

**REVIEW OF EXITING GROUP CONTRIBUTION METHODS
FOR PREDICTING OF THE (p,ρ,T) DATA OF EVEN ALKYL CHAINS
(C₂, C₄, C₆, C₈) IMIDAZOLIUM IONIC LIQUIDS WITH [NTf₂]⁻ ANION**

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Abstract

A wide literature analysis of exiting Group Contribution Methods (GCM) for predicting the thermophysical properties of ionic liquids (ILs) was analysed. The various possibilities for a linear generalized equation for lattice potential energies/enthalpies of ILs; an approach to estimate thermo-chemical radius and close packed single ion volume data for ions of salt types was discussed. The literature recommendations for “ideal” volumetric behaviour of ILs, a constant variation of the molar volume with the addition of carbon atoms on alkyl chain were attended during the investigations. The new research applications in the field of hetero-segmented statistical associating fluid theory (hetero-SAFT) to describe (p,ρ,T) data of imidazolium ILs was discussed. The following four ILs with [NTf₂]⁻ anion (F₆C₂O₄NS₂):

- 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIM][NTf₂],
 - 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIM][NTf₂],
 - 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [HMIM][NTf₂],
 - 1-Octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [OMIM][NTf₂]
- were examined for these methods and obtained fitting results were discussed. The chemical structure of these ILs was analysed and divided into the various groups. The molar volume and density of these ILs, at reference temperature ($T = 298.15$ K) and ambient pressure ($p = 0.101$ MPa), is defined as the reference point. As the next step, predicting the density of ILs across a wide range of temperatures and at reference pressure $p_0 = 0.101$ MPa were carried out. The measured in our laboratory (p,ρ,T) data of these ILs across a wide temperature range and at high pressures were compared with the predicted values using a GCM and good agreement between them was obtained

Keywords: *group contribution method, density, high temperature, ionic liquid, molar volume*

Introduction

There are various non-experimental methods and models for analyzing/predicting thermophysical properties of ionic liquids (ILs). One from them is an empirical/theoretical GCM. They adopted an equation of state arising from more general thermodynamic or statistical mechanical theories. The primary benefit of applying this method is the accuracy of molar volume ($V_m / \text{m}^3 \cdot \text{mol}^{-1}$) calculations. For this purpose, ILs are divided into cations and anions,

and these groups are then separated into smaller groups, such as $-\text{CH}_2-$, $-\text{CH}_3-$, $-\text{CF}_3-$, $-\text{NTf}_2-$, etc. The GCM application to the even alkyl chains (C_2 , C_4 , C_6 , C_8) ILs with $[\text{NTf}_2]^-$ anion ($\text{F}_6\text{C}_2\text{O}_4\text{NS}_2$) is discussed in this paper.

Literature Analysis of Various Methods

Jenkins *et al.* [1] (1999) proposed a predictive method involving a linear generalized equation for lattice potential energies/enthalpies of ILs; it developed an approach to estimate thermochemical radius and close packed single ion volume data for ions of salt types that had not yet been determined. In doing so, they provided an extended database of ion parameters. The molecular volume is calculated from the unit cell parameters, and this relationship is then used to estimate the combined radii ($r_a + r_c$) of salts and predict individual ion radii. The density is determined as:

$$\rho = \frac{M}{N_A \cdot V_m}, \quad (1)$$

where M is molecular mass, N_A is Avogadro constant, and V_m is the molecular volume of salt (i.e., the linear sum of cation and anion volumes). Esperança *et al.* [2] (2006) also noted an impressive degree of linearity in the plots of molar volume (V_m) of ILs versus the number of carbons in the alkyl chain (n), and proposed to calculate the molar volume as sum of effective volume of cations (V_c^*) and anions (V_a^*):

$$V_m = V_c^* + V_a^*, \quad (2)$$

Additionally, Slattery *et al.* [3] (2007) proposed the molar volume of ILs as the sum of individual contributions of the cations and anions. They suggested using the crystallographic data or quantum chemical calculations for estimating contributions from particular ions, which was used by Rebelo *et al.* [4] (2007) for the 1-alkyl-3-methylimidazolium ILs. Based on the results, the authors decided that molar volume increases proportionally to the number of CH_2 units in the alkyl chain attached to the cation.

