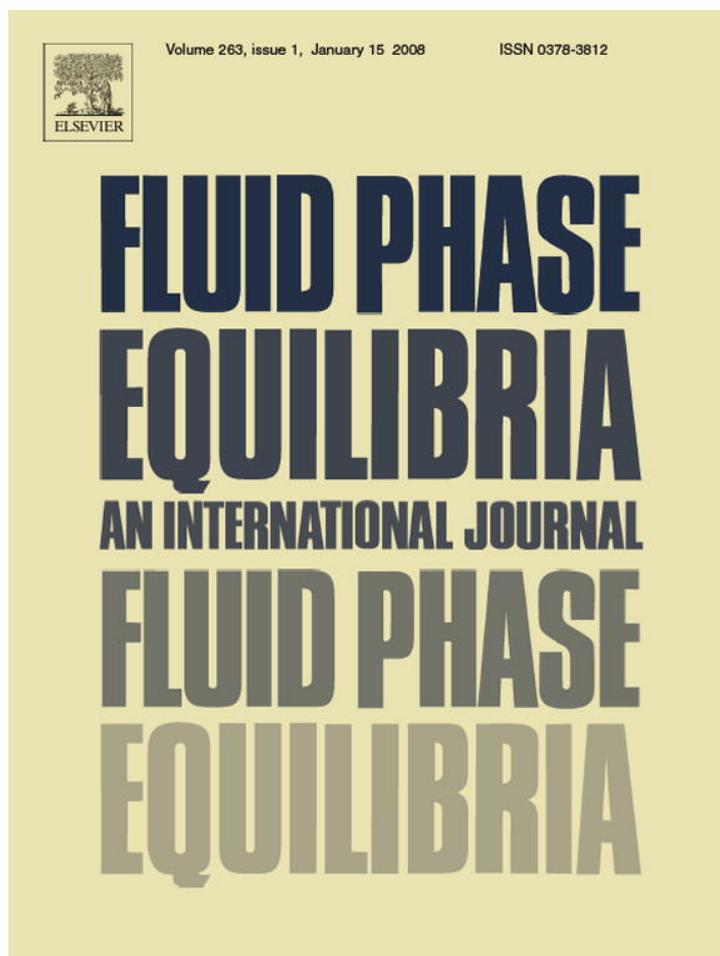


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Extension of the Ye and Shreeve group contribution method for density estimation of ionic liquids in a wide range of temperatures and pressures

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Abstract

An extension of the Ye and Shreeve group contribution method [C. Ye, J.M. Shreeve, *J. Phys. Chem. A* 111 (2007) 1456–1461] for the estimation of densities of ionic liquids (ILs) is here proposed. The new version here presented allows the estimation of densities of ionic liquids in wide ranges of temperature and pressure using the previously proposed parameter table. Coefficients of new density correlation proposed were estimated using experimental densities of nine imidazolium-based ionic liquids. The new density correlation was tested against experimental densities available in literature for ionic liquids based on imidazolium, pyridinium, pyrrolidinium and phosphonium cations. Predicted densities are in good agreement with experimental literature data in a wide range of temperatures (273.15–393.15 K) and pressures (0.10–100 MPa). For imidazolium-based ILs, the mean percent deviation (MPD) is 0.45% and 1.49% for phosphonium-based ILs. A low MPD ranging from 0.41% to 1.57% was also observed for pyridinium and pyrrolidinium-based ILs.

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1. Introduction

Ionic liquids (ILs) are a combination of bulky, asymmetric N-containing organic cations (e.g., imidazole, pyrrole, pyridine, etc.) and anions of wide variety, ranging from simple inorganic ions (e.g., halides) to more complex organic species (e.g., triflate). Since a large number of cationic and anionic structures

combinations are possible it is impossible to measure the thermophysical properties for all conceivable ionic liquids. During the last few years, measurements of the thermophysical and thermodynamic properties of ILs have increased remarkably but they are by no means exhaustive [1–34]. Although experimental measurements are available for common fluids, experimental data for many new fluids of industrial interest are non-existent or tend

