

This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Density of ionic liquids

Mäki-Arvela, Päivi

Published in:
Encyclopedia of ionic liquids

DOI:
[10.1007/978-981-10-6739-6](https://doi.org/10.1007/978-981-10-6739-6)

Published: 16/06/2020

Document Version
Accepted author manuscript

Document License
Publisher rights policy

[Link to publication](#)

Please cite the original version:
Mäki-Arvela, P. (2020). Density of ionic liquids. In S. Zhang (Ed.), *Encyclopedia of ionic liquids* Springer. <https://doi.org/10.1007/978-981-10-6739-6>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Density of ionic liquids

PÄIVI MÄKI-ARVELA

Åbo Akademi University, Turku/Åbo, Finland

Introduction

The experimentally measured densities of ionic liquids are important, since they can be used to develop equations of state, which describe non-ideal behaviour of ionic liquids. The density and from it derived volumetric parameters of ionic liquids are required for developing new industrial processes [1]. Density is decreasing with increasing temperature due to increasing kinetic energy, which in turn increases the volume of ions. After linear fitting the parameters a and b for the temperature dependence of density are determined from

$$\rho = b - aT \quad (1)$$

in which ρ denotes density and T temperature in Kelvin. In this work the method, how to determine the density of ionic liquids is reported. The main emphasis is put on comparison of the density of ionic liquids based on their structure. Some regularities have been observed in the density of ionic liquids depending on the type [2] and size of the ions [3, 4] and molecular weight of anions [5] and different functional groups, i.e. unsaturated functional groups [6] or groups which can form hydrogen bonds [7] in ionic liquids decrease typically ionic liquid density.

Instruments and Method to Determine Density of Ionic Liquids

Density of ionic liquids is typically measured using an oscillating U-tube densimeter, which gives a period of vibration for a certain fluid [1]. The obtained period of vibration is correlated

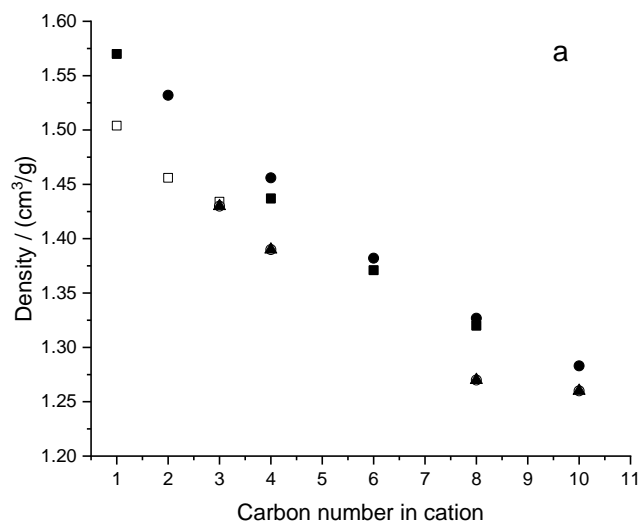
with density, which is obtained by calibrating the apparatus with for example water and air with known density [8]. For accurate calibration of density values, bidistilled ultra pure water was used [9]. The sample treatment during density measurements under an inert atmosphere is also recommended [10]. Temperature control is extremely important for density measurements and typically deviation in temperature should be smaller than ± 2 mK [10]. Typically three measurements at least have been done for determination of ionic liquid densities [9] and the error in repeatability of density values was for [bmim][Tf₂N] ca. $\pm 7 \cdot 10^{-5}$ g·cm⁻³ [9]. Since experimentally determined densities can be used in thermodynamic modelling (see below), it is important to compare and validate the obtained values with literature data, if possible. Since ionic liquids are hygroscopic and can contain traces of water, large deviations in experimentally derived densities in comparison to those reported in literature can occur [11].

Comparison of Ionic Liquid Densities based on Their Structure

The main emphasis in the comparison of ionic liquid densities based on their structure is to give an idea of which structural details in the molecular structure of ionic liquid affect density. The main correlations found for decreasing IL density are: 1) the long alkyl chain length of either anion or cation in IL, 2) for cyclic compounds a large ring size, 3) a large heteroatom in e.g. imidazolium based IL, 4) cyclic ILs with no charge delocalization occurring, 5) saturated ILs have usually lower density than unsaturated ones, 6) no electronegative atoms are present in IL structure, 7) no hydrogen bonding groups present in IL structure. Some examples of these effects are given below and in Table 1.

Density of the ionic liquid decreased with both increasing alkyl chain length of the cation, when anion is the same, for example in imidazolium based ionic liquids with bis(trifluoromethyl sulfonyl)imides (Tf₂N) (structure 1) [12, 13], phenyl substituted imidazolium ring with varying alkyl chain length (structure 3) [14, 15] and in pyrrolidinium based ionic liquids (structure 17,

22) (Fig. 1a) [16] et al. 2009). For example phenylalkyl methylimidazolium bis(trifluoromethylsulfonyl) imide, [(Ph)emim][Tf₂N] has higher density than [(Ph)pmim][Tf₂N] (structure 3) [15]. Furthermore the larger size of cyclic substituent in imidazolium based bis(trifluoromethyl sulfonyl)imides decreased the IL density of ionic liquid, e.g. cyclopentylalkyl- (e.g. [(cyclopemim)][Tf₂N] (structure 4) [15] has higher density than [(cyclohmim)][Tf₂N] (structure 2) [18]. When cation is large, the density of ionic liquid is low due to dispersive interactions and steric hindrance [1].