Ye and Shreeve [5] (2007) reported a method of group additivity for estimating density of ILs and salts. A linear relationship between the density in solid and liquid states of ionic liquids was reported. They applied this method towards estimating the thermochemical radius and closed packed volume of single ions, which was then used to analyse GCM for ILs at room temperature and ambient pressure. Volume parameters of groups and fragments for salts were calculated, and densities for various ILs were predicted.

Gardas and Coutinho [6] (2008) extended the model of Ye and Shreeve [5] across the wider temperature range $T = (273.15 \text{ to } 393.15 \text{ K})$ and pressures $p = (0.1 \text{ to } 100 \text{ MPa})$. The new density correlation was checked using experimental literature densities for imidazolium, pyridinium, pyrrolidinium, and phosphonium cations ILs. They also used the Jenkins *et al.* [1] procedure, from equation (1), to obtain the pressure and temperature dependent molecular volume (V_m):

$$V_m = V_0(a + bT + cp), \quad (3)$$

where $V_0/\text{m}^3 \cdot \text{molecule}^{-1}$ is the molecular volume at room temperature and ambient pressure

(calculated using the ion and group parameters taken from the investigations of Jenkins *et al.* [1]), $a = (1+x)$ with $x = -(\alpha_p T_0 + \kappa_T p_0)$, b is α_p (the isobaric expansivity), and c is κ_T (the isothermal compressibility). In this case, eqn. (1) for the calculation of density (ρ) can be writing as:

$$\rho = \frac{M}{N_A \cdot V_0 (a + bT + cp)} \quad (4)$$

The coefficients a , b , and c were obtained by fitting of available experimental values.

Jacquemin *et al.* [7, 8] (2008) developed another form of GCM, based on the “ideal” volumetric behaviour of ILs. They analysed already published literature values and indicated that, for a range of anions, the molar volumes vary linearly as a function of the number of carbons in the alkyl chain; a constant variation of the molar volume was found with the addition of two carbon atoms on this alkyl chain, irrespective of the anion. They used this moment in the first paper [7], to calculate molar volumes (V_m) of cations and anions:

$$V_k^* \text{ or } V_a^* = N_A \cdot \left(\frac{4\pi r^3}{3} \right), \quad (5)$$

where V_k^* or $V_a^*/m^3 \cdot \text{molecule}^{-1}$ is the molecular volume of cation or anion, respectively, at room temperature and ambient pressure, and r is the radius of the cation or anion hard sphere. The authors predicted the temperature dependence of various ILs. The contribution of two $-\text{CH}_2-$ groups to the molar volume was obtained from the difference between the molar volume of [EMIM][NTf₂] and [BMIM][NTf₂], as a function of temperature. In another publication, Jacquemin *et al.* [8] (2008) used this method for the prediction of density at higher pressures, up to $p = 207$ MPa. Effective molar volumes of the constituting ions were considered temperature and pressure dependent. Being able to predict density across a wide range of temperatures and at high pressures make it possible to define important thermophysical properties, such as isothermal compressibility and the thermal expansion coefficient. The authors analysed the 1-alkyl-3-methylimidazolium effective molar volumes as a function of the alkyl chain, at a fixed temperature, and decided that there existed a linear trend. $[\text{C}_n\text{MIM}]^+$ cations beginning from $n = 0$ were used to test this method and a new relationship was calculated, expressed as a function of δT :

$$V_{[\text{C}_n\text{MIM}]^+}^* (\delta T) = V_{[\text{C}_0\text{MIM}]^+}^* (\delta T) + n \cdot a^* , \quad (6)$$

where a^* is the contribution to the molar volume of each extra $-\text{CH}_2-$ group on the alkyl chain and n is the total number of $-\text{CH}_2-$ groups in that alkyl chain, Jacquemin *et al.* [8]. Temperature dependence of effective molar volumes was described using a second order polynomial equation and pressure was calculated using a Tait-type equation with four adjustable parameters. A large number of IL density values found in the literature were used during the development of the model and a $\Delta V_m/V_m = \pm 0.36\%$ mean percent deviation of IL molar volumes was obtained.