Abbreviations: IL, ionic liquid; PVT, pressure, volume and temperature; EOS, equation-of-state; AAV, average atom volume; MPD, mean percent deviation; [C₂mim][NTf₂], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C₃mim][NTf₂], 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C₄mim][NTf₂], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C₅mim][NTf₂], 1-pentyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C₆mim][NTf₂], 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C₇mim][NTf₂], 1-heptyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C₈mim][NTf₂], 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C₁₀mim][NTf₂], 1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C₂mim][BF₄], 1-ethyl-3-methylimidazolium tetrafluoroborate; [C₄mim][BF₄], 1-butyl-3-methylimidazolium tetrafluoroborate; [C₈mim][BF₄], 1-octyl-3-methylimidazolium tetrafluoroborate; [C₄mim][PF₆], 1-butyl-3-methylimidazolium hexafluorophosphate; [C₆mim][PF₆], 1-hexyl-3-methylimidazolium hexafluorophosphate; [C₈mim][PF₆], 1-octyl-3-methylimidazolium hexafluorophosphate; [C₄mim][C(CN)₃], 1-butyl-3-methylimidazolium tricyanomethane; [C₄mim][MeSO₄], 1-butyl-3-methylimidazolium methylsulphate; [(C₆H₁₃)₃P(C₁₄H₂₉)][NTf₂], trihexyl(tetradecyl) phosphonium bis[(trifluoromethyl) sulfonyl]imide; [(C₆H₁₃)₃P(C₁₄H₂₉)][Cl], trihexyl(tetradecyl) phosphonium chloride; [(C₆H₁₃)₃P(C₁₄H₂₉)][Ac], trihexyl(tetradecyl) phosphonium acetate; [C₂py][NTf₂], 1-ethylpyridinium bis[(trifluoromethyl) sulfonyl]imide; [C₂py][BF₄], 1-ethylpyridinium tetrafluoroborate; [C₄py][BF₄], 1-butylpyridinium tetrafluoroborate; [C₄mpy][BF₄], 1-butyl-4-methyl pyridinium tetrafluoroborate; [C₄mpyr][NTf₂], 1-butyl-1-methyl pyrrolidinium bis[(trifluoromethyl) sulfonyl]imide.

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to be restricted to limited regions of the phase diagram. It is necessary to accumulate a sufficiently large data bank on the fundamental physical and chemical properties of ILs, not only for process and product design, but also for the development of adequate correlations and predictive methods for the estimation of these properties in wide ranges of pressure and temperature.

The relationship between pressure, volume and temperature is one of the most fundamental and useful from both a theoretical and a practical standpoint. *PVT* data are particularly important to describe the thermodynamic behavior of fluids and are important for efficient design of chemical products and processes.

The two most commonly used methods of calculating *PVT* properties are equation-of-state (EOS) and *PVT* correlations. The EOSs are computationally demanding, in particular for complex fluids, where they require adequate knowledge and representation of the molecular interactions. On the other hand, *PVT* correlations involve simple mathematical computations and they only require readily available experimental data for a small number of representative compounds.

Several researchers [35–40] proposed different types of parameters for atoms or groups for the density estimation of neutral molecules by group contribution. Hofmann [41] achieved the same by the average atom volume (AAV) method. Density of both neutral molecule as well as ionic species can be computed by high-level ab initio calculations [42,43] which are very expensive and time-consuming. Rebelo and co-workers [12,13,44,45] have proposed a simple model for ILs molar volume prediction, where the molar volume of a given ionic liquid is considered as the sum of the effective molar volumes occupied by the cation and the anion. Using this approach, for a given IL knowing the effective size of the anion it is possible to determine the molar volume of the cation and vice versa. Moreover, it was verified that there is a proportional increment with the methyl groups and that is irrespective to the anion identity. Thus, it was possible to use the molar volumes presented by Rebelo and co-workers [12,13,44,45] for the estimation of the volume of a new anion or cation group. This method has been applied by us to describe the densities of ionic liquids measured at our laboratory [34,46]. On the development of Rebelo's approach Jacquemin [47] also proposed a group contribution method for the ionic liquids density.

In 1999 Jenkins and Roobottom [48] proposed a predictive method for lattice potential energies/enthalpies of ionic solids. They developed an approach to estimate thermochemical radius and close packed single ion volume data for ions for which no salts have yet been prepared, by virtue of the extended database of ion parameters which they provided. The capability of prediction of the molecular (formula unit) volume of new and as yet unprepared materials by combination of single ion volumes can also provide an estimate of the density of that material, considering the fact that effective close-packing ion volumes are additive. Thus the density may be estimated by

$$\rho = \frac{W}{NV} \quad (1)$$

where ρ is the density in kg m^{-3} , W is the molar mass in kg mol^{-1} , N is the Avogadro constant and V is the molecular

volume of the salt, in $\text{m}^3 \text{ molecule}^{-1}$ unit, which is assumed as the linear sum of the volumes of cation (V_+) and anion (V_-).

This method was recently extended to ionic liquids by Ye and Shreeve [49] with success but limited to the estimation of densities at atmospheric pressure and room temperature. Based on this approach it is here proposed an extension of the Ye and Shreeve group contribution method for the estimation of ionic liquids densities in a wide range of temperatures (273.15–393.15 K) and pressures (0.10–100 MPa).

A limited amount of literature data is available on densities of ILs binary mixtures [50–52] and they show that the ILs mixtures studied can be considered as quasi-ideal mixtures. Therefore the ability of the density model here proposed will be evaluated for the estimation of the density of homogeneous binary mixtures of ILs having same cation or anion by comparison with available literature values.

2. Discussion

Most of the ionic liquids are based on imidazolium, phosphonium, pyridinium, pyrrolidinium and tetraalkylammonium cations with anions, such as BF_4^- , PF_6^- , (bis(trifluoromethanesulfonyl) amide (NTf_2^-) and so forth. Therefore, combining the known volumes of cations with the volumes of other functional groups, it is a very convenient way to derive the molecular volume of the various substituted imidazolium, phosphonium, pyridinium or pyrrolidinium-based ionic liquids.