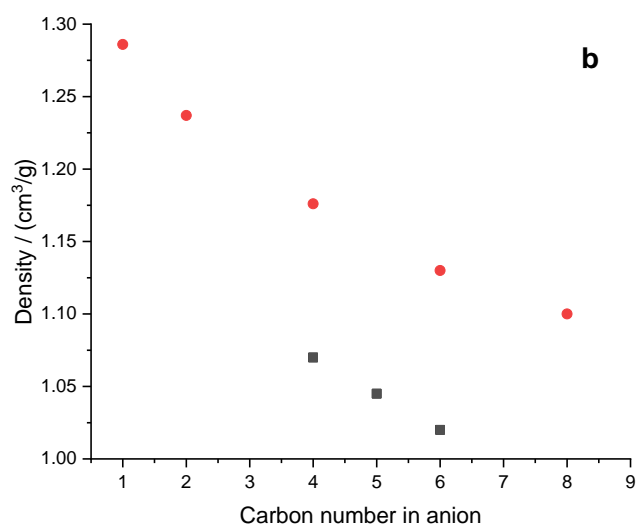


Fig. 1 a) Effect of alkyl chain length in a) cation, symbols (\square) IL 3, (\blacksquare) IL 1, (\bullet) IL 16 and (\blacktriangle) IL 17 and b) anion in ionic liquid on its density, symbols (\bullet) IL 15, (\blacksquare) IL 35. Numbers of ionic liquids are the same as in Table 1.

Analogously to alkyl chain length in cation, also longer anion carbon chain length in ionic liquids decreased its density, as was the case in 1-ethyl-3-methylimidazolium alkyl sulfates (structure 15) (Fig. 1b) [10], in N-2-hydroxyethylammonium alkylates (structure 33) [20] and in N-methyl-2-hydroxy ethyl ammonium alkylates (structure 34) [4]. In these cases the cation is the same and only anion is changing. The reason for the decreased density of ionic liquid with a long alkyl chain is a larger free volume, which decreased its densities due to steric hindrance to obtain high packaging level [4]. In addition, it can be noted that N-methyl-2-hydroxy ethyl ammonium alkylates (structure 34) [4] are protic ionic liquids, which have high electrostatic interactions between cation and anion and thus their densities are lower than those for aprotic ionic liquids, e.g. imidazolium based ionic liquid (structure 1) [12]. In general aprotic ionic liquids have higher level of packaging in comparison to protic ionic liquids [4].

The size of hetero atom in ionic liquid, for example trimethylsilyl containing imidazolium based IL (structure 5) [27] with a silicon exhibiting a larger size than carbon, exhibits lower density

than the corresponding IL with carbon (structure 5). Analogously the density of the ionic liquid with a phosphorus atom (structure 33) is lower than with nitrogen atom (structure 34), since phosphorus is larger than nitrogen [3].

The density of ionic liquids is also higher for imidazolium based ionic liquids having anion with a higher molecular weight as shown in Fig. 2, in which a correlation for five different imidazolium based ionic liquids with different anions at 303 K was made based on the data in [5].

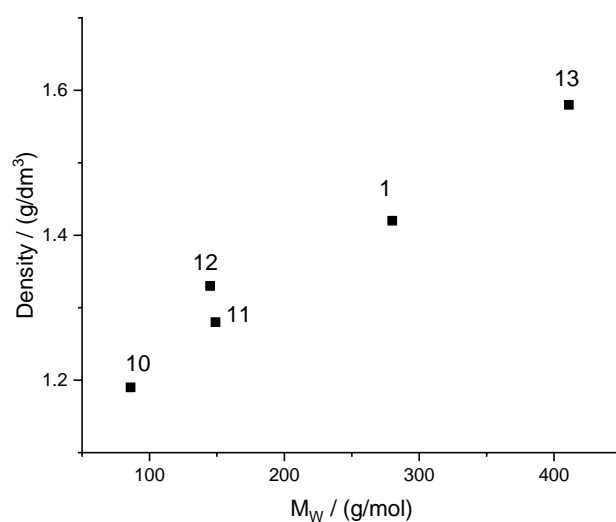


Fig. 2 Density of 1-butyl-3-methylimidazolium based ionic liquids with different anions as a function of the molecular weight (M_w) of the anion. The numbers refer to the ionic liquids noted in Table 1.

The unsaturation in ionic liquid makes it more compact due to the fact the unsaturated structures have more dense structure. One example is a comparison of densities for imidazolium, pyrrolidinium and pyridinium based ionic liquids. The following decreasing density order has been confirmed for these ILs: [bpy][Tf₂N] (structure 16) [25] > [bmim][Tf₂N] (structure 1) [12] > [bmpyr][Tf₂N] (structure 17) [16] indicating that imidazolium has higher mobility than

the heterocyclic ionic liquids, while pyridinium IL packs more efficiently, which can be caused by charge localisation in pyridinium cation. In addition, density of [(allylmpi)][Tf₂N] (structure 29) [6] is higher than that for [pmpi][Tf₂N] (structure 25) [19].

The presence of electron-withdrawing groups increases the density of ionic liquids. The unsaturated alkenyl chain in pyrrolidinium cation increases the density of [(allylm)mpyr][Tf₂N] (structure 23) [23] in comparison to the corresponding saturated one, [pmpyr][Tf₂N] (structure 17) [7]. The presence of two unsaturated alkenyl chains in pyrrolidinium cation in [(allylm)₂pyr][Tf₂N] (structure 19) [23], however, makes the molecule symmetric, which decreases its density. In this case the cation is large. High density of IL has also been observed for phenyl substituted pyrrolidinium containing ionic liquids than with cyclohexyl containing ones, i.e. the ionic liquid, [(Phm)mpyr][Tf₂N] (structure 20) with a phenyl ring exhibits a higher packing density than [(cycloh)mpyr][Tf₂N] (structure 21) and the latter one has a higher density [14].

