



# Ionic and molar volumes of room temperature ionic liquids

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## ABSTRACT

A large set of ionic volumes of the constituent ions of a variety of (non-protic) RTILs is used for the estimation of their molar volumes, hence their densities, at various temperatures by means of two fitting parameters only. The difference between the sum of the ionic volumes of the cation and the anion per mole and the actual molar volume is ascribed to the expansion of the RTIL on melting.

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## 1. Introduction

The physical properties of room temperature ionic liquids (RTILs) can be predicted according to many approaches as reviewed recently by Coutinho et al. [1], including from group contributions as reviewed by Gardas and Coutinho [2]. An approach called volume based thermodynamics has also been employed for this purpose as developed by Beichel et al. [3], involving the individual ionic volumes of the constituting cations,  $v_+$ , and anions,  $v_-$ . The molar volumes of the RTILs are given by:

$$V = N_A(v_+ + v_-) \quad (1)$$

where  $N_A$  is Avogadro's number, and the predicted densities  $\rho = M/V$  are obtained from these and the molar masses  $M$ . Rather than using ionic volumes, van der Waals volumes of the ions,  $v_{vdW}^{+/-}$ , have also been employed for this purpose [4]. These are related to the ionic volumes obtained directly from the crystal structures as:

$$v_{vdW+} + v_{vdW-} = (v_{cell}/Z)P = (v_+ + v_-)P \quad (2)$$

where  $v_{cell}$  is the unit cell volume of the crystalline RTIL containing  $Z$  formula units and  $P$  is the packing fraction. The values of  $P$  vary slightly among various classes of RTILs [4], but are, on the average,  $0.6875 \pm 0.0055$ , i. e., within  $<1\%$ . Therefore, values of  $(v_+ + v_-)$  may be reconstituted from the reported  $(v_{vdW+} + v_{vdW-})$  values in [4] by division of the latter by 0.6875. Ionic volumes have been reported by several authors [3,5–7] and a representative list for commonly encountered RTILs is shown in Table 1. The ionic volumes are generally reported at

an unspecified temperature and pressure, presumed to be those at the standard ambient conditions, 298.15 K and 0.1 MPa.

There is an almost inexhaustible variety of RTILs that have been synthesized and applied, and many of their physical properties, including their densities, have been measured. In order to remain realistic this paper deals with the most popular groups among the RTILs, many members of which are commercially available. These include salts of the 1-alkyl-3-methylimidazolium, 1-alkylpyridinium (with possible 2, 3, or 4-methyl substitution), 1-alkyl-1-methylpyrrolidinium and other non-symmetrical quaternary ammonium, and quaternary phosphonium cations.

According to Eq. (1) the molar volumes  $V$  of the RTILs should be, with the specified units:

$$V/\text{cm}^3 \text{mol}^{-1} = 602.2[(v_+ + v_-)/\text{nm}^3]. \quad (3)$$

The calculated  $V$  at ambient conditions from Eq. (3) and the ionic volumes in Table 1 (second column) leads to too small values, as is demonstrated in Fig. 1 for 174 of the common types of RTILs with cations as mentioned above and a variety of anions.

It is attempted to improve the reliability of the calculation of the molar volumes of RTILs in the simplest manner that would still agree better with the experimental values. The latter, together with the isobaric expansibilities have been compiled recently by the author [8] and a few additional newly reported values have also been considered here.

### 1.1. The ionic volume database

The ionic volumes shown in Table 1 for monatomic and small polyatomic anions ( $\text{SCN}^-$ ,  $\text{NO}_3^-$ ) are taken from Jenkins et al. [9] or the  $v_j$

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**Table 1**  
Ionic volumes of the constituents of RTILs (tw = this work, see text).