A simple and accurate GCM was developed by Lazzús [9] (2010) to estimate the molar volume of ILs at $T = 298.15$ K and atmospheric pressure:

$$V_0 = C + \sum_i n_i \Delta V_{c_i} + \sum_j n_j \Delta V_{a_j}, \quad (7)$$

where $C = 0.042$ is the constant of fitting, n_i and n_j are the occurrence of the groups i and j in the compound, and ΔV_c and ΔV_a are the contributions of the cation and anion groups to the molar volume, respectively. The GCM method is based on the principle of polylinearity, which was used during the prediction of density:

$$\rho_{T,p} = \rho_0 + \alpha(T - T_0) + \beta(p - p_0), \quad (8)$$

where ρ_0 is the density (at $T_0 = 298.15$ K and $p_0 = 0.1$ MPa), $\alpha = -0.719$, and $\beta = 0.5698$. The molar volumes and density at these state parameters were calculated for the 210 ILs with available literature information. Afterwards, the model was tested for another 100 ILs that lacked experimental density values. Based on the results, linear dependency of density on temperature and pressure was assumed and the universal coefficients – using the 3530 (p, ρ, T) data of 76 ILs at $T = (258.15$ to $393.15)$ K and $p = (0.1$ to $207)$ MPa – were obtained.

Qiao *et al.* [10] (2010) developed the next linear GCM for predicting (p, ρ, T) data of many ILs. They analysed all molecular structures, and 51 groups were selected for the GCM to calculate density (dependent on temperature and pressure) in linear form:

$$\rho_{T,p} = A + B(p/\text{MPa}) + C(T/\text{K}), \quad (9)$$

where A , B , and C are the parameters depending on the number n_i of group i in the compound as follows:

$$A = \sum_{i=1}^{51} n_i a_i + a_0; B = \sum_{i=1}^{51} n_i b_i + b_0; C = \sum_{i=1}^{51} n_i c_i + c_0 \quad (10)$$

Here, a_i , b_i , and c_i are contributions of group i for A , B , and C , respectively. These parameters were applied to fit about 6500 literature density values.

Some studies have used hetero-segmented statistical associating fluid theory (hetero-SAFT) to describe (p, ρ, T) data of imidazolium ILs, but an electrostatic interaction was not taken into account by some authors. Including an explicit electrostatic term to the residual Helmholtz energy, which can substantially improve density prediction results, is an idea proposed by Wang *et al.* [11] in 2009 and [12] in 2010. Applying this idea to ILs is substantially limited, however, because it assumes whole alkyl chains are distinct functional groups, rather than considering methyl and methylene units to be basic building blocks; this point is discussed by Padaszynski and Domanska [13] (2012), who also published a new simple generalized correlation for predicting (p, ρ, T) data of ILs. While developing their method they used literature data on density for 1,028 ILs, which they then divided into 177 functional groups. The complete set of functional groups was divided into three main subsets: cation cores, anions cores, and substituted groups. Results found the reference molar volume of 828 ILs, predicted through optimization of the sum of squared residuals between calculated and experimental values. The authors indicated that the method developed by Jacquemin *et al.* [7-8] is very accurate for predicting density at high pressures and across a wide range of temperatures. A Tait-type equation, with four adjustable parameters, was used to define high-pressure density values. Padaszynski and Domanska [13] used a Tait-type equation in another form to predict density results at high pressures.