Recently Ye and Shreeve [49] proposed of group additivity method for the estimation of densities of room-temperature ionic liquids (RTILs) and salts. They estimated the density by using Eq. (1) and for that purpose molecular volumes are either calculated following Jenkins' procedure described above, or directly taken from literature [45]. Eq. (1) can be used to estimate the densities of a broad range of ionic liquids with a good accuracy but its application is restricted to 298.15 K and atmospheric pressure. This model is here extended to make it valid for a wide range of temperatures (273.15–393.15 K) and pressures (0.10–100 MPa), as described below.

The isothermal compressibility, κ_T , is defined as

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (2)$$

and the isobaric expansivity, α_P is defined as

$$\alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (3)$$

Combining the pressure and temperature dependence of the molecular volume and integrating this equation the dependency of the molecular volume in pressure and temperature is obtained as

$$V = V_0 e^{(x + \alpha_P T + \kappa_T P)} \quad (4)$$

where V_0 is constant and x is equal to $-(\alpha_P T_0 + \kappa_T P_0)$.

Expanding Eq. (4) in a Taylor series and retaining just the first members of the series Eq. (4) is simplified on

$$V = V_0(a + bT + cP) \quad (5)$$

Table 1
Ionic liquids [34,46], with studied temperature range (293.15–393.15 K), used to obtain coefficients a , b and c of Eq. (6)

Ionic liquid	W (g mol ⁻¹)	Volume (Å ³)		Pressure range (MPa)	Data points	Expt. average density (kg m ⁻³)	Calc. average density (kg m ⁻³)	Mean percent deviation (%)
		Cation	Anion					
[C ₂ mim][NTf ₂]	391.31	182	248	0.10–30.00	96	1492.9	1489.1	0.25
[C ₇ mim][NTf ₂]	461.45	322	248	0.10–30.00	96	1323.8	1324.7	0.11
[C ₈ mim][NTf ₂]	475.48	350	248	0.10–30.00	96	1297.6	1301.1	0.29
[C ₂ mim][BF ₄]	197.97	182	73	0.10–30.00	96	1279.1	1270.4	0.69
[C ₄ mim][BF ₄]	226.02	238	73	0.10–10.00	77	1171.5	1176.0	0.39
[C ₈ mim][BF ₄]	282.13	350	73	0.10–10.00	77	1074.7	1079.3	0.42
[C ₆ mim][PF ₆]	312.24	294	107	0.10–10.00	77	1259.7	1260.0	0.08
[C ₈ mim][PF ₆]	340.29	350	107	0.10–10.00	77	1204.8	1204.9	0.07
[C ₄ mim][C(CN) ₃]	229.28	238	126	0.10–30.00	96	1029.3	1030.7	0.18
Total					788	1242.8	1242.9	0.28

where V_0 is the molecular volume at the reference temperature (T_0) and pressure (P_0) in m³ molecule⁻¹, whereas the coefficients a are $(1+x)$, b is α_P and c is κ_T . The b and c constants will be taken as ionic liquid independent as the α_P and κ_T for most of the ionic liquids investigated seem to have a fairly constant value.

Using Eq. (5), it is possible to obtain a pressure and temperature dependent version of Eq. (1):

$$\rho = \frac{W}{NV_0(a + bT + cP)} \quad (6)$$

The coefficients a , b and c can be estimated by fitting Eq. (6) to experimental data. Here they were estimated by correlating the experimental densities of nine ILs previously measured by us [34,46] covering the density range (986.7–1547.1 kg m⁻³), temperature range (293.15–393.15 K) and pressure range

