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Insights into interactions between 1-butyl-3-methylimidazolium dicyanamide and molecular solvents: γ -valerolactone, γ -butyrolactone and propylene carbonate. Volumetric properties and MD simulations

Nebojša Zec^{1,2*}, Abdenacer Idrissi³, Marija Bešter-Rogač⁴, Milan Vraneš² and Slobodan Gadžurić²

¹*German Engineering Materials Science Centre (GEMS) at Heinz Maier-Leibnitz Zentrum (MLZ) Helmholtz-Zentrum Geesthacht GmbH, Lichenbergstr. 1, 85748 Garching bei München, Germany*

²*Faculty of Science, Department of Chemistry, Biochemistry and Environmental Protection, University of Novi Sad, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia*

³*University of Lille, Science and Technology, LASIR (UMR CNRS A8516), Bât. C5, Cité Scientifique, 59655 Villeneuve d'Ascq Cedex, France*

⁴*Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, 1000 Ljubljana, Slovenia*

Abstract

Experimental densities of the binary mixtures containing 1-butyl-3-methylimidazolium dicyanamide ionic liquid, [C₁C₄im][DCA] and molecular solvent: γ -valerolactone (γ VL) or propylene carbonate (PC) were measured at temperatures from (273.15 to 323.15) K and at a pressure of 0.1 MPa over the whole composition range. Related excess molar volumes were calculated and fitted using Redlich-Kister's polynomial equation and compared with previously measured IL + γ -butyrolactone (γ BL) mixture. Obtained values are negative in the whole range of ionic liquid mole fraction and at all temperatures. Molecular dynamics simulations were applied to quantify the intermolecular interactions in pure liquids and binary mixtures, hydrogen bond, dipole-dipole and stacking interactions. Excess molar volumes obtained from MD simulations follow the trend observed in the experiment. Orientational correlations were characterized by several combined angular and distance distribution functions between first neighbour molecules. Results suggest that strength of solvent-solvent interactions plays a significant role in the observed difference in volumetric properties of these binary mixtures. Calculated hydrogen bond geometry indicates that the hydrogen bond interaction in the three molecular solvents is weak and follows the order PC > γ BL > γ VL.

¹ * Corresponding author: Tel: +49 89 289 10748; E-mail: nebojsa.zec@hzg.de

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1 Introduction

Mixtures of ionic liquids (ILs) and molecular solvents (MS) are widely studied in recent years from experimental, theoretical and computational point of view [[1]; [2]; [3]; [4]; [5]; [6]; [7]; [8]]. One of the major practical problems concerning ILs, their high viscosity, can be addressed by mixing with appropriate low viscous molecular solvents. By reducing viscosity and altering other physicochemical properties, possibilities are opened for different practical applications of these binary mixtures [9]. Among them, energy applications of ILs, such as in batteries, fuel and solar cells, supercapacitors and actuators, are still the promising ones [10].

Dicyanamide anion based ILs have well-known favourable properties such as low viscosity and low melting point [[11]; [12]], efficient mass transport [13] and a relatively high electrical conductivity [14]. In addition, wide electrochemical window makes them excellent candidates for electrochemical devices [15].

In our previous work, we showed that mixture of IL and γ -butyrolactone (γ BL) could be applied as an electrolyte for Li-ion batteries, with TiO₂ nanotube arrays electrode in particular [16].

Since reliable physicochemical data and knowledge about interactions between components of a mixture are necessary for developing a new class of electrolytes, in this work, we investigated ionic liquid 1-butyl-3-methylimidazolium dicyanamide [C₁C₄im][DCA] + molecular solvents mixtures by using computational and experimental approach.

Molecular liquids such as γ -valerolactone (γ VL), γ -butyrolactone (γ BL) and propylene carbonate (PC) have a high boiling point and low melting point. These are non-corrosive liquids suitable for electrochemical cells operating over a wide temperature range for a long time, which makes them suitable solvent candidates to be used to improve volumetric and transport properties of ILs.

In this paper, the density of [C₁C₄im][DCA] binary mixtures with γ VL and PC were examined in the temperature range from (273.15 to 323.15) K, at a pressure of 0.1 MPa. Calculated volumetric

parameters are compared with a previously measured binary system with γ BL [6]. Molecular dynamics simulations were applied to quantify the intermolecular interactions in pure liquids and binary mixtures, hydrogen bond, dipole-dipole and stacking interactions.

2 Experimental section

2.1 Materials

Ionic liquid [C₁C₄Im][DCA] (≥ 0.98), was purchased from IOLITEC and dried under vacuum at 353 K for 24 h before use. Propylene carbonate and γ -valerolactone (Aldrich, $\omega \geq 0.99$) were dried and kept in the dry box in the nitrogen atmosphere. The summary of the provenance and purity of the samples is given in Table 1. The water content in ionic liquid was estimated to be 211 ppm by Karl Fischer titration, which is appropriate for this type of measurements. Binary mixtures covering the whole composition range of [C₁C₄Im][DCA] and molecular solvents were prepared by measuring appropriate amounts of the components on a Sartorius analytical balance. The standard uncertainty of mass fraction is estimated $7.5 \cdot 10^{-4}$.

TABLE 1. Provenance and purity of the samples.

Chemical name	Provenance	Purification method	Purity specified by the supplier		
			Mass fraction purity	Halides	Water content by Karl-Fischer titration
[bmim][DCA]	IOLITEC	vacuum drying	> 0.98	< 0.02 ^a	189 ppm
γ -butyrolactone	Aldrich	vacuum drying	≥ 0.99	/	71 ppm
γ -valerolactone	Aldrich	vacuum drying	≥ 0.99	/	52 ppm
propylene carbonate	Aldrich	vacuum drying	0.99	/	50 ppm

^aspecified by the supplier

2.2 Density measurements

The density of pure components and binary mixtures were measured at a pressure of 0.1 MPa using a vibrating tube densimeter, Anton Paar DMA5000 with a declared reproducibility of $1 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$. The calibration of densimeter was performed using the density data for dry air and water. The instrument was thermostated within 0.001 K, and viscosity related errors in the density were automatically corrected over full viscosity range, thus the major source of measuring error were gas bubbles entrapped in the measuring cell filled with a sample. Therefore, the measuring cell was filled very carefully to minimize the probability of such error. The total volume of the samples used for density measurements was approximately 1 cm^3 . The relative standard uncertainty of determining the density was estimated to be 0.4%.

