције између молекула чисте компоненте, за обе испитиване смеше при свим условима. Упркос јаким интеракцијама између јона, тестирани модели су показали способност квалитативног предсказивања.

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