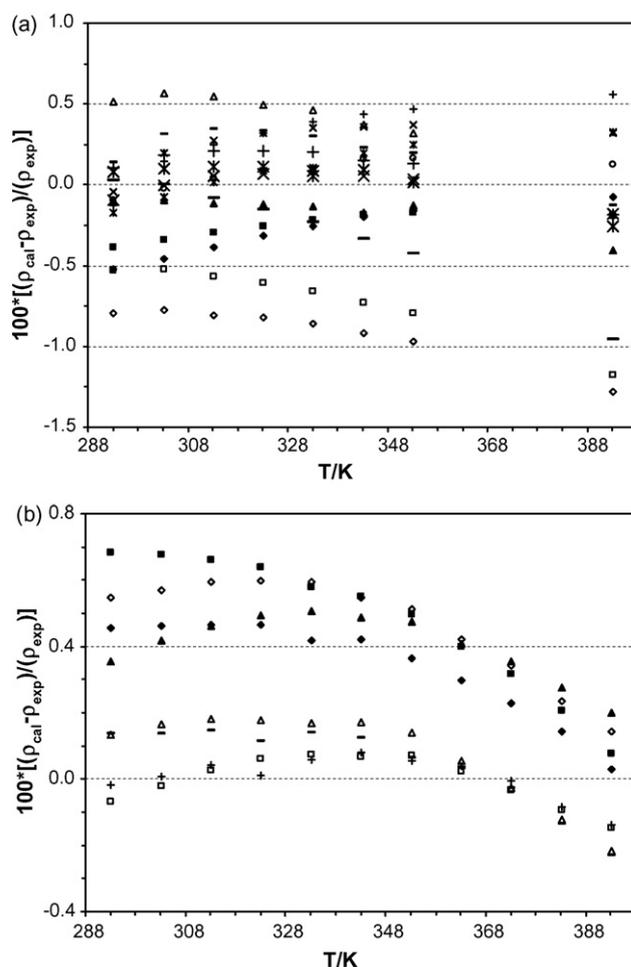


Fig. 1. Relative deviations between the calculated and experimental density data as a function of temperature: (a) [C₂mim][NTf₂]: (◆) at 0.10 MPa, (▲) at 10.00 MPa, (▲) at 30.00 MPa; [C₇mim][NTf₂]: (*) at 0.10 MPa, (○) at 10.00 MPa, (✱) at 30.00 MPa; [C₈mim][NTf₂]: (+) at 10.00 MPa, (✱) at 10.00 MPa, (−) at 30.00 MPa; [C₂mim][BF₄]: (◇) at 0.10 MPa, (□) at 10.00 MPa, (−) at 30.00 MPa; [C₄mim][C(CN)₃]: (×) at 10.00 MPa, (+) at 10.00 MPa, (Δ) at 30.00 MPa. (b) [C₄mim][BF₄]: (◆) at 0.10 MPa, (■) at 10.00 MPa; [C₈mim][BF₄]: (▲) at 0.10 MPa, (◇) at 10.00 MPa; [C₆mim][PF₆]: (□) at 0.10 MPa, (Δ) at 10.00 MPa; [C₈mim][PF₆]: (+) at 0.10 MPa, (−) at 10.00 MPa.

Table 2
Prediction of densities of imidazolium-based ionic liquids

Ionic liquid	W (g mol ⁻¹)	Volume (Å ³)		Temperature range (K)	Pressure range (MPa)	Data points	Mean percent deviation (%)	Reference
		Cation	Anion					
[C ₂ mim][NTf ₂]	391.31	182	248	293.1–353.1	0.10	13	0.38	[26]
[C ₃ mim][NTf ₂]	405.34	210	248	298.15–333.15	0.10–59.59	165	0.21	[13]
[C ₄ mim][NTf ₂]	419.36	238	248	298.15–328.20	0.10–59.10	168	0.22	[11]
[C ₅ mim][NTf ₂]	433.39	266	248	298.15–333.15	0.10–59.59	165	0.18	[13]
[C ₆ mim][NTf ₂]	447.42	294	248	298.15–333.15	0.10–50.75	156	0.34	[11]
[C ₈ mim][NTf ₂]	475.48	350	248	298.15–358.15	0.10	14	0.22	[16]
[C ₂ mim][BF ₄]	197.97	182	73	293.15–323.15	0.101	07	3.56	[21]
[C ₄ mim][BF ₄]	226.02	238	73	298.34–332.73	0.10–59.92	67	0.80	[10]
				278.15–333.15	0.1–60.0	26	0.64	[15]
				293.15–353.15	0.10–20.00	20	0.21	[23]
[C ₈ mim][BF ₄]	282.13	350	73	298.2–323.2	0.10–69.39	07	2.02	[17]
				273.1–363.1	0.10	13	0.44	[19]
				298.15–323.15	0.–100	144	1.15	[10]
				298.2–323.2	0.10–69.39	06	1.39	[17]
				293.15–353.15	0.10–20.00	20	0.32	[23]
[C ₄ mim][PF ₆]	284.18	238	73	283.13–343.27	0.10	13	0.07	[22]
				273.1–363.1	0.10	14	0.14	[24]
				298.23–353.47	0.10	10	0.14	[25]
				283.15–323.15	0.10	09	0.23	[14]
				289.10–309.15	0.10	11	0.34	[27]
[C ₆ mim][PF ₆]	312.24	294	107	278.15–318.15	0.10	09	0.08	[28]
[C ₈ mim][PF ₆]	340.29	350	107	298.2–323.2	0.10–69.73	06	1.69	[17]
				273.1–363.1	0.10	13	0.11	[19]
Total						1086	0.45	

(0.10–30.00 MPa) as described in detail in Table 1. A total amount of circa 800 density data points were used. The values of coefficient a , b and c obtained are $8.005 \times 10^{-1} \pm 2.333 \times 10^{-4}$, $6.652 \times 10^{-4} \pm 6.907 \times 10^{-7} \text{ K}^{-1}$ and $-5.919 \times 10^{-4} \pm 2.410 \times 10^{-6} \text{ MPa}^{-1}$, respectively, at 95% level of confidence. The relative deviations between calculated and experimental density data are presented in Fig. 1(a) and (b). The mean percent deviation of calculated densities from the experimental densities is 0.28%. The experimental density (Y), for the nine ILs used to obtain coefficient a , b and c of Eq. (6), is essentially identical to its calculated density (X): $Y = (1.0001 \pm 0.0003)X$ (correlation coefficient: $R^2 = 0.9989$, at 95% level of confidence).