2.3 MD Simulations

Molecular dynamics simulation were carried out using GROMACS 4.5.5 simulation package [17]. Initial systems containing 864 molecules, generated by Packmol [18] and placed randomly in a cubic simulation box, were equilibrated at room temperature. The simulation of IL/molecular solvent mixtures was carried out at ambient conditions of pressure and temperature equal to 1 bar and 298K, respectively. The ionic liquid molar fraction, XIL, are 0.0, 0.05, 0.10, 0.15, 0.20, 0.30, 0.40, 0.5, 0.60, 0.70, 0.80, 1.0. The system was equilibrated in isothermal-isobaric (NPT) ensemble of 500 ps. This step was followed by 5 ns calculation performed in canonical (NVT) that was used to obtain reliable information on the structure of the mixture. A Velocity-rescaling thermostat maintained the temperature, and Berendsen barostat set the pressure at 1 atm throughout the simulation with relaxation times of 0.1 and 0.5 ps, respectively. Equations of motion were integrated using Verlet leap-frog algorithm with a time-step of 0.5 fs. The long-range electrostatic interactions equal to 1.4 nm were accounted by the computationally efficient Particle-Mesh-Ewald (PME) algorithm and similar to cut-off distance for the real-space component. The 12-6 Lennard-Jones interactions are treated by the conventional shifted force technique with a switch region between 1.2 and 1.3 nm. Cross interactions between different atom types were derived using standard Lorentz-Berthelot combination rule. All the

other properties presented here were derived from 500 ps trajectory in NVT ensemble and analyzed using TRAVIS-1.14.0 code [19]. Force field parameters for γ VL and γ BL were taken from work of Aparicio and Alcalde. [20], while parameters for PC were taken from work of Takeuchi et al [21]. $[C_1C_4Im][DCA]$ parameters were taken from work of Mondal and Balasubramanian [22].

3 Results and discussion

3.1 Densities of pure components

All experimental density data presented in this work for pure $[C_1C_4Im][DCA]$ and γ BL, as well as comparison with literature data, are published in our previous works [[6]; [23]].

Densities of pure γ VL and PC were measured in the temperature range from (273.15 to 333.15) K in steps of 5 K, and the results are presented in Table 2.

TABLE 2. Experimental density values (d) of investigated ionic liquid and molecular solvents in the temperature range $T = (273.15 - 333.15)$ K at atmospheric pressure $p = 0.1$ MPa.

T / K	$d / g \cdot cm^{-3}$			
	$[C_1C_4Im][DCA]^a$	γ BL ^b	γ VL	PC
273.15	1.075196	1.149155	1.072741	1.226273
278.15	1.072131	1.144229	1.068026	1.220903
283.15	1.068945	1.139314	1.063311	1.215540
288.15	1.065724	1.134403	1.058602	1.210191
293.15	1.062518	1.129493	1.053895	1.204853
298.15	1.059326	1.124588	1.049191	1.199524
303.15	1.056152	1.119684	1.044483	1.194198
308.15	1.052992	1.114782	1.039776	1.188886
313.15	1.049849	1.109874	1.035065	1.183581
318.15	1.046721	1.104965	1.030351	1.178287

323.15	1.043606	1.100053	1.025633	1.172991
328.15	1.040507	1.095137	1.020915	1.167704
333.15	1.037427	1.090216	1.016185	1.162415

^aRef [6]
^bRef [23]
Relative standard uncertainty: $u(d) = 0.4\%$. $u(p) = 1.5\%$.
Standard uncertainty: $u(T) = 0.015$ K.

Comparison with the available literature values for pure PC is presented in Figure 1. It is found that deviations of our experimental results obtained for PC from the literature values are less than 0.15% in the whole range of temperature, except in the case of the values measured by Guevara et al [24] where deviations are between 0.3% and 0.5%. Experimental densities for γ VL are measured by Aparicio and Alcalde in the wide temperature range, and results agree very well with our data with deviations up to 0.05% [20].

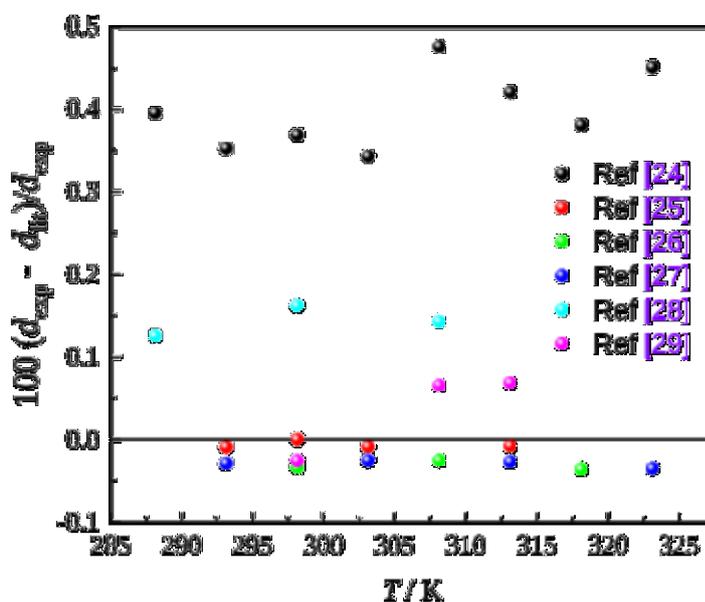


Figure 1. Plot of relative deviations vs. temperature between our experimental density data for propylene carbonate and those from the literature [[24]; [25]; [26]; [27]; [28]; [29]].