Electronegative atoms in ionic liquid increase their density and thus [(F₃p)₂mim][Tf₂N] (structure 9) exhibits higher density than [(F₃p)im][Tf₂N] (structure 8) [21]. Piperidinium containing [(F₃b)mpi][Tf₂N] (structure 26) with its higher molecular weight and fluorine content has higher density than the corresponding [bmpi][Tf₂N] (structure 25) [26].

The alkyl chain structure in cation has an impact on the density of corresponding imidazoloim based IL. When, for example, the ionic liquid [ipmpyr][Tf₂N] (structure 18) has an isopropyl group, the IL exhibits higher density [16] in comparison to [pmpyr][Tf₂N] (structure 17) [16], which has a linear alkyl group.

The functional group with ability for hydrogen bonding in the side chain increases the packing density of ionic liquid, e.g. [(HOe)mpi][Tf₂N] (structure 27) [7], which has higher density than [pmpi][Tf₂N] with the same carbon number in the side chain (structure 25) [7]. The ether group

in (structure 24) has a higher packing density [7] in comparison to the ionic liquid [pmpyr][Tf₂N] (structure 17) with carbon atoms [16] and thus the density of is lower than that for [(mOm)m pyr][Tf₂N] (structure 24) [7]. Analogously higher density was measured for [(mOe)m pi][Tf₂N] (structure 28) [7] in comparison to [bmp i][Tf₂N] (structure 25) [19] and for [(mOe)m mo][Tf₂N] (structure 32) [22] in comparison to [bm mo][Tf₂N] (structure 31) [22].

Modelling of Ionic Liquid Densities

Several methods exist to model ionic liquid densities, such as COSMO-RS model based on quantum chemistry [30], group contribution equation of state based on electrolyte perturbation theory [11], or using Predictive-Soave-Redlich-Kwong (PSRK) method [31]. Furthermore, density of ionic liquids was predicted using molecular volume of ionic liquids [32, 33]. It was stated in [34] that the accuracy of COSMO-RS is not sufficient to predict density. The details of some thermodynamical models to predict ionic liquid density [11, 31-33] are described below.

Density of ionic liquids was predicted using molecular volume of ionic liquids [33]. In this method density ρ is related to molecular volume V_m as follows:

$$V_m = \left(\frac{M_w}{\rho} \right) N_A \quad (2)$$

In which M_w is molecular weight and N_A denotes Avogadro's number. V_m is a sum of cation V_{cat} and anion volumes V_{an} .

$$V_m = V_{cat} + V_{an} \quad (3)$$

It is possible to derive an equation for cation volume from crystal structures and thereafter assess the volume not occupied by cation, i.e. V_{an} . In the new model proposed by Montalban et al [33] density of alkyl imidazolium based ionic liquids was predicted via calculating

theoretically van der Waals volume of the ion. When comparing van der Waals volume with the ionic volume of anion, it was observed that different anions exhibited different increment value of volume to van der Waals volume of ion depending on the geometry charge distribution etc. This increment is varying with the alkyl chain length of the anion and temperature and it takes also into account interionic distances. Based on experimental data of ionic liquid densities an equation for temperature dependence of the volume of anion and number of carbon atoms was derived. For example the anion volume for BF_4^- anion is the following:

$$V_{\text{BF}_4} = V_{\text{BF}_4\text{theo}}(1.083 + 0.365 \cdot 10^{-3}T) \quad (4)$$

in which $V_{\text{BF}_4\text{theo}}$ is the volume of BF_4^- ion van der Waals volume and T temperature in Kelvin and this equation can also be written as a function of number of carbon atoms in alkyl chain. Experimental errors for densities of several imidazolium based ionic liquids with BF_4^- , PF_6^- NTf_2^- anions were below 0.3 %.

Another method to predict ionic liquid densities is Predictive-Soave-Redlich-Kwong (PSRK) method [31]. In this method cohesion function $\alpha(t)$, containing reduced temperature T_r and acentric factor ω of ionic liquid, is used. Acentric factor describes the structural deviation of ionic liquid from spherical shape and T_r is the ratio between temperature and critical temperature of ionic liquid. The prediction starts with taking into account the saturated density of ionic liquid and assuming an adjustable parameter δ . Thereafter a temperature dependent cohesion function denoted as $\alpha(t)$ or $f(T_r)$ is calculated, for example

$$\alpha(t) = [1 + (1.367\omega + 0.4132)(1 - \sqrt{T_r})]^2 \quad (5)$$

as proposed in [35]. Thereafter density is calculated from

$$\rho_0(\text{exp}) = \frac{\rho_c}{\rho_c [1 + \delta(f(T_r) - 1)^{1/3}]} \quad (6)$$

Followed by calculation of $\rho_0(\text{calc})$ from

$$\rho_0(\text{calc}) = 1 + d1 \left(1 - \frac{T_r}{f(T_r)}\right)^{1/3} + d2 \left(1 - \frac{T_r}{f(T_r)}\right)^{2/3} + d3 \left(1 - \frac{T_r}{f(T_r)}\right)^1 + d4 \left(1 - \frac{T_r}{f(T_r)}\right)^{4/3} \quad (7)$$

In eq. (7) constants values of $d1$ to $d4$ are given in [31]. Thereafter the saturated ionic liquid density is estimated from:

$$\frac{\rho_s}{\rho_c} = \rho_0(\text{calc}) \left[1 + \delta(f(T_r) - 1)^{1/3}\right] \quad (8)$$

The adjustable parameter δ is optimized by minimizing the sum of the difference between specific experimental density and calculated density. Typically the average absolute deviation in δ was 1.10-1.13 % and the estimated densities are close to experimental ones.