For the density calculation, volume parameters of ions and groups were directly taken from literature [48], except for two anions, $[\text{C}(\text{CN})_3]^-$ and $[\text{CH}_3\text{CO}_2]^-$. Following Jenkins' procedure [48], volume of anion, $[\text{C}(\text{CN})_3]^-$, is estimated as 123 \AA^3 from the values of $[\text{C}(\text{NO}_2)_3]^-$ (141 \AA^3), NO_2 (36 \AA^3) and CN (30 \AA^3), and volume of anion, $[\text{CH}_3\text{CO}_2]^-$, is estimated as 85.5 \AA^3 from $[\text{CF}_3\text{CO}_2]^-$ (141 \AA^3), F (12.5 \AA^3) and H (5 \AA^3).

Experimental densities available in literature for ILs based on imidazolium, pyridinium, pyrrolidinium and phosphonium-based ionic liquids, were predicted by using Eq. (6). Predicted densities are in good agreement with experimental literature data. Table 2 shows predicted densities with the mean percent deviation (MPD) of 1086 data points of total 12 imidazolium-

Table 3
Prediction of densities of phosphonium, pyridinium and pyrrolidinium-based ionic liquids

Ionic liquid	W (g mol ⁻¹)	Volume (Å ³)		Temperature range (K)	Pressure range (MPa)	Data points	Mean percent deviation (%)	Reference
		Cation	Anion					
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)] [NTf ₂]	764.01	947	248	298.15–333.43	0.21–65.01	126	0.24	[12]
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)] [Cl]	519.32	947	47	298.13–333.14	0.19–65.00	134	2.43	[12]
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)] [Ac]	542.91	947	85.5	298.15–334.11	0.21–65.01	144	1.69	[12]
[C ₂ py] [NTf ₂]	388.31	174	248	298.15–333.15	0.10	08	0.43	[20]
[C ₂ py] [BF ₄]	194.97	174	73	293.1	0.10	01	1.14	[53]
[C ₄ py] [BF ₄]	223.02	230	73	298.2–323.2	0.10–71.46	06	1.57	[17]
[C ₄ mpy] [BF ₄]	237.05	258	73	298.15–323.15	0.101	05	0.62	[18]
[C ₄ mpyr] [NTf ₂]	422.41	253	248	298.15–348.15	0.10	11	0.41	[16]
Total						435	1.43	

based ILs containing NTf_2^- , BF_4^- and PF_6^- anions.

The mean percent deviation (MPD) was defined as

$$\text{MPD} (\%) = \frac{100 \times \sum_{i=1}^{N_p} |(\rho_{\text{cal}} - \rho_{\text{exp}}) / \rho_{\text{exp}}|_i}{N_p} \quad (7)$$

where N_p represents the number of data points.

The experimental densities (Y) of imidazolium-based ILs containing NTf_2^- , BF_4^- and PF_6^- anions display a very good agreement with corresponding predicted densities (X) from Eq. (6): $Y = (0.9968 \pm 0.0004)X$ (correlation coefficient: $R^2 = 0.9903$, at 95% level of confidence). For 12 imidazolium-based ILs, from Rebelo and co-workers [10,11,13–15], Gmehling and co-workers [16,26], Harris et al. [19,24], Gu and Brennecke [17], Zhang et al. [21], Jacquemin et al. [22], Tomida et al. [23], Kabo et al. [25], Kumelan et al. [27] and Pereiro et al. [28], the MPD is 0.48%; 42.6% of the estimated densities were within absolute deviation of 0.00–0.20, 27.1% were within 0.201–0.40, 11.0% were within 0.401–0.60, 8.0% were within 0.601–1.00, 7.5% were within 1.001–2.00 and only 3.9% were within 2.001–3.78.

Predicted densities with the mean percent deviation (MPD) of phosphonium, pyridinium and pyrrolidinium-based ILs are shown in Table 3. The experimental densities (Y) of phosphonium-based ILs containing NTf_2^- , Cl^- and CH_3CO_2^- anions display a very good relationship with corresponding predicted densities (X) from Eq. (6): $Y = (1.0133 \pm 0.0010)X$ (correlation coefficient: $R^2 = 0.9874$, at 95% level of confidence). For phosphonium-based ILs, from Rebelo and co-workers [12], the MPD is 1.49%; 8.2% of the estimated densities were within absolute deviation of 0.00–0.20, 23.0% were within 0.201–0.40, 37.4% were within 0.401–2.00 and 31.4% were within 2.001–2.61. The low MPD ranging from 0.41% to 1.57% was also observed for pyridinium and pyrrolidinium-based ILs. It is also shown in Fig. 2 that the experimental densities of ILs, containing imidazolium, pyridinium, pyrrolidinium and phosphonium cations, display a very good linear relationship with the corresponding predicted densities.