In Table 3. density values obtained by MD simulations at 298.15 K are presented and compared with experimental data. For all investigated pure liquids densities are reproduced within acceptable limits for structural investigation.

Table 3. Comparison of experimental density values and values obtained from MD simulations for investigated ionic liquid and molecular solvents at 298.15 K

	[C ₁ C ₄ Im][DCA]	PC	γ VL	γ BL
Experimental value / g·cm ⁻³	1.05933	1.19952	1.04919	1.12459
MD Simulation / g·cm ⁻³	1.03132	1.18906	1.06315	1.12650
Deviation %	2.64	1.01	-0.94	-0.18

3.2 Volumetric parameters

Densities of ([C₁C₄Im][DCA] + γ VL and ([C₁C₄Im][DCA] + PC) mixtures were measured in the temperature range from (273.15 to 323.15) K and presented as a function of temperature in Table S1 and also in Figure S1 in the supporting information, along with data for previously measured system [C₁C₄Im][DCA] + γ BL. From these results, it can be seen that the density increases slightly in the binary mixture [C₁C₄Im][DCA] + γ VL with the ionic liquid mole fraction since densities of pure components have very similar values. Since propylene carbonate has a higher density than IL, in the system [C₁C₄Im][DCA] + PC density decreases with increasing mole fraction of IL, which is the same situation as in the case of [C₁C₄Im][DCA] + γ BL.

Values of the excess molar volume, V^E , were calculated from the experimental and simulation density of the mixture, d , densities of the pure components, d_i , the corresponding mole fractions, x_i , and molar masses, M_i , using the following equation:

$$V^E = x_1 M_1 \left(\frac{1}{d} - \frac{1}{d_1} \right) + x_2 M_2 \left(\frac{1}{d} - \frac{1}{d_2} \right) \quad (1)$$

where x_1 , M_1 and d_1 relate to IL and x_2 , M_2 and d_2 relate to molecular solvent. Values of the excess molar volumes are graphically presented in Figure 2 using a Redlich-Kister-type polynomial equation [30] where Y^E represents the excess property:

$$V^E = x_2 \sum_{i=0}^n A_i (1 - 2x_2)^i \quad (2)$$

Values of the excess molar volumes were fitted by a method of the least squares. Here, A_i refers to the adjustable parameters and n is the number of the coefficients in the equation. The coefficients of the Redlich-Kister's equation, as well as the standard deviations of the fit, are given in Table S3 in the supporting information.

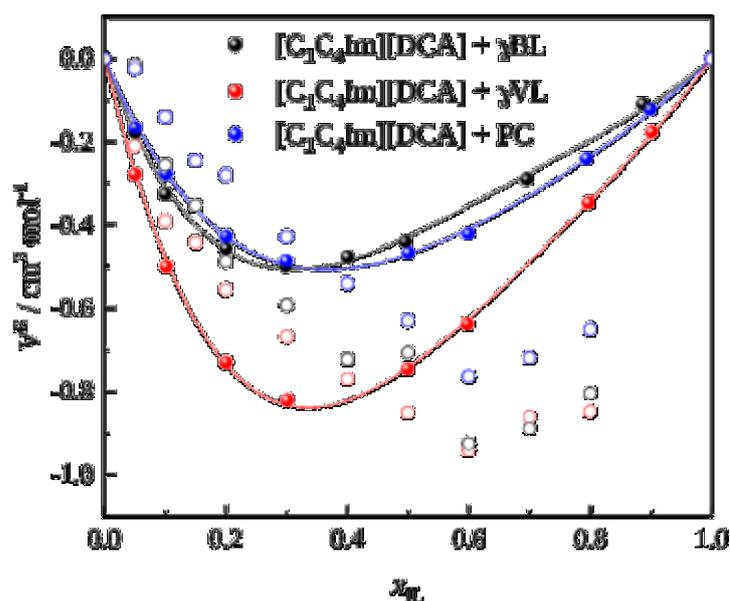


Figure 2. Excess molar volumes of investigated binary mixtures at $T = 298.15$ K. Lines represent Redlich Kister polynomial fit. Empty circles represent values obtained by MD simulations.

Negative values of excess molar volumes (Figure 2) in the whole range of IL mole fraction and at all temperatures indicate stronger interactions between molecular solvents and IL compared to the pure components. To understand which interactions can contribute to negative excess volumes structural analysis from MD simulation trajectories has been performed. In order to explain at a molecular level the behavior of the excess volume and particularly the negative values, we started from the established correlation between the weak interactions in lactones (γ BL, γ VL, δ -valerolactone and ϵ -caprolactone), and the negative excess volume in a mixture of these lactones with $[C_1C_4im][NTf_2]$

[31]. Indeed, it was shown by Papović et al. that lactones with weaker intermolecular interactions in the pure state have more negative values of the excess volume.

However, negative excess molar values are a consequence of complex interactions (ion-ion, ion-solvent, solvent-solvent) as well as of shape and size of molecules. First, we used molecular dynamics simulations to quantify the intermolecular interactions between ions of the IL and molecular solvents. Hydrogen bond, dipole-dipole and stacking interactions are the main interactions in these systems. To investigate possible hydrogen bonding between an acidic hydrogen on imidazolium C² carbon and carboxylic oxygen of molecular solvents. Interactions were quantified by calculating the two distances shown in Figure 3, the first one between H¹⋯Oⁱ, and the distance between, C²⋯Oⁱ, where *i* indicates the carboxylic oxygen in molecular solvents.