Based on the above review of available methods, as well as a comparison to literature

values, we find that present measured (p,ρ,T) results for the studied ILs are in good agreement with findings from other researchers. This allowed us to use present data to further assess models available in the literature, and to evaluate and predict the volumetric properties of ILs. Resultantly, we used the predictive capability of five main GCM, published by Gardas and Coutinho [6], Jacquemin *et al.* [7-8], Lazzús *et al.* [9], Qiao *et al.* [10] and Paduszynski and Domanska [13]. The For this particular ILs – under these temperature and pressure conditions – the Paduszynski and Domanska [13] GCM was more accurate, within a predictive capability ($\Delta\rho/\rho = \pm 0.07\%$) close to the overall uncertainty of the density data reported herein. The various important information of Gardas and Coutinho [6], Jacquemin *et al.* [7-8], Lazzús *et al.* [9], and Qiao *et al.* [10] were attended during the calculations.

As an example, we present accuracy predictions of (p,ρ,T) data for ILs with $[\text{NTf}_2]^-$ anion ($\text{F}_6\text{C}_2\text{O}_4\text{NS}_2$)⁻:

- 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIM][NTf₂],
- 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIM][NTf₂],
- 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [HMIM][NTf₂],
- 1-Octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [OMIM][NTf₂].

The chemical structure of cation $[\text{EMIM}]^+$ is $\text{C}_8\text{H}_{11}\text{N}_2$, of cation $[\text{BMIM}]^+$ - $\text{C}_{10}\text{H}_{15}\text{N}_2$, of cation $[\text{HMIM}]^+$ - $\text{C}_{12}\text{H}_{19}\text{N}_2$ and of cation $[\text{OMIM}]^+$ - $\text{C}_{14}\text{H}_{23}\text{N}_2$ (Figure 1):

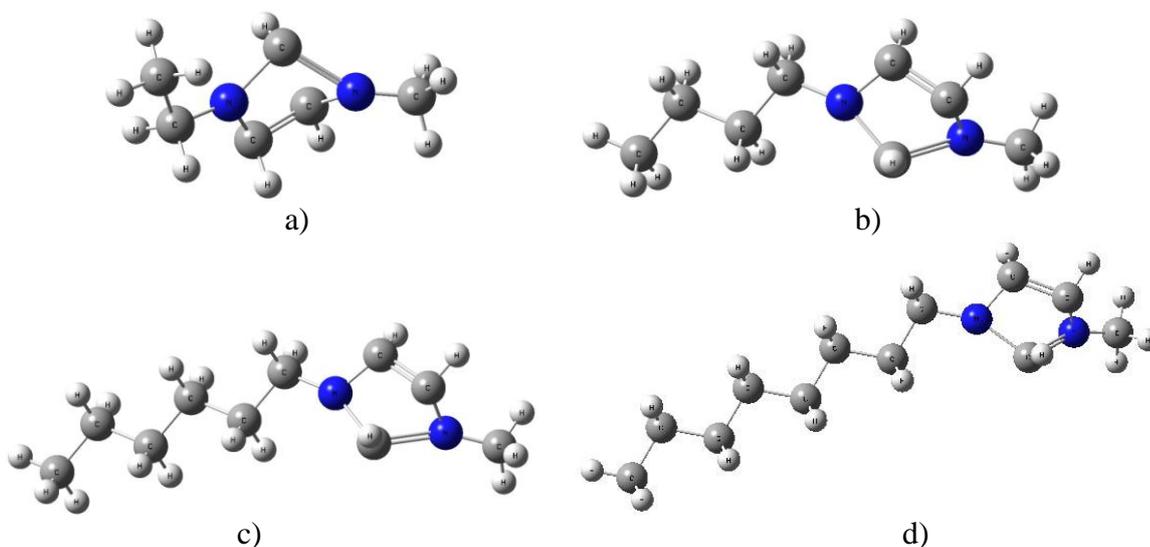


Fig. 1. Chemical structures of $[\text{C}_n\text{MIM}]^+$ cations: a) $[\text{EMIM}]^+$, b) $[\text{BMIM}]^+$, c) $[\text{HMIM}]^+$, d) $[\text{OMIM}]^+$, where in dark grow described carbon (C), in light grow - hydrogen (H), in blue - nitrogen (N)

As seen in Figure 1, these cations can be divided into the following groups: a) a central imidazolium group (there are three C–H groups in the central chain); b) N–CH₂ and N–CH₃

bonds (in the central chain); c) a CH₃ group (in the linear alkyl chain); d) CH₂ groups (in the linear alkyl chain for n = 2 is 0, for n = 4 is 2, for n = 6 is 4, for n = 8 is 6).