Group contribution equation of state based on electrolyte perturbation theory was used to predict ionic liquid density at different temperatures and pressures [11]. In this method the pressure of a system including ionic liquid was written according to Helmholtz free energy as:

$$P = P^{hs} + P^{dis} + P^{elec} \quad (9)$$

which includes a hard-sphere repulsion term, a dispersive attraction term and electrostatic interaction contribution to pressure, respectively. In this method both hard sphere and dispersive repulsion term, which contain density:

$$P^{hs} = \frac{6kT}{\pi} \left[\frac{\xi_0}{(1-\xi_3)} + \frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{(3-\xi_3)\xi_2^3}{(1-\xi_3)^3} \right] \quad (10)$$

in which k is Boltzmann's constant. Dispersive attraction pressure is given by:

$$\frac{P^{dis}}{\rho kT} = \frac{1}{\bar{r}} \sum_{m=1}^4 mA_{1m} \left(\frac{\xi_3}{\tau}\right)^m + \frac{1}{\bar{r}^2} \sum_{m=1}^4 mA_{2m} \left(\frac{\xi_3}{\tau}\right)^m \quad (11)$$

in which $\xi_n = \frac{\pi}{6} \sum_i \rho_i d_i^n$ ($n = 0,1,2,3$), $\tau = \pi \frac{\sqrt{2}}{6}$ and \tilde{T} is dimensionless temperature defined as $\tilde{T} = kT/\varepsilon$. Furthermore, d_i denotes hard-sphere diameter of group I, which can be calculated as a function of temperature and it is related to temperature-independent soft-core Lennard-Jones fluid diameter σ_i :

$$\frac{d_i}{\sigma_i} = \frac{1+0.2977\tilde{T}}{1+0.3316\tilde{T}+\frac{1.0477\tilde{T}^2}{1000}} \quad (12)$$

The coefficients A_{1m} and A_{2m} in eq. (11) and more details are given in [11]. It was experimentally confirmed in the work of Wang et al. [11] that hard sphere repulsion and dispersive interaction remain the same when a physical mixture of molecular liquids is converted to ionic liquid, while electrostatic interactions are changed. Electrostatic interaction in ionic liquids has been estimated by mean spherical approximation (MSA) by Wang et al. [11]. The electrostatic pressure contribution is defined as:

$$P^{elec} = -kT \left[\frac{\Gamma^3}{3\pi} + \frac{1}{8} \left(\frac{aP_n}{\Delta} \right)^2 \right] \quad (13)$$

in which Γ is inverse shielding length, ε is dispersion energy, σ_i denotes soft-sphere diameter. Group contribution equation of state was used to calculate ε and σ_i [37]. Finally the objective function defined as the absolute value of the difference between experimental and calculated density divided by experimental density was minimized. The results for predicting density of imidazolium based ionic liquids show that the maximum average relative deviation in density has been below 2.76% [11]. In another work [38] the average relative deviation (ARD) of the density for different imidazolium based ionic liquids increased with increasing length of the alkyl group in cation, which might be due to increasing non-sphericity when alkyl group length increases. The ARD for density predictions of 1-methylimidazolium dimethylphosphate, trimethylphosphate, triethylphosphate and tributylphosphate were, however, below 1% [38].

Density of ionic liquids has also been predicted using linear Yukawa isotherm regularity (LYIR) derived based on an effective nearest neighboring pair attractive interaction of the Yukawa potential [39, 40], since effective attraction range between ion pairs and their changes at different temperatures are related to molecular structure of anion and cation segments. Ionic liquid was considered to be as a one-centered spherical united atom. In LYIR method compressibility factor of the fluid is described by Carnahan-Starling (CS) equation of state [Mahboub409], and defined as

$$Z - Z_{CS} = A + B\rho^{1/3} \quad (14)$$

in which Z_{CS} is

$$Z_{CS} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \pi r^2 \quad (15)$$

In eq. (15) packing fraction $\eta = (\pi/6)\rho\sigma^3$ and σ denotes the finite distance at which interparticle potential is zero. Density was calculated using the following equation for the compressibility of the reference fluid, Z_{CS} :

$$Z_{CS} + A + B\rho^{1/3} - \frac{p}{RT} = 0 \quad (16)$$

Parameters A and B were obtained by fitting experimental data to eq. (14) (see details in [39]).

$$p^{elec} = -kT \left[\frac{\Gamma^3}{3\pi} + \frac{1}{8} \left(\frac{aP_n}{\Delta} \right)^2 \right] \quad (17)$$

where k denotes Boltzmann's constant and the inverse shielding length Γ is defined as:

$$\Gamma = \frac{a}{2} \left[\sum_i \rho_i \left(\frac{z_i - \left(\frac{\pi}{2\Delta} \right) d_i^2 P_n}{1 + \Gamma d_i} \right)^2 \right]^{1/2} \quad (18)$$

which contains the following terms: $a^2 = 4\pi\beta e^2$ and P_n is defined as

$$P_n = \frac{1}{\Omega} \sum_i \frac{\rho_i d_i Z_i}{1 + \Gamma d_i} \quad (19)$$

in which Ω is:

$$\Omega = 1 + \frac{\pi}{2\Delta} \sum_i \frac{\rho_i d_i^3}{1 + \Gamma d_i} \quad (20)$$