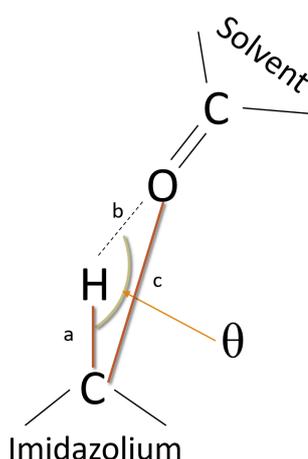


Figure 3. Angle θ between C² – H¹ and intermolecular H¹⋯Oⁱ bonds.

In the case of a linear hydrogen bond and then a strong one, the C²⋯Oⁱ distance will be equal to the sum of C²⋯H¹ bond and the intermolecular H¹⋯Oⁱ distances, while in the case of a bent hydrogen bonding, with a given θ angle, the C²⋯Oⁱ distance is shorter and can be estimated using the Eq. 3.

$$c^2 = a^2 + b^2 - 2ab\cos\theta \quad (3)$$

where *a*, *b* and *c* are distances $r(\text{C}^2\cdots\text{H}^1)$, $r(\text{H}^1\cdots\text{O}^i)$, $r(\text{C}^2\cdots\text{O}^i)$ respectively (Figure 3). We calculated these distances using the nearest neighbour approach, and their behaviour is illustrated in Figure 4.

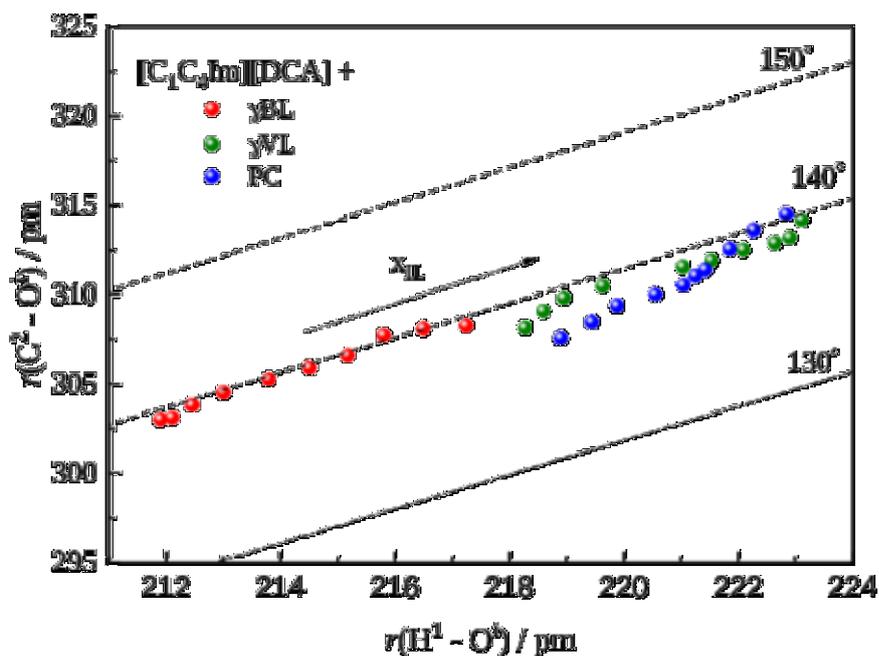


Figure 4. The distance between imidazolium C^2 and solvents carbonyl oxygen O^i as a function of the distance between imidazolium hydrogen H^1 on C^2 and same O^i . Lines are guided to the eye and represent distances calculated with Eq. 3 for different angles.

The comparison between the calculated values indicates clearly that the hydrogen bond interaction is not pronounced and is similar in the case of all three investigated solvents. Distances between H^1 and oxygen of the solvent are between 2.1 and 2.2 Å with the angle of around 140° and slightly change with increasing IL mole fraction.

The hydrogen bond interactions in pure solvents were quantified by calculating the two distances, the first one between $H^i \cdots O^i$, and the distance between $C^i \cdots O^i$, where i indicates the position of the C and H atoms (Figure 5). In the case of a linear hydrogen bond and then a strong one, the $C^i \cdots O^i$ distance will be equal to the sum of $C^i - H^i$ bond and the intermolecular $H^i \cdots O^i$ distances, while in the case of a bent hydrogen bonding, with a given θ angle, the $C^i \cdots O^i$ distance is shorter, and angle can be estimated using the equation 3. We calculated these distances using the nearest neighbour approach, and their behaviour is illustrated in Figure 5. The comparison between the calculated values and those obtained in the case of a linear hydrogen bonding geometry indicates that the hydrogen bond interaction in the three liquids is the most pronounced in pure PC and is the weakest in γ VL. It was

already shown by neutron scattering and computational techniques that PC molecules form head to tail clusters [32] in opposite to γ BL and γ VL where H-bonding less pronounced [20].