Table 4
Density prediction of binary mixtures of imidazolium-based ionic liquids having common anion or cation

Binary mixture	Temperature range (K)	Data points	Mean percent deviation (%)	Reference
Binary mixtures of ILs having common anion				
$[\text{C}_6\text{mim}][\text{BF}_4] + [\text{C}_2\text{mim}][\text{BF}_4]$	298.15–308.15	135	1.24	[52]
$[\text{C}_6\text{mim}][\text{BF}_4] + [\text{C}_4\text{mim}][\text{BF}_4]$	298.15–308.15	108	0.60	[52]
$[\text{C}_2\text{mim}][\text{NTf}_2] + [\text{C}_{10}\text{mim}][\text{NTf}_2]$	298.15–333.15	14	2.63	[51]
$[\text{C}_4\text{mim}][\text{NTf}_2] + [\text{C}_{10}\text{mim}][\text{NTf}_2]$	298.15–333.15	08	2.09	[51]
$[\text{C}_6\text{mim}][\text{NTf}_2] + [\text{C}_{10}\text{mim}][\text{NTf}_2]$	298.15–333.15	14	1.62	[51]
$[\text{C}_8\text{mim}][\text{NTf}_2] + [\text{C}_{10}\text{mim}][\text{NTf}_2]$	298.15–333.15	06	2.08	[51]
$[\text{C}_4\text{mim}][\text{NTf}_2] + [\text{C}_8\text{mim}][\text{NTf}_2]$	298.15–333.15	08	0.64	[51]
$[\text{C}_2\text{mim}][\text{NTf}_2] + [\text{C}_8\text{mim}][\text{NTf}_2]$	298.15–333.15	10	1.01	[51]
Binary mixtures of ILs having common cation				
$[\text{C}_4\text{mim}][\text{MeSO}_4] + [\text{C}_4\text{mim}][\text{BF}_4]$	298.15–308.15	144	1.28	[52]
$[\text{C}_4\text{mim}][\text{PF}_6] + [\text{C}_4\text{mim}][\text{BF}_4]$	298.15–308.15	126	0.14	[52]
$[\text{C}_4\text{mim}][\text{PF}_6] + [\text{C}_4\text{mim}][\text{NTf}_2]$	298.15–333.15	10	0.13	[51]
$[\text{C}_4\text{mim}][\text{PF}_6] + [\text{C}_4\text{mim}][\text{NTf}_2]$	298.15–333.15	10	0.16	[51]
$[\text{C}_4\text{mim}][\text{BF}_4] + [\text{C}_4\text{mim}][\text{NTf}_2]$	303.15–333.15	16	0.79	[51]

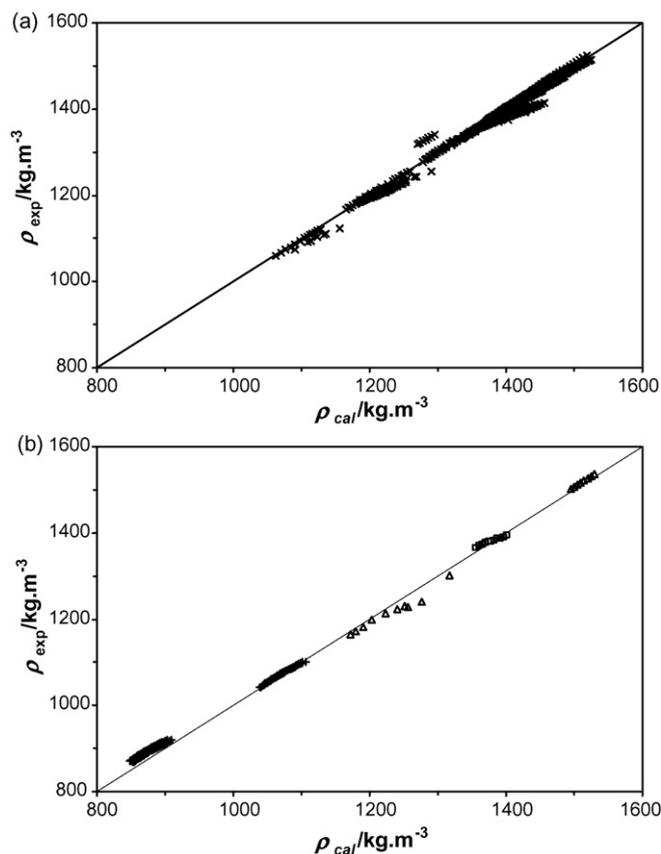


Fig. 2. Experimental densities vs. calculated densities of ionic liquids: (a) (x) imidazolium cation; (b) (Δ) pyridinium, (\square) pyrrolidinium, and (+) phosphonium cations.

Torres [50] was the first to show that homogeneous binary mixtures of ionic liquids can be considered ideal. The experimental data of Lopes et al. [51] and Navia et al. [52] further confirmed that densities of homogeneous binary mixtures of ILs having same cation or anion do not deviate significantly from the ideal mixture and can be considered as quasi-ideal mixture. The proposed model was here evaluated for the estimation

of densities of mixtures of ionic liquids by comparing its predictions with the data by Lopes et al. [51] and Navia et al. [52]. The deviations between the estimated densities and the literature data [51,52] at 298.15 K are reported in Table 4 and deviations at other temperatures are of similar. The predicted densities for mixtures of ionic liquids are thus in good agreement with experimental data showing that the model can provide a good estimate for densities of mixtures as for pure ionic liquids.