The chemical structure of anion [NTf₂]⁻ is F₆C₂O₄NS₂ (Fig. 2):

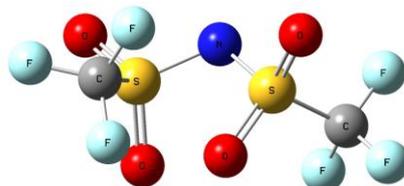


Fig. 2. Chemical structure of [NTf₂]⁻ anion, where in light blue is fluor (F), in light grey - carbon (C), in red - oxygen (O), in yellow - phosphor (S) and in blue - nitrogen (N)

After analysing the chemical structure of these ILs, we determined that it is possible to divide the structure into the following groups:

- Central C₃H₃ imidazolium group without N connection;
- N-CH₂ or N-CH₃ bonds in the central chain;
- CH₂ group in a linear alkyl chain;
- CH₃ group in a linear alkyl chain;
- F₆C₂O₄NS₂⁻ [NTf₂]⁻ anion connection.

The molar volume of these ILs, at reference temperature ($T = 298.15$ K) and ambient pressure ($p = 0.101$ MPa), is defined as the reference point. The bond length between atoms and their van der Waals radii are used as the basis for calculations of effective molar volumes. The molar volume at these reference state parameters is calculated as the sum of effective volumes of cations and anions:

$$V_m(T_0, p_0) = V_k^* + V_a^*, \quad (11)$$

$$V_k^* \text{ or } V_a^* = N_A \cdot \left(\frac{4\pi r^3}{3} \right), \quad (12)$$

where V_k^* and V_a^* are the effective volumes of cations and anions, respectively, N_A is Avogadro number ($N_A = 6,022 \cdot 10^{23} \text{ mol}^{-1}$), and r is the group's radius (i.e., sum of the bond length between atoms and their van der Waals radius). With this, we can calculate the effective volumes of all groups [7, 8, 13]:

- Central C₃H₃ imidazolium group without N connection: $V_{m,i} = 0.00005974 \text{ m}^3 \cdot \text{mol}^{-1}$;
- N-CH₃ connection in the central chain: $V_{m,\text{NCH}_3} = 0.00001199 \text{ m}^3 \cdot \text{mol}^{-1}$;
- N-CH₂ connection in the central chain: $V_{m,\text{NCH}_2} = 0.000002881 \text{ m}^3 \cdot \text{mol}^{-1}$;
- CH₂ group in a linear alkyl chain: $V_{m,\text{CH}_2} = 0.00001673 \text{ m}^3 \cdot \text{mol}^{-1}$;
- CH₃ group in a linear alkyl chain: $V_{m,\text{CH}_3} = 0.00002616 \text{ m}^3 \cdot \text{mol}^{-1}$;
- F₆C₂O₄NS₂⁻ [NTf₂]⁻ anion connection: $V_{m,\text{NTf}_2} = 0.0001582 \text{ m}^3 \cdot \text{mol}^{-1}$.