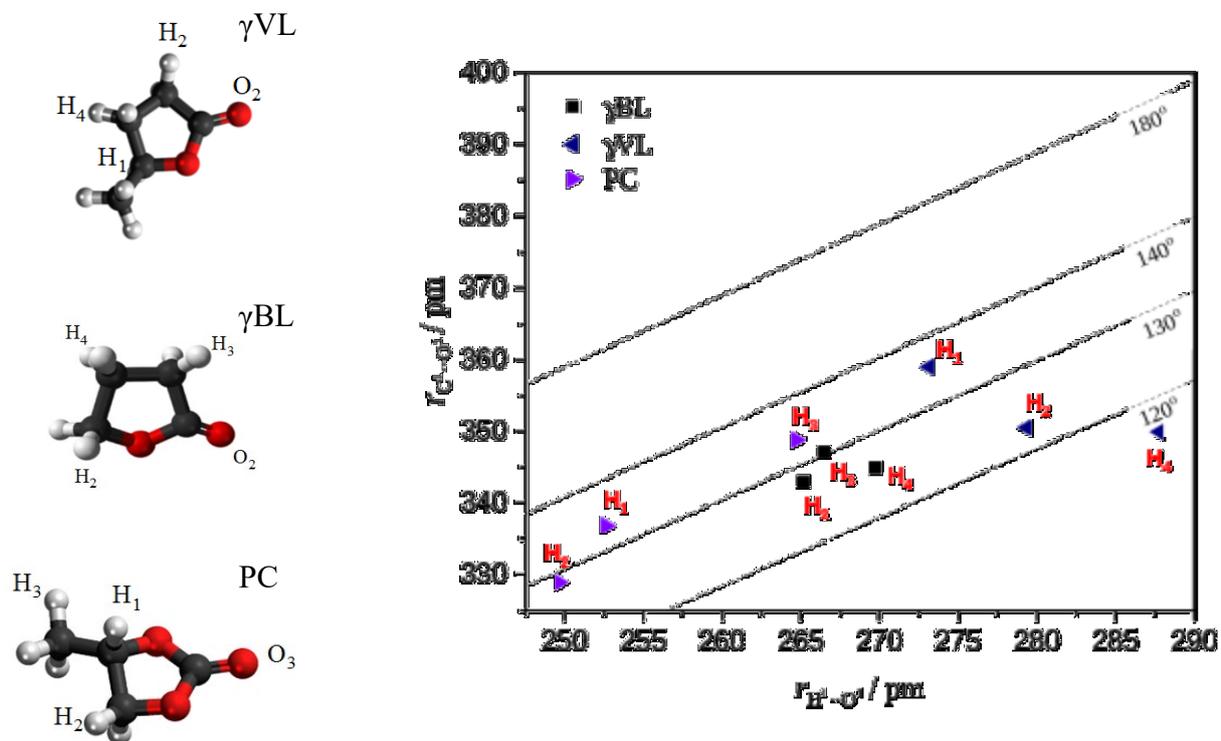


Figure 5. The distance between carbonyl oxygen O^i and carbon atoms C^i as a function of the distance between carbonyl oxygen O^i and hydrogen atoms H^i . Lines are guided to the eye and represent distances calculated with Eq. 3 for different angles.

Combined angular and distance distributions (CDFs)

To study the orientational aspects in more detail, we have decided to calculate several combined angular and distance distributions where the angles are defined in Figure 6, while the distance is that between a reference center of the ring (CoR) and that of the first neighbour.

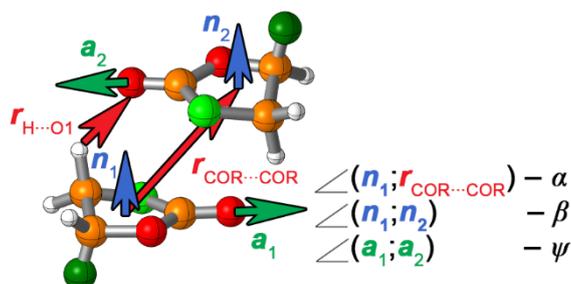


Figure 6. Schematic representation of the γ BL, γ VL and PC dimer with geometric characteristics used for the description of the mutual orientation of the molecules in neat liquids. For imidazolium rings, same notation is used.

The first investigated angle, designated here as α , is the angle between the normal vector of the γ BL, γ VL and PC ring plane of the reference molecule and the distance vector connecting the ring centers of the reference and observed molecules. Thus, positions above/below the reference molecule would correspond to α angle around 0° and 180° , while the perfect in-plane arrangement of the observed molecules would contribute to the α values close to 90° . The second investigated angle is β , formed by the normal vectors of the ring planes between the reference and observed molecules. As in the previous case, a perfectly parallel arrangement of the planes corresponds to β values of 0° and 180° , whereas the values around 90° are indicative of a T-shaped relative arrangement of the two ring planes. This angle gives information on the stacking between the rings of the molecules. The third angle designated as ψ is that between the vectors along C=O bonds in the reference and observed molecules. The ψ values close to 0° and 180° indicate a parallel and antiparallel orientation, respectively. Thus, this angle gives information about the relative orientation of molecular dipoles.

The behaviour of these distributions is given in Figure 7. In all the studied molecular solvent the above/below orientation, as indicated by the distribution of α angle, is not fulfilled and the above

orientation characterises the orientation between two molecular solvent molecules in γ_{BL} , γ_{VL} while the below orientation characterize that in PC. In investigated solvents, the stacking orientation can be ranked in the following decreasing order: γ_{BL} , γ_{VL} , PC as shown by the intensity in these distributions. Finally, the distribution of ψ angle shows that the antiparallel dipole-dipole orientation occurs in γ_{BL} while the parallel one occurs in the two other molecular solvents. These results point out to the fact that hydrogen bonding and dipole-dipole interactions are weaker in the case of γ_{VL} and correlates with the more negative values (as a comparison with γ_{BL} and PC) of the excess volume.

In Figure 8. are presented CDFs of cation-cation interactions in $[C_1C_4im][DCA] + \gamma_{BL}$ system for different compositions. The same behaviour is observed in all three systems. In pure IL cation above/below orientation is observed (α angle), as well as stacking between imidazolium cations (β angle). Parallel/antiparallel orientation is not pronounced as can be seen from ψ angles. As expected, all cation-cation interactions are reduced by adding molecular solvent.