3. Conclusions

The Ye and Shreeve's group contribution method for estimation of ionic liquids densities was here successfully extended to predict densities of ILs for a wide range of temperature (273.15–393.15 K) and pressure (0.10–100 MPa). The validity of this new method was checked by predicting experimental densities available in literature, 1521 data points, of ionic liquids based on imidazolium, pyridinium, pyrrolidinium and phosphonium cations. For 12 imidazolium-based ILs, the mean percent deviation (MPD) is 0.45% and for phosphonium-based ILs, the MPD is 1.49%. The low MPD ranging from 0.41% to 1.57% was also observed for pyridinium and pyrrolidinium-based ILs. Predicted densities of pure and homogeneous binary mixtures of ILs having same cation or anion are in good agreement with available experimental literature values.

List of symbols

a, b, c	coefficients of density correlation
N_p	number of data points
P	pressure
T	temperature
V	molecular volume
V_+	volume of cation
V_-	volume of anion
W	molar mass

Greek letters

α_p	thermal expansivity
κ_T	isothermal compressibility
ρ	density

Subscripts

cal	calculated property
exp	experimental property

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References

- [1] K.N. Marsh, J.A. Boxall, R. Lichtenthaler, *Fluid Phase Equilib.* 219 (2004) 93–98.
- [2] A. Heintz, *J. Chem. Thermodyn.* 37 (2005) 525–535.
- [3] S. Zhang, N. Sun, X. He, X. Lu, X. Zhang, *J. Phys. Chem. Ref. Data* 35 (2006) 1475–1517.
- [4] H. Tokuda, K. Hayamizu, K. Ishii, M.A.B.H. Susan, M. Watanabe, *J. Phys. Chem. B* 108 (2004) 16593–16600.
- [5] H. Tokuda, K. Hayamizu, K. Ishii, M.A.B.H. Susan, M. Watanabe, *J. Phys. Chem. B* 109 (2005) 6103–6110.
- [6] H. Tokuda, K. Hayamizu, K. Ishii, M.A.B.H. Susan, M. Watanabe, *J. Phys. Chem. B* 110 (2006) 2833–2839.
- [7] C.P. Fredlake, J.M. Crosthwaite, D.G. Hert, S.N.V.K. Aki, J.F. Brennecke, *J. Chem. Eng. Data* 49 (2004) 954–964.
- [8] U. Domanska, *Pure Appl. Chem.* 77 (2005) 543–557.
- [9] U. Domanska, *Thermochim. Acta* 448 (2006) 19–30.
- [10] R.G. Azevedo, J.M.S.S. Esperança, V. Najdanovic-Visak, Z.P. Visak, H.J.R. Guedes, M. Nunes da Ponte, L.P.N. Rebelo, *J. Chem. Eng. Data* 50 (2005) 997–1008.
- [11] R.G. Azevedo, J.M.S.S. Esperança, J. Szydłowski, Z.P. Visak, P.F. Pires, H.J.R. Guedes, L.P.N. Rebelo, *J. Chem. Thermodyn.* 37 (2005) 888–899.
- [12] J.M.S.S. Esperança, H.J.R. Guedes, M. Blesic, L.P.N. Rebelo, *J. Chem. Eng. Data* 51 (2006) 237–242.
- [13] J.M.S.S. Esperança, Z.P. Visak, N.V. Plechkova, K.R. Seddon, H.J.R. Guedes, L.P.N. Rebelo, *J. Chem. Eng. Data* 51 (2006) 2009–2015.
- [14] J. Troncoso, C.A. Cerdeirina, Y.A. Sanmamed, L. Romani, L.P.N. Rebelo, *J. Chem. Eng. Data* 51 (2006) 1856–1859.
- [15] L.P.N. Rebelo, V. Najdanovic-Visak, Z.P. Visak, M. Nunes da Ponte, J. Szydłowski, C.A. Cerdeirina, J. Troncoso, L. Romani, J.M.S.S. Esperança, H.J.R. Guedes, H.C. de Sousa, *Green Chem.* 6 (2004) 369–381.
- [16] R. Kato, J. Gmehling, *J. Chem. Thermodyn.* 37 (2005) 603–619.
- [17] Z. Gu, J.F. Brennecke, *J. Chem. Eng. Data* 47 (2002) 339–345.
- [18] A. Heintz, D. Klasen, J.K. Lehmann, *J. Solution Chem.* 31 (2002) 467–476.
- [19] K.R. Harris, M. Kanakubo, L.A. Woolf, *J. Chem. Eng. Data* 51 (2006) 1161–1167.
- [20] R. Kato, J. Gmehling, *Fluid Phase Equilib.* 226 (2004) 37–44.
- [21] S. Zhang, X. Li, H. Chen, J. Wang, J. Zhang, M. Zhang, *J. Chem. Eng. Data* 49 (2004) 760–764.
- [22] J. Jacquemin, P. Husson, V. Majer, M.F. Costa Gomes, *Fluid Phase Equilib.* 240 (2006) 87–95.
- [23] D. Tomida, A. Kumagai, K. Qiao, C. Yokoyama, *Int. J. Thermophys.* 27 (2006) 39–47.
- [24] K.R. Harris, L.A. Woolf, M. Kanakubo, *J. Chem. Eng. Data* 50 (2005) 1777–1782.
- [25] G.J. Kabo, A.V. Blokhin, Y.U. Paulechka, A.G. Kabo, M.P. Shymanovich, J.W. Magee, *J. Chem. Eng. Data* 49 (2004) 453–461.
- [26] M. Krummen, P. Wasserscheid, J. Gmehling, *J. Chem. Eng. Data* 47 (2002) 1411–1417.
- [27] J. Kumelan, A.P.S. Kamps, D. Tuma, G. Maurer, *Fluid Phase Equilib.* 228–229 (2005) 207–211.
- [28] A.B. Pereiro, E. Tojo, A. Rodriguez, J. Canosa, J. Tojo, *J. Chem. Thermodyn.* 38 (2006) 651–661.
- [29] A.B. Pereiro, P. Verdia, E. Tojo, A. Rodriguez, *J. Chem. Eng. Data* 52 (2007) 377–380.
- [30] A.B. Pereiro, A. Rodriguez, *J. Chem. Eng. Data* 52 (2007) 600–608.
- [31] A.B. Pereiro, A. Rodriguez, *J. Chem. Thermodyn.* 39 (2007) 978–989.
- [32] A.B. Pereiro, J.L. Lejido, A. Rodriguez, *J. Chem. Thermodyn.* 39 (2007) 1168–1175.
- [33] T.L. Greaves, A. Weerawardena, C. Fong, I. Krodkiewska, C.J. Drummond, *J. Phys. Chem. B* 110 (2006) 22479–22487.
- [34] R.L. Gardas, M.G. Freire, P.J. Carvalho, I.M. Marrucho, I.M.A. Fonseca, A.G.M. Ferreira, J.A.P. Coutinho, *J. Chem. Eng. Data* 52 (2007) 80–88.
- [35] O. Exner, *Collect. Czech. Chem. Commun.* 32 (1967) 1–23.
- [36] J. Stine, Report DE81032016, Los Alamos National Laboratory, Los Alamos, NM, 1981.
- [37] C.M. Tarver, *J. Chem. Eng. Data* 24 (1979) 136–145.