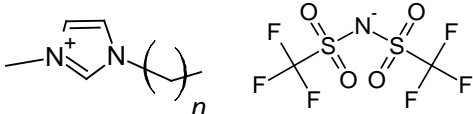
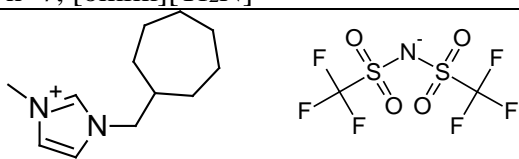
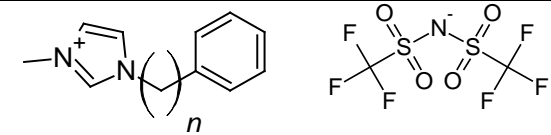
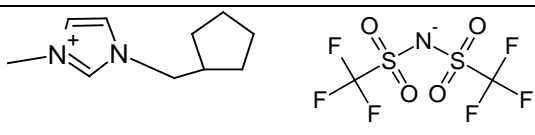
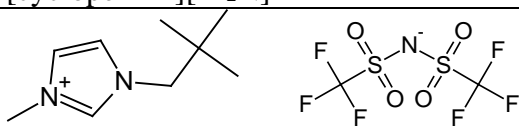
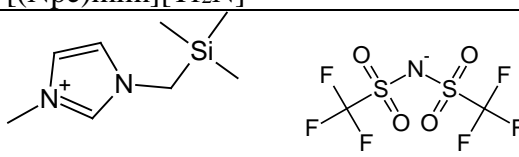
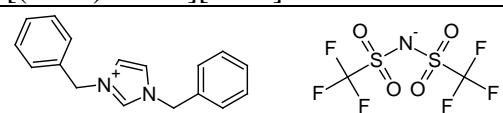
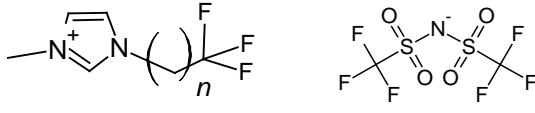
Δ in eq. (20) is defined as $\Delta = 1 - \frac{\pi}{6} \sum_i \rho_i d_i^3$ and inverse shielding length Γ is given as a function of density:

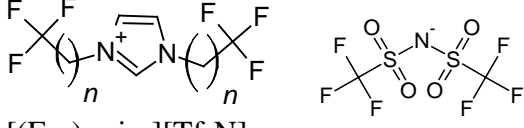
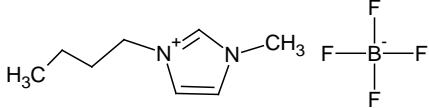
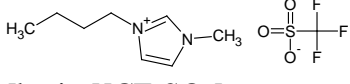
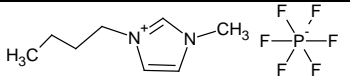
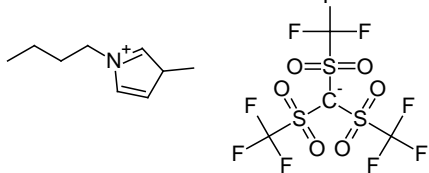
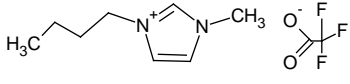

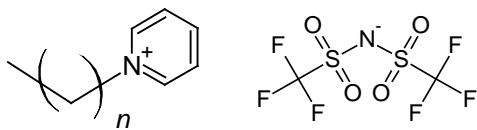
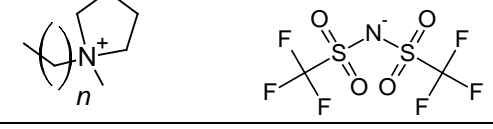
$$\Gamma = \frac{a}{2} (\sum_{i=1}^N \rho_i Z_i^2)^{1/2} \quad (21)$$

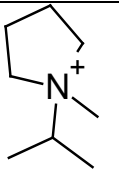
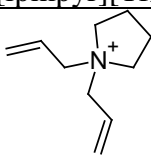
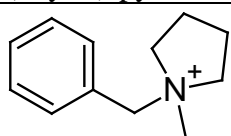
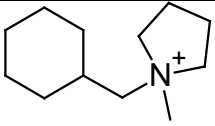
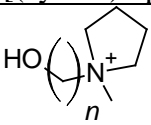
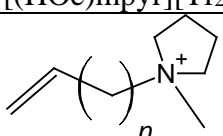
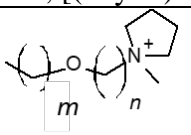
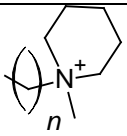
When densities were calculated for several methylimidazolium based ionic liquids, the relative errors between experimental and LYIR equation of state calculated densities were typically below 0.01% for [emim][Tf₂N] [39].

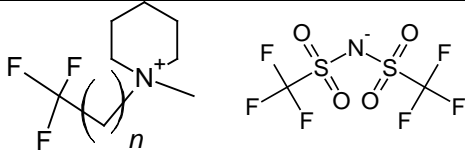
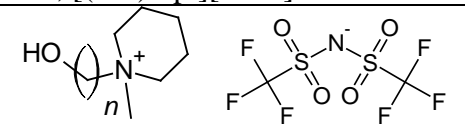
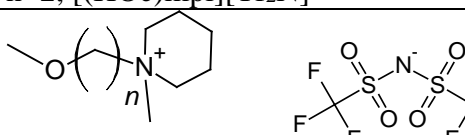
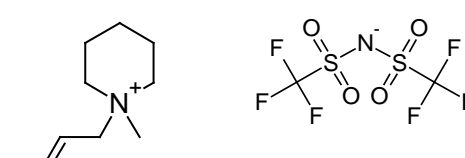
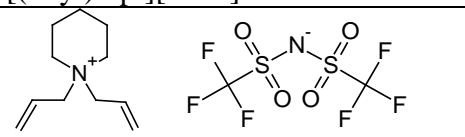
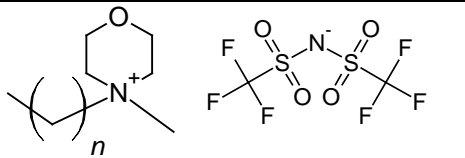
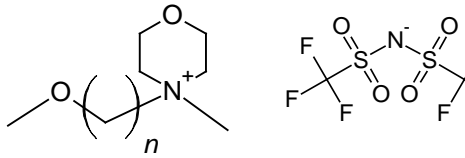
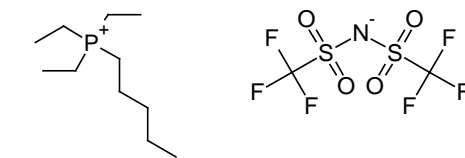
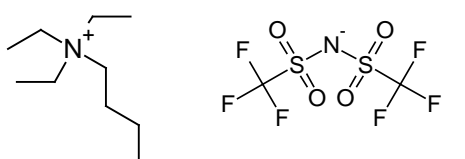
As a conclusion it can be stated that several methods, such as perturbation-based linear Yukawa isotherm regularity, the use of mean spherical approximation for electrostatic interactions in ionic liquid and density prediction using molecular volume, can be successfully applied to predict ionic liquid density.