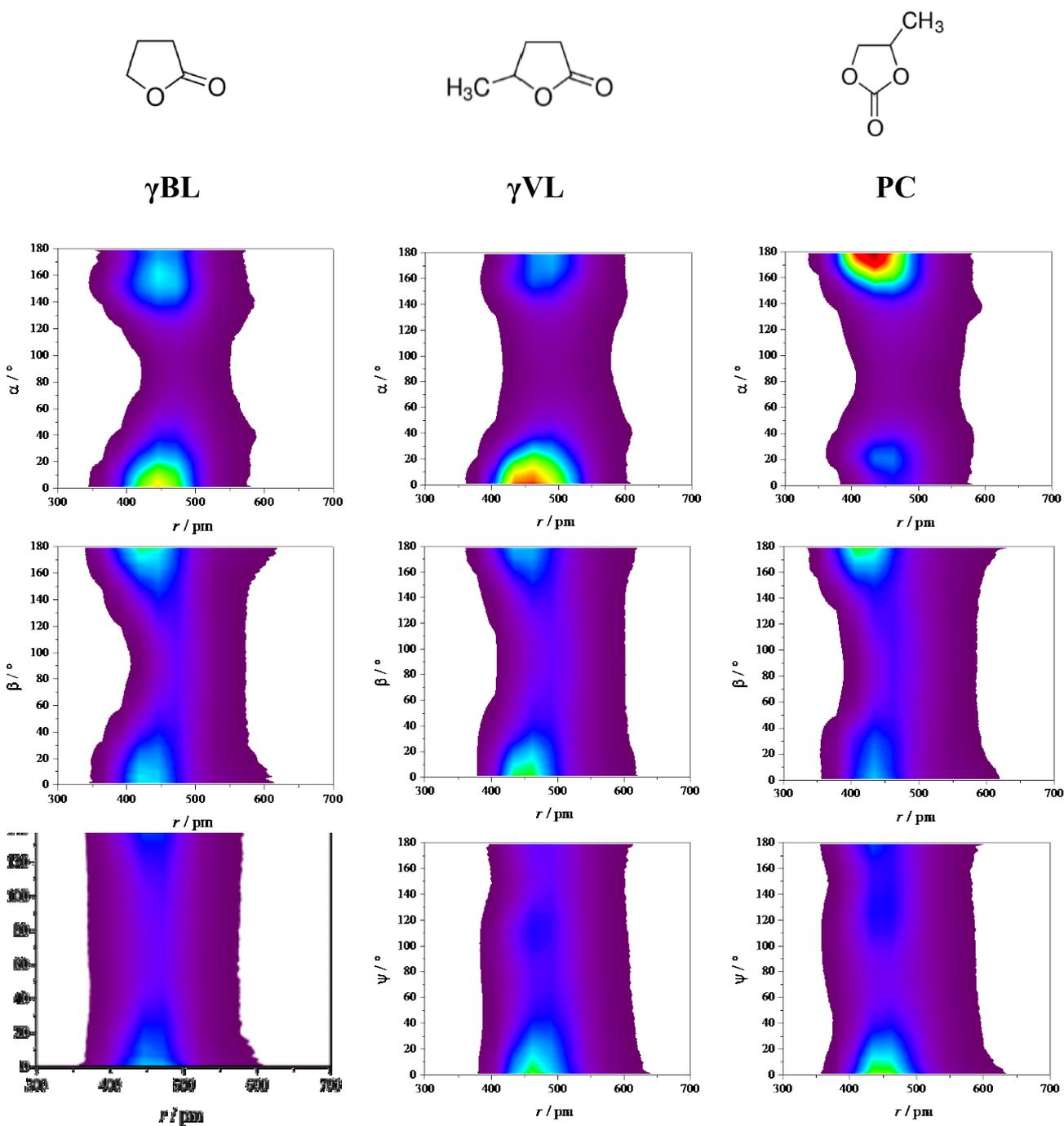


Figure 7. Combined Distribution Functions (CDFs) of solvent-solvent interactions in investigated pure solvents, where r represents the distance between centers of the imidazolium rings. Angles α , β , and ψ are explained in text and schematically presented in **Figure 6**.