- [38] H.L. Ammon, *Struct. Chem.* 12 (2001) 205–212.
- [39] H.L. Ammon, S. Mitchell, *Propell. Explos. Pyrot.* 23 (1998) 260–278.
- [40] S. Beaucamp, N. Marchet, D. Mathieu, V. Agafonov, *Acta Crystallogr. B* 59 (2003) 498–504.
- [41] D.W.M. Hofmann, *Acta Crystallogr. B* 58 (2002) 489–493.
- [42] H.R. Karfunkel, R.J. Gdanitz, *J. Comput. Chem.* 13 (1992) 1171–1183.
- [43] K.E. Gutowski, J.D. Holbrey, R.D. Rogers, D.A. Dixon, *J. Phys. Chem. B* 109 (2005) 23196–23208.
- [44] L.P.N. Rebelo, V.N. Visak, R.G. de Azevedo, J.M.S.S. Esperança, M.N. da Ponte, H.J.R. Guedes, Z.P. Visak, H.C. de Sousa, J. Szydłowski, J.N.C. Lopes, T.C. Cordeiro, *Ionic liquids IIIA: fundamentals, progress, challenges, and opportunities properties and structure*, in: R.D. Rogers, K.R. Seddon (Eds.), *ACS Symposium Series 901*, American Chemical Society, Washington, DC, 2005, pp. 270–291 (Chapter 21).
- [45] L.P.N. Rebelo, J.N.C. Lopes, M.S.S. Jose, H.J.R. Esperança, J. Guedes, V.N. Lachwa, Z.P. Visak, *Acc. Chem. Res.* 40 (2007) 1114–1121.
- [46] R.L. Gardas, M.G. Freire, P.J. Carvalho, I.M. Marrucho, I.M.A. Fonseca, A.G.M. Ferreira, J.A.P. Coutinho, *J. Chem. Eng. Data* 52 (2007) 1881–1888.
- [47] J. Jacquemin, PhD Thesis, Université de Clermont Ferrand, France, 2006.
- [48] H.D.B. Jenkins, H.K. Roobottom, *Inorg. Chem.* 38 (1999) 3609–3620.
- [49] C. Ye, J.M. Shreeve, *J. Phys. Chem. A* 111 (2007) 1456–1461.
- [50] M.-J. Torres, PhD Thesis, The Queen's University of Belfast, Belfast, 2001.
- [51] J.N.C. Lopes, T.C. Cordeiro, J.M.S.S. Esperança, H.J.R. Guedes, S. Huq, L.P.N. Rebelo, K.R. Seddon, *J. Phys. Chem. B* 109 (2005) 3519–3525.
- [52] P. Navia, J. Troncoso, L. Romani, *J. Chem. Eng. Data* 52 (2007) 1369–1374.
- [53] H. Zhao, S.V. Malhotra, R.G. Luo, *Phys. Chem. Liq.* 41 (2003) 487–492.