Now, we can calculate the ILs molar volumes V_m at $T_0 = 298.15$ K and $p_0 = 0.1$ MPa separately using each groups contribution:

$$V_{m,[EMIM][NTf_2]} = V_{m,i} + V_{m,NCH_3} + V_{m,NCH_2} + 0 \cdot V_{m,CH_2} + V_{m,CH_3} + V_{m,F_6C_2O_4NS_2} = (0.00005974 + 0.00001199 + 0.000002881 + 0 \cdot 0.00001673 + 0.00002616 + 0.0001582) = 0.000258971 \text{ m}^3 \cdot \text{mol}^{-1}.$$

$$V_{m,[BMIM][NTf_2]} = V_{m,i} + V_{m,NCH_3} + V_{m,NCH_2} + 2 \cdot V_{m,CH_2} + V_{m,CH_3} + V_{m,F_6C_2O_4NS_2} = (0.00005974 + 0.00001199 + 0.000002881 + 2 \cdot 0.00001673 + 0.00002616 + 0.0001582) = 0.000292431 \text{ m}^3 \cdot \text{mol}^{-1}.$$

$$V_{m,[HMIM][NTf_2]} = V_{m,i} + V_{m,NCH_3} + V_{m,NCH_2} + 4 \cdot V_{m,CH_2} + V_{m,CH_3} + V_{m,F_6C_2O_4NS_2} = (0.00005974 + 0.00001199 + 0.000002881 + 4 \cdot 0.00001673 + 0.00002616 + 0.0001582) = 0.000325891 \text{ m}^3 \cdot \text{mol}^{-1}.$$

$$V_{m,[OMIM][NTf_2]} = V_{m,i} + V_{m,NCH_3} + V_{m,NCH_2} + 6 \cdot V_{m,CH_2} + V_{m,CH_3} + V_{m,F_6C_2O_4NS_2} = (0.00005974 + 0.00001199 + 0.000002881 + 6 \cdot 0.00001673 + 0.00002616 + 0.0001582) = 0.000359351 \text{ m}^3 \cdot \text{mol}^{-1}.$$

After defining the molar volumes of ILs at the reference point ($T_0 = 298.15$ K and $p_0 = 0.1$ MPa), we can calculate the density of them at this point [13]:

$$\rho(T_0, p_0) = \frac{M}{V_m(T_0, p_0)}, \quad (13)$$

where M is the molecular mass of the ILs, in $\text{kg} \cdot \text{mol}^{-1}$ and it is for [EMIM][NTf₂] is $M(\text{C}_8\text{H}_{11}\text{F}_6\text{N}_3\text{O}_4\text{S}_2) = 0.3913155 \text{ kg} \cdot \text{mol}^{-1}$; for [BMIM][NTf₂] – $M(\text{C}_{10}\text{H}_{15}\text{N}_3\text{F}_6\text{O}_4\text{S}_2) = 0.4193692 \text{ kg} \cdot \text{mol}^{-1}$; for [HMIM][NTf₂] – $M(\text{C}_{12}\text{H}_{19}\text{N}_3\text{F}_6\text{O}_4\text{S}_2) = 0.4474230 \text{ kg} \cdot \text{mol}^{-1}$; and for [OMIM][NTf₂] – $M(\text{C}_{14}\text{H}_{23}\text{N}_3\text{F}_6\text{O}_4\text{S}_2) = 0.4754767 \text{ kg} \cdot \text{mol}^{-1}$.

The next step is predicting the density of ILs across a wide range of temperatures and at reference pressure $p_0 = 0.1$ MPa [13]:

$$\rho(T, p_0) = \frac{M}{V_m \cdot (T_0, p_0) \cdot [1 + a_0(T - T_0)]} = \frac{\rho(T_0, p_0)}{1 + a_0 \cdot (T - T_0)}, \quad (14)$$

where a_0 is an adjustable parameter (given in Table 1 for the investigated ILs). At $T = T_0$, the density is equal to the reference density $\rho(T, p) = \rho(T, p_0)$.