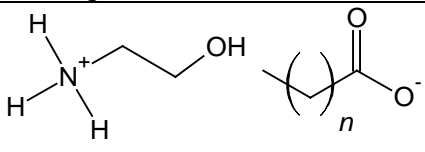
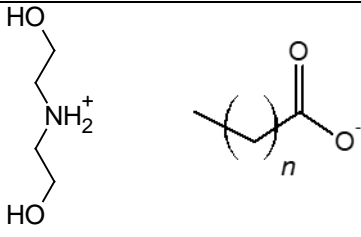
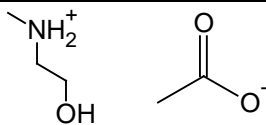
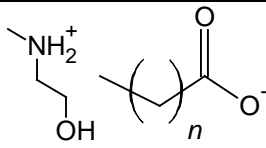
Comparison of ionic liquid densities. Notation: n denotes number of carbon atoms minus one in ionic liquid, Table 1

Entry	Structure and name of ionic liquid	Density (g/cm ³)	Temperature (K)	Reference
Imidazolium cation				
1	 n=0, [mmim][Tf ₂ N]	1.570	298.15	[13]
	n=3, [bmim][Tf ₂ N]	1.437	298.15	[12]
	n=5, [hmim][Tf ₂ N]	1.371	298.15	[12]
	n=7, [omim][Tf ₂ N]	1.320	298.15	[12]
2	 [cyclohmim][Tf ₂ N]	1.432	293.15	[18]
3	 n=1, [(Ph)mmim][Tf ₂ N]	1.504	298.15	[14]
	n=2, [(Ph)emim][Tf ₂ N]	1.456	298.15	[15]
	n=3, [(Ph)pmim][Tf ₂ N]	1.434	298.15	[15]
4	 [cyclopemim][Tf ₂ N]	1483	293.15	[17]
5	 [(Npe)mim][Tf ₂ N]	1.50	295	[27]
6	 [(TMS)mmim][Tf ₂ N]	1.46	295	[27]
7	 [BnBnim][Tf ₂ N]	1.434	298.15	[24]
8	 n=2, [(F ₃ p)mim][Tf ₂ N]	1.44	no temp. reported	[21]

9	 $[(F_3p)_2mim][Tf_2N]$	1.85	no temp. reported	[21]
10	 $[bmim][BF_4]$	1.42	303.15	[12]
11	 $[bmim][CF_3SO_3]$	1.53	303.15	[12]
12	 $[bmim][PF_6]$	1.62	303.15	[12]
13	 $[bmim][triflate]$	1.57	298.15	[5]
14	 $[bmim][CF_3CO_2]$	1.43	303.15	[12]
15	 $n=0, [emim][mSO_4]$	1.286	298.15	[10]
	$n=1, [emim][eSO_4]$	1.237	298.15	[10]
	$n=3, [emim][bSO_4]$	1.176	298.15	[10]
	$n=5, [emim][hSO_4]$	1.130	298.15	[10]
	$n=7, [emim][oSO_4]$	1.096	298.15	[10]
Pyridinium cation				
16	 $n=1, [epy][Tf_2N]$	1.532	298.15	[25]
	$n=3, [bpy][Tf_2N]$	1.456	298.15	[25]
	$n=5, [hpv][Tf_2N]$	1.382	298.15	[25]
	$n=7, [opy][Tf_2N]$	1.3268	Temp. not given	[28]
	$n=9, [dpy][Tf_2N]$	1.2835	Temp. not given	[28]
Pyrrolidinium cation				
17	 $[pyr][Tf_2N]$	1.43	298.15	[16]

	n=2, [pmpyr][Tf ₂ N]			
	n=3, [bmpyr][Tf ₂ N]	1.39	303.15	[16]
	n=5, [hmpyr][Tf ₂ N]	1.33	303.15	[16]
	n=7, [ompyr][Tf ₂ N]	1.27	303.15	[16]
	n=9, [dmpyr][Tf ₂ N]	1.26	303.15	[16]
18	 [ipmpyr][Tf ₂ N]	1.46	303.15	[16]
19	 [(allylm) ₂ pyr][Tf ₂ N]	1.40	no temp. reported	[23]
20	 [(Phm)pyr][Tf ₂ N]	1.438	293.15	[14]
21	 [(cycloh)mpyr][Tf ₂ N]	1.379	293.15	[14]
22	 [(HOe)mpyr][Tf ₂ N]	1.5044	no temp. reported	[7]
23	 n=1, [(allylm)mpyr][Tf ₂ N]	1.43	no temp. reported	[23]
24	 m=0, n=1, [(mOm)mpyr][Tf ₂ N]	1.4827	298.15	[7]
Piperidium cation				
25	 n=2, [pmpi][Tf ₂ N]	1.4070	303.15	[19]
	n=3, [bmpi][Tf ₂ N]	1.3765	303.15	[19]