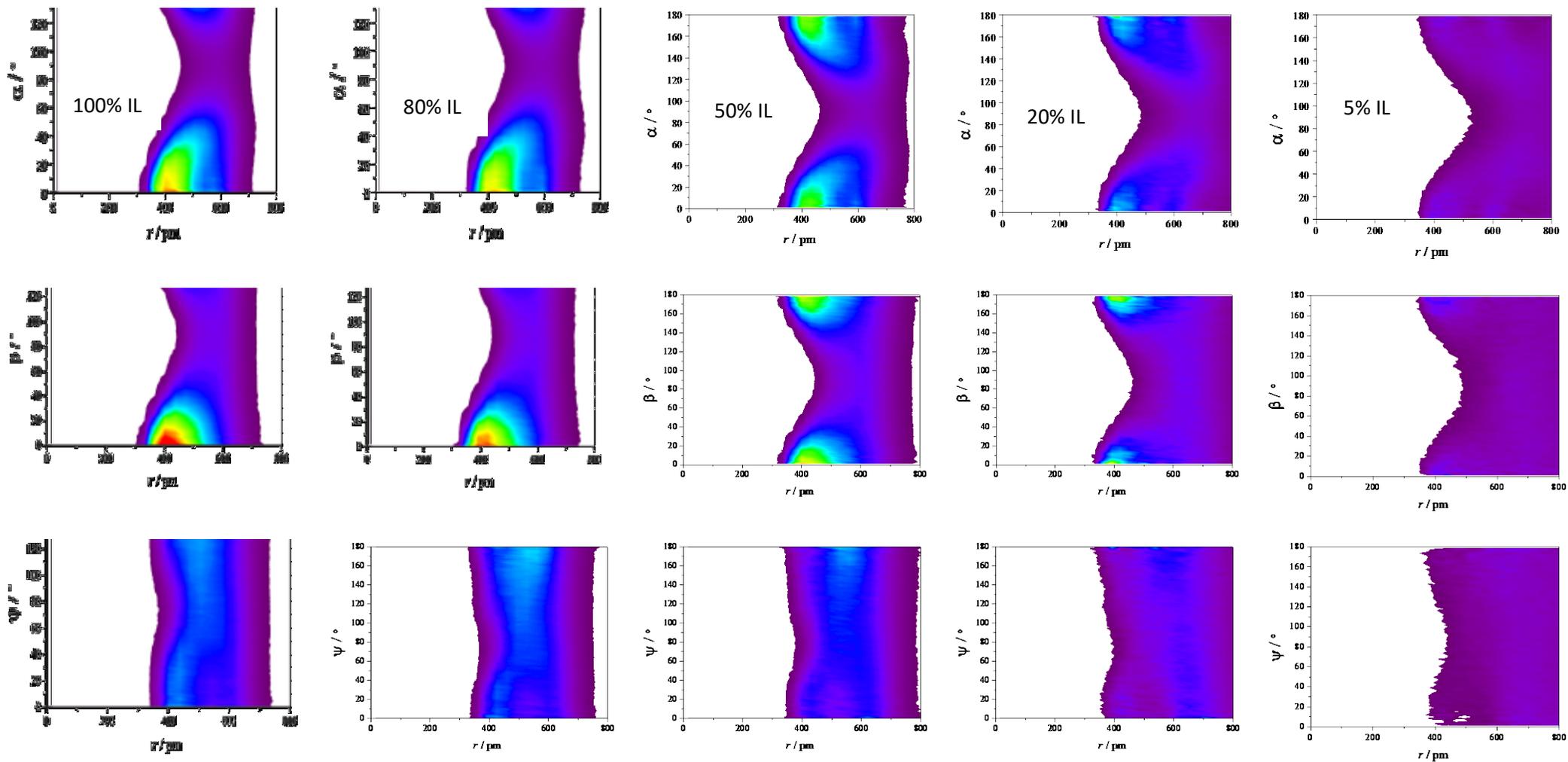


Figure 8. Combined Distribution Functions (CDFs) of cation-cation interactions in investigated IL + γ BL system for different compositions, where r represents the distance between centers of the imidazolium rings. Angles α , β , and ψ are explained in text and schematically presented in **Figure 6**.

Another information that we can obtain from the simulation is to quantify the change in the interactions between the constituents (cation-anion, cation-cation, anion-anion, cation-solvent and anion-solvent) of the mixture. This is quantified through the calculation of the average distance between a reference constituent and its close nearest neighbour (center of mass). The short distance between two constituents is correlated with strong interaction, although one needs to characterize the orientation to quantify the interactions fully. The behaviour of these average distances as a function of the ionic liquid mole fraction is shown in Figure 9.

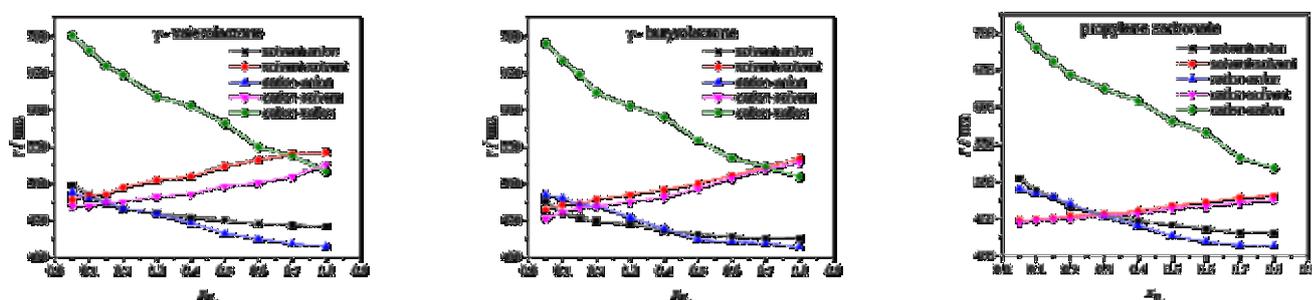


Figure 9. Center of mass distances between components of three investigated mixtures

Knowing the molar volumes of the pure components, V^0 for $[C_1C_4im][DCA]$ and V^0 for solvents, the partial molar volumes of the components, V_1 and V_2 can be calculated from the expressions (3) and (4), using the parameters A_i obtained from equation (2) and presented in Table S3:

$$V_1 = V_1^0 + (1-x) \sum_{i=0}^{i=n} A_i (1-x)^i - x(1-x) \sum_{i=0}^{i=n} A_i (1-x)^{i-1} \quad (3)$$

$$V_2 = V_2^0 + x \sum_{i=0}^{i=n} A_i (1-x)^i + 2x^2(1-x) \sum_{i=0}^{i=n} A_i (1-x)^{i-1} \quad (4)$$

In the case when $x_1 = 0$ or $x_2 = 0$, the equations (3) and (4) may be transformed into:

$$V_1^E = V_1^\infty + \sum_{i=0}^{i=n} A_i^E \quad (x_1 \rightarrow 0) \quad (5)$$

$$V_2^E = V_2^\infty + \sum_{i=0}^{i=n} A_i^E B_i \quad (x_2 \rightarrow 0) \quad (6)$$

where V_1^∞ and V_2^∞ are the partial molar volumes of the components at infinite dilution. Useful information about solute-solvent interactions can be obtained knowing the partial molar properties at infinite dilution. At infinite dilution, solute-solute interactions can be neglected. Thus rearrangement of the equations (5) and (6) gives partial excess molar volumes at infinite dilution of the components