Lastly, we can predict the (p,ρ,T) data of ILs across a wide temperature range and at high pressures. Most of the literature investigations used the Tait-type equation for this purpose [13]:

$$\rho(T, p) = \frac{\rho(T, p_0)}{1 - C \cdot \ln[1 + (p - p_0)B(T)]}, \quad (15)$$

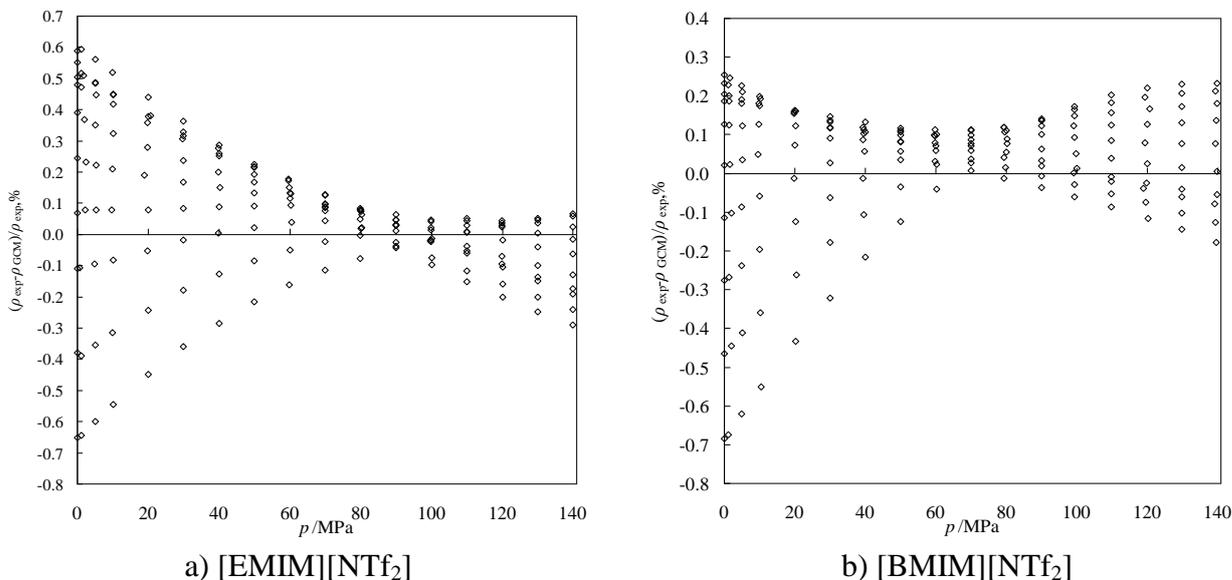
where $B(T) = \frac{1 + b_1 \cdot (T - T_0)}{b_0}$ and C are the coefficients of Tait equation, and b_0 and b_1 are the adjustable coefficients (given in Table 1 for the investigated ILs). In eqn. (15), if pressure is equal to the reference pressure ($p = p_0$), then the density will be equal to the reference density $\rho(T, p) = \rho(T, p_0)$.

Predicted densities across a wide range of temperatures and at ambient and high pressures were compared with the experimental (p, ρ, T) results measured in our laboratory for [EMIM][NTf₂] from [14], for [BMIM][NTf₂] from [15], for [HMIM][NTf₂] from [16] and for [OMIM][NTf₂] from [17]. The molecular mass dependence of all four empiric coefficients is appr. linear and it is good possibility to interpolation of them for odd alkyl chains (C₃, C₅, C₇) ILs with [NTf₂]⁻ anion (F₆C₂O₄NS₂), which is planned in next research works of our group.

Table 1. Coefficients of Tait equation and adjustable coefficients for the GCM predictions of ILs density.