26	 <p>n=1, [(F₃b)mpi][Tf₂N]</p>	1.48	298.15	[26]
27	 <p>n=2, [(HOe)mpi][Tf₂N]</p>	1.4922	303.15	[7]
28	 <p>n=2, [(mOe)mpi][Tf₂N]</p>	1.4294	303.15	[7]
29	 <p>[(allyl)mpi][Tf₂N]</p>	1.42	no temp. reported	[23]
30	 <p>[(allyl)₂pi][Tf₂N]</p>	1.45	no temp. reported	[6]
Morpholinium cation				
31	 <p>n=3, [bmmo][Tf₂N]</p>	1.439	298.15	[29]
32	 <p>n=2, [(mOe)mмо][Tf₂N]</p>	1.5055	298.15 K	[22]
33	 <p>[TepP][Tf₂N]</p>	1.296	298.15	[3]
34		1.318	298.15	[3]

	[Te(pe)a][Tf ₂ N]			
Protic ionic liquids				
35	 n=2, [2-OHea][but]	1.07	298.16	[20]
	n=3, [2-OHea][pen]	1.045	298.15	[20]
	n=4, [2-OHea][hex]	1.020	298.15	[20]
	 n=4, [(2-OHe) ₂ a][hex]	1.058	298.15	[20]
36	 [2-OHmea][ac]	1.093	298.15	[4]
37	 n=1, [2OHmea][prop]	1.061	298.15	[4]
	n=2, [2-OHmea][but]	1.031	298.15	[4]

Notation

a ammonium

a allyl

ac acetate

b butyl

but butanoate

d dodecyl

e ethyl

F fluoro

h hexyl

hex hexanoate

im imidazolium,
ip isopropyl
m methyl
o octyl
O oxy, ether
OH -ol, alcohol
prop propionate
p propyl
P phosphonium
pe pentyl
pen pentanoate
Ph phenyl
pi piperidinium
py pyridinium
pyr pyrrolidinium
SO₃⁻ sulfonate
T tri
Tf₂N bis(trifluoromethylsulfonyl)imide
triflate tris(trifluoromethylsulfonyl)methide

References

1. Sas D, Ivanis OG, Kijevcanin GR, Gonzales ML, Dominguez B, Radovic A (2018)
Densities and derived volumetric properties of ionic liquids with [Nf₂] and [NTf₂]
anions at high pressures. J Chem Eng Data 63: 954-964

2. Hudleston JG, Visser AE, Reichert WM, Willauer HD, Broker GA, Rogers RD (2001) Characterization and composition of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem* 3: 156-164
3. Seki S, Hayamizu K, Tzuzuki S, Fujii K, Umebayashi Y, Mitsugi T, Kobayashi T, Ohno Y, Kabayasi T, Mita Y, Miyashiro H, Ishigoru SI (2009) Relationship between center atom species (N,P) and ionic conductivity, viscosity, density, self-diffusion coefficient of quaternary cation room-temperature ionic liquids. *Phys Chem Chem Phys* 18: 3509-3514
4. Santos D, Santos M, Franceschi E, Dariva C, Barison A, Mattedi S (2016) Experimental density of ionic liquids and thermodynamic modeling with group contribution equation of state based on the lattice fluid theory. *J Chem Eng Data* 61: 348-353
5. Fredlake CP, Crostwaite JM, Hert DG, Aki SNVK, Brennecke, Thermophysical properties of imidazolium-based ionic liquids 82004) *J Chem Eng Data* 49: 954-964
6. Yim T, Choi CY, Mun J, Oh SM, Kim YG (2009) Synthesis and properties of acyclic ammonium-based ionic liquids with allyl substituents as electrolytes. *Molecules* 14: 1840-1851
7. Wu TY, Su SG, Wang HP, Lin YC, Gung ST, Lin MW, Sun IW (2011) Electrochemical studies and self diffusion coefficients in cyclic ammonium based ionic liquids with allyl substituents. *Electrochim Acta* 56: 3209-3218
8. Lagourette B, Boned C, Saint-Guirons H, Xans P, Zhou H (1992) Densimeter calibration method versus temperature and pressure. *Meas Sci Technol* 3: 699-703
9. Vranes M, Dozic S, Djeric V, Gadzuric S (2012) Physicochemical characterization of 1-butyl-3-methylimidazolium and 1-butyl-1-methylpyrrolidinium bis (trifluoromethyl-sulfonyl)imide. *J Chem Eng Data* 57: 1072-1077

10. Costa AJL, Esperanza JMSS, Marrucho IM, Rebelo LPN (2011) Densities and viscosities of 1-ethyl-3-methylimidazolium *n*-alkyl sulfates. *J Chem Eng Data* 56: 3433-3441
11. Wang J, Li Z, Li C, Wang Z (2010). Density prediction of ionic liquids at different temperatures and pressures using a group contribution equation of state based on electrolyte perturbation theory. *Industrial & Engineering Chemistry Research*. 49 (9): 4420-4425
12. Tokuda H, Hayamizu K, Ishii K, Bin Hasan SMA, Watanabe M (2004), Physicochemical properties and structures of room temperature ionic liquids. I. Variation of anionic species. *J Phys Chem B* 108:16593-16600
13. Dzueba SV, Batsch RA (2002) Influence of structural variations in 1-alkyl(aralkyl)-3-methylimidazolium hexafluorophosphates and bis(trifluoromethylsulfonyl)imides on physical properties of the ionic liquids. *Chem Phys Chem* 3: 161-166
14. Shirota H, Matsozaki H, Ramati S, Wishart JF (2015) Effects of aromaticity in cations and their functional groups on the low-frequency spectra and physical properties of ionic liquids. *Phys Chem B* 119, 29: 9173-9187
15. Mandai T, Matsumara A, Imanari M, Nishikawa K (2012) Effects of cyclic-hydrocarbon substituents and linker length on physicochemical properties and reorientational dynamics of imidazolium-based ionic liquids. *J Phys Chem B* 116: 2090-2095.
16. Appetecchi GB, Montanino M, Zane D, Carewski M, Alessandri F, Passerini S (2009) Effect of the alkyl group on the synthesis and the electrochemical properties of *N*-alkyl-*N*-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide ionic liquids. *Electrochim Acta* 54: 1325-1332