$(V_1^E)^\infty$ and $(V_2^E)^\infty$ $(V_1^E)^\infty (V_2^E)^\infty$:

$$(V_1^E)^\infty = \sum_{i=0}^{i=n} A_i^E \quad (7)$$

$$(V_2^E)^\infty = \sum_{i=0}^{i=n} A_i^E B_i \quad (8)$$

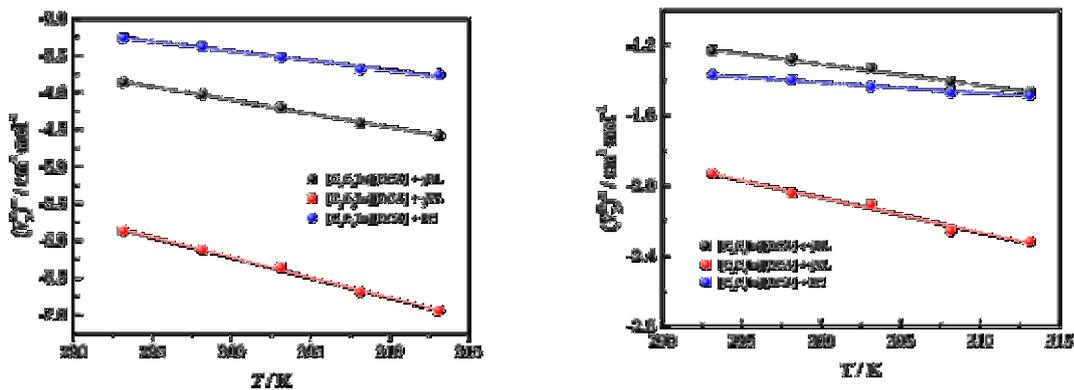


Figure 10. Partial excess molar volumes at infinite dilution of IL $(V_1^E)^\infty$ and solvent $(V_2^E)^\infty$ for three investigated systems

The partial molar volumes at infinite dilution are presented in Figure 10. Negative values of these properties for both components also indicate the stronger ion-dipole interactions between ions and solvent molecules compared to the interactions in pure components. This is consistent with the claim that intermolecular interactions in pure solvents follow the order PC > γ BL > γ VL.

On the basis of the volumetric data, one can also calculate the isobaric thermal expansivity.

Thermal expansion coefficients, α_p and α_{ip} , for the pure components and mixtures, respectively, are defined as:

$$\alpha_p = \frac{1}{V_i} \left(\frac{\partial V_i}{\partial T} \right)_P \quad (9)$$

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (10)$$

At constant molality, the expression (12) can be written as:

$$\alpha_p = - \frac{1}{\alpha} \left(\frac{\partial \alpha}{\partial T} \right)_P \quad (11)$$

In addition, the excess thermal expansion coefficient α_p^E was calculated using the equation (12):

$$\alpha_p^E = \alpha_p - \sum_{i=1}^{i=2} \phi_i \alpha_{ip} \quad (12)$$

where ϕ_i is the volume fraction of component i , defined as:

$$\phi_i = \frac{V_i}{\sum_{i=1}^{i=2} V_i} \quad (13)$$

The obtained results are presented in Figure 11.

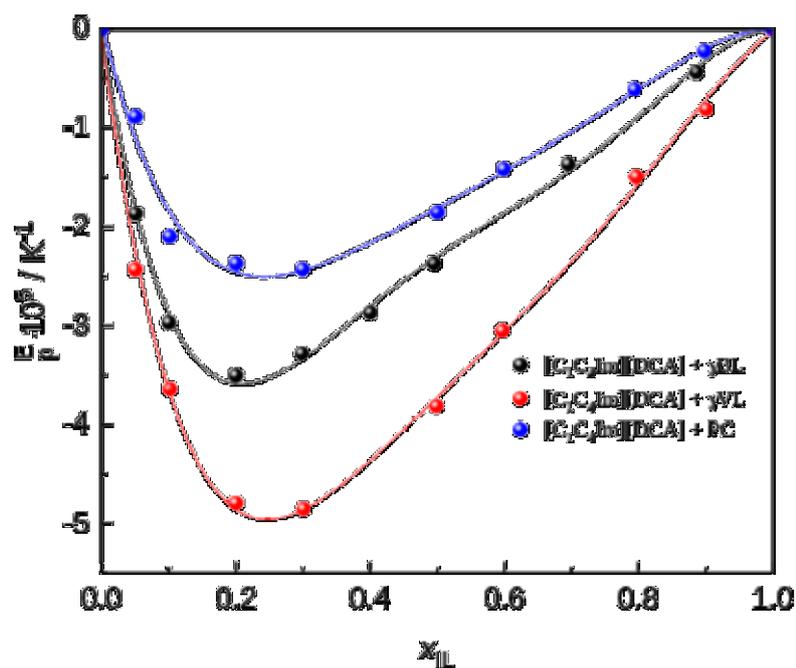


Figure 11. Excess thermal expansion coefficient α_p^E for three investigated binary mixtures

As shown in Figure 11, the α_p^E deviation is negative over the whole composition range for all three systems. Expansivity coefficients are related to the fluctuation of the cross term of enthalpic interaction and interaction volume of liquids and mixtures. The excess amount may reflect the molecular orientation and packing of mixtures. Positive α_p^E values indicate pronounced self-association while more negative values of excess thermal expansion coefficient obtained in our case with order $PC > \gamma_{BL} > \gamma_{VL}$ may indicate the weakest solvent-solvent interactions in case of γ_{VL} .

4 Conclusions

Densities of ([C₁C₄Im][DCA] + γ VL and ([C₁C₄Im][DCA] + PC) mixtures were measured in the temperature range from (273.15 to 323.15) K and volumetric properties are compared with data for previously measured system [C₁C₄Im][DCA] + γ BL. Negative excess molar volume values in the whole range of IL mole fraction and at all temperatures indicate stronger interactions between molecular solvents and IL compared to the pure components. In order to understand which interactions can contribute to negative excess volumes structural analysis from MD simulation trajectories has been performed. Orientational correlations were characterized by several combined angular and distance distribution functions between first neighbour molecules. Results suggest that strength of solvent-solvent interactions plays a significant role in the observed difference in volumetric properties of these binary mixtures. Calculated hydrogen bond geometry indicates that the hydrogen bond interaction in the three pure molecular solvents is weak and follows the order PC > γ BL > γ VL.

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