IL	a_0	b_0 / MPa	b_1 /K ⁻¹	C	$\Delta\rho/\rho$, %
[EMIM][NTf ₂]	0.00060	173	0.0012	0.097	± 0.1152
[BMIM][NTf ₂]	0.00062	176	0.0018	0.096	± 0.0852
[HMIM][NTf ₂]	0.00064	179	0.0024	0.095	± 0.1265
[OMIM][NTf ₂]	0.00066	182	0.0030	0.094	± 0.1174

A plot of the deviation between experimental and predicted values, using GCM density data for all four investigated ILs is shown in Fig. 3. From these figures it is to be seen, that the experimental density values of [EMIM][NTf₂], [BMIM][NTf₂], [HMIM][NTf₂] and [OMIM][NTf₂] are predicting using GCM method with the average percent deviation (APD) of measurement uncertainties. Large percent deviation (PD) are located around the ambient pressure, and they are decreasing by the increasing of pressure for [EMIM][NTf₂], [BMIM][NTf₂], [HMIM][NTf₂], except [OMIM][NTf₂], where the PD are smaller around the ambient pressure and increase at high pressures.



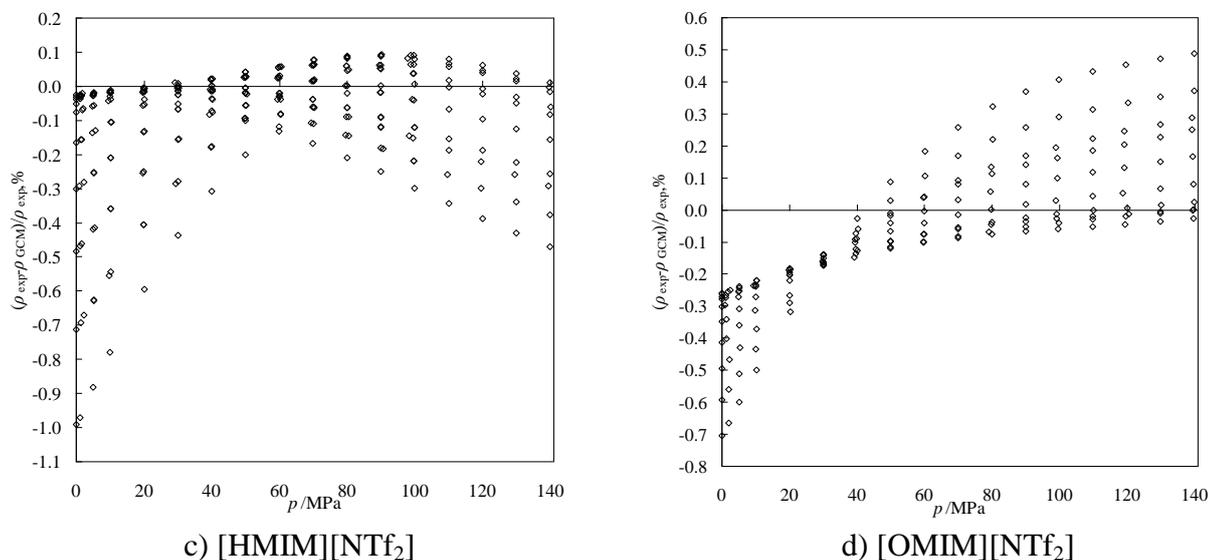


Fig. 3. A plot of the deviation between experimental $\rho_{\text{exp.}}$ and GCM predicted density ρ_{GCM} values of investigated ILs: a) [EMIM][NTf₂], b) [BMIM][NTf₂], c) [HMIM][NTf₂] and d) [OMIM][NTf₂]

Conclusion

A wide literature analysis of exiting GCM for predicting the thermophysical properties of ILs were described. The four ILs with [NTf₂]⁻ anion (F₆C₂O₄NS₂), like as [EMIM][NTf₂], [BMIM][NTf₂], [HMIM][NTf₂], [OMIM][NTf₂] were predicted using the GCM described by Paduszynski and Domanska [13] included the additional information of Jacquemin *et al.* [7-8], Gardas and Coutinho [6], Lazzús *et al.* [9], and Qiao *et al.* [10]. The measured (p,ρ,T) results for these ILs are in good agreement with the prediction of them using GCM. The molecular mass dependence of all four empiric coefficients is approximately linear and it is good possibility to interpolation of them for odd alkyl chains (C₃, C₅, C₇) ILs with [NTf₂]⁻ anion (F₆C₂O₄NS₂).

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