17. Mandai T, Masu H, Imanari M, Nishikawa K (2012) Comparison between cycloalkyl- and *n*-alkyl-substituted imidazolium-based ionic liquids in physicochemical properties and reorientational dynamics. *J Phys Chem B* 116: 2059-2064
18. Mandai T, Imanari M, Nishikawa K (2011) Correlation between hydrocarbon flexibility and physicochemical properties for cyclohexyl-imidazolium based ionic liquids studied by ¹H and ¹³C NMR. *Chem Phys Let* 507: 100-104
19. Bhattejee A, Carvalho PJ, Coutinho JAP (2014) The effect of the cation aromaticity upon the thermophysical properties of piperidinium- and pyridinium-based ionic liquids. *Fluid Phase Equilib* 375: 80-88
20. Pinto RR, Mattedi S, Aznai M (2015) Synthesis and physical properties of three protic ionic liquids with the ethylammonium cation. *Chem Eng Transactions* 43 1165-1170
21. Singh RP, Manandhar S, Sheeve JM (2002) New dense fluoroalkyl-substituted imidazolium ionic liquids. *Tetrahedron Lett* 43: 9497-9499
22. Zhou BZ, Matsumoto H, Tatsumi K (2006) Cyclic quaternary ammonium ionic liquids with perfluoroalkyltrifluoroborates: Synthesis, characterization, and properties. *Chem Eur J* 12: 2196-2212
23. Yim T, Lee H, Kim H, Mun J, Kim S, Oh S, Kim Y (2007) Synthesis and properties of pyrrolidinium and piperidinium Bis(trifluoromethanesulfonyl)imide ionic liquids with allyl substituents. *Bull Korean Chem Soc* 28: 1567-1572
24. Tao R, Tamas G, Xue L, Simon SL, Quitevis EL (2014) Thermophysical properties of imidazolium-based ionic liquids: The effect of aliphatic versus aromatic functionality. *J Chem Eng Data* 59: 2717-2724
25. Bittner B, Wrobel RJ, Milchert EJ (2012) Physical properties of pyridinium ionic liquids. *J Chem Thermodyn* 55: 159-165

26. Le MLP, Alloin F, Strobel P, Lepretre JC, Cointeaux L, del Valle C (2012) Electrolyte based on fluorinated cyclic quaternary ammonium ionic liquids. *Ionics Kiel* 18: 817-827
27. Shirota H, Castner EW (2005) Why are viscosities lower for ionic liquids with $-\text{CH}_2\text{Si}(\text{CH}_3)_3$ vs $-\text{CH}_2\text{C}(\text{CH}_3)_3$ substitutions on the imidazolium cations? *J Phys Chem B* 109: 21576-21585
28. Yunus NM, Mutalib Am Man Z, Bustam MA, Murugesan T (2010) Thermophysical properties of 1-alkylpyridinium bis (trifluoromethylsulfonyl) imide ionic liquids. *J Chem Thermodyn* 42: 491-495
29. Galinski M, Stepniak I (2009) sMorpholium-based ionic mixtures as electrolytes in electrochemical double layer capacitors. *J Appl Electrochem* 39: 1949-1953.
30. Klamt A (1995) Conductor-like screening model for real solvents: A new approach to the quantitative calculation of solvation phenomena, *The J Phys Chem* 99 (7): 2224-2235
31. Patel NK, Joshipura MH (2013) Generalized PSRK model for prediction of liquid density of ionic liquids. *Procedia Engineering* 51: 386-394
32. Montalbán MG, Collado-González M, DíazBanos FG, Villora G (2017) Predicting density and refractive index of ionic liquids Ch. 15, 339-368, Intech, open science
33. Montalban MG, Bolívar CL, Diaz Banos FG, VÍllora G (2015). Effect of temperature, anion, and alkyl chain length on the density and refractive index of 1-alkyl-3-methylimidazolium-based ionic liquids. *J Chem & Eng Data* 60(7): 1986-1996
34. Kato R, Gmehling J (2005). Measurement and correlation of vapor–liquid equilibria of binary systems containing the ionic liquids [EMIM][(CF₃SO₂)₂N],[BMIM][(CF₃SO₂)₂N],[MMIM][(CH₃)₂PO₄] and oxygenated organic compounds respectively water. *Fluid Phase Equilibria* 231(1): 38-43

35. Joshipura MH, Dabke SP, Subrahmanyam N (2010) Modeling vapour pressure using compound specific cohesion factor relationship. *Journal of the Taiwan Institute of Chemical Engineers* 41(5): 570-578
36. Cotterman RL, Schwarz, BJ, Prausnitz JM (1986). Molecular thermodynamics for fluids at low and high densities. Part I: Pure fluids containing small or large molecules. *AIChE journal* 32(11): 1787-1798
37. Martin MG, Siepmann JI (1998) Transferable potentials for phase equilibria. 1. United-atom description of n-alkanes. *J Phys Chem B* 102(14): 2569-2577.
38. Wang J, Li C, Shen C, Wang Z (2009) Towards understanding the effect of electrostatic interactions on the density of ionic liquids. *Fluid phase equilibria* 279(2): 87-91.
39. Mahboub MS, Farrokhpour H (2016) Molecular thermodynamic modeling of ionic liquids using the perturbation-based linear Yukawa isotherm regularity. *J Phys Cond Matter* 28(23): 235101
40. Mahboub MS, Farrokhpour H, Parsafar GA (2016). Linear Yukawa Isotherm Regularity for dense fluids derived based on the perturbation theory. *Fluid Phase Equilibria* 409: 105-112