Ion*	$v/\text{nm}^3$	Ref.	$v/\text{nm}^3$	Ref.	$v/\text{nm}^3$	Ref.
$C_n\text{mim}^+$	$0.106 + 0.0230n$	tw	$0.111 + 0.022n^a$	[6]	$0.103 + 0.027n^b$	[7]
$C_n\text{Py}^+$	$0.096 + 0.0239n$	tw	$0.102 + 0.024n$	[5]	$0.099 + 0.025n$	[4] <sup>c</sup>
$C_n(C_m)_3\text{N}^+$	$0.034 + 0.024(n + 3m)$	tw				
$C_n\text{MePyr}^+$	$0.119 + 0.0234n$	tw	$0.238^c$	[9]	$0.132 + 0.025n$	[4] <sup>e</sup>
$C_n(C_m)_3\text{P}^+$	$0.133 + 0.021(n + 3m)$	tw	$0.499^d$	[10]		
$C_2\text{mmim}^+$	0.173	[3]	$0.183^e$	[4]		
$C_4\text{mmim}^+$	0.220	[3]	$0.229^e$	[4,6]	0.275	[17]
$C_4(4M)\text{Py}^+$	0.221	[6]				
$C_5(4M)\text{Py}^+$	0.238	[6]				
$C_2\text{MPip}^+$	0.192	[11]				
$C_3\text{MPip}^+$	0.208	[3]				
$\text{Cl}^-$	0.047	[5,12]	0.033	[7]		
$\text{Br}^-$	0.056	[5,12]				
$\text{I}^-$	0.072	[12]				
$\text{NO}_3^-$	0.064	[5,12]	0.062	[3]	$0.058^e$	[4]
$\text{SCN}^-$	0.071	[12]	0.075	[3]		
$\text{CH}_3\text{CO}_2^-$	0.078	[3]	0.086	[13]	0.071	[7]
$\text{CF}_3\text{CO}_2^-$	0.103	[3]	0.108	[5]	0.103	[7]
$\text{BF}_4^-$	0.079	[3]	0.073	[4,5]	0.078	[7]
$\text{PF}_6^-$	0.111	[3]	0.105	[6,7]	0.100	[4]
$\text{AlCl}_4^-$	0.156	[9]				
$\text{FeCl}_4^-$	0.155	[9]				
$\text{N}(\text{FSO}_2)_2^-$	0.139	[14]	0.148	[3]		
$\text{NTF}_2^-$	0.230	[3]	0.232	[6]	0.246	[7]
$\text{N}(\text{CN})_2^-$	0.089	[3,6]	0.069	[7]	$0.080^e$	[4]
$\text{B}(\text{CN})_4^-$	0.156	[15]				
$\text{CH}_3\text{SO}_3^-$	0.099	[3,5]	0.096	[7]	$0.095^e$	[4]
$\text{CF}_3\text{SO}_3^-$	0.126	[3]	0.130	[6,7]	0.128	[7]
$\text{MePhSO}_3^-$	0.196	[3]	0.208	[7]	$0.195^e$	[4]
$C_n\text{SO}_4^-$	$0.080 + 0.027n^b$	[7]				
$\text{PF}_3(\text{C}_2\text{F}_5)_3^-$	0.334	[3]	0.383	[16]		

\* The following abbreviations are employed:  $C_n = \text{H}(\text{CH}_2)_n$ ,  $\text{mim}^+ = 1$ -alkyl-3-methylimidazolium,  $\text{mmim}^+ = 1$ -alkyl-2,3-dimethylimidazolium,  $\text{Py}^+ = 1$ -alkylpyridinium,  $(4M)\text{Py}^+ = 1$ -alkyl-4-methylpyridinium,  $\text{MePyr}^+ = 1$ -alkyl-1-methylpyrrolidinium,  $\text{Pip}^+ = 1,1$ -dialkylpiperidinium,  $\text{TdHx}_3 = \text{tetradecyltrihexyl}$ ,  $\text{NTF}_2^- = \text{bis}(\text{trifluoromethylsulfonyl})\text{amide}$ ,  $\text{MePhSO}_3^- = p$ -toluenesulfonate (tosylate).

<sup>a</sup> For  $2 \leq n \leq 8$ ,  $m = 1$  or  $2$ .

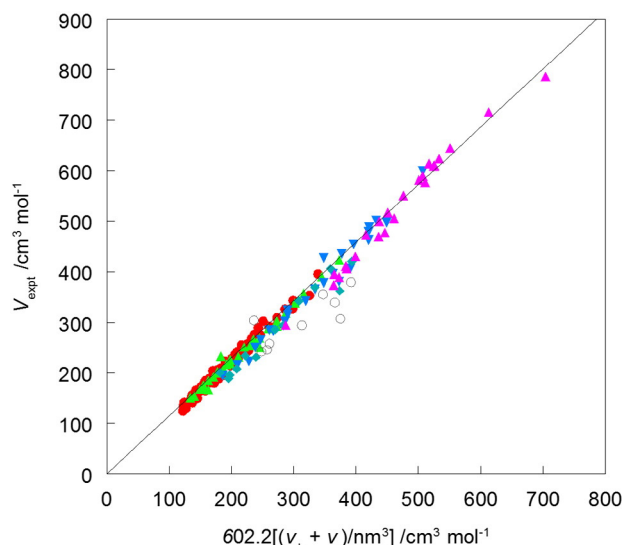
<sup>b</sup> For  $C_n\text{mim}$   $2 \leq n \leq 10$  and for  $C_n\text{SO}_4$   $n = 1, 2, 8$ .

<sup>c</sup> For  $n = 4$  with the ionic volume of  $\text{TaCl}_6^-$  from [9].

<sup>d</sup> For  $\text{Bu}_4\text{P}^+$ , [17], but  $\text{MeBu}_3\text{N}^+$  has  $v = 0.388 \text{ nm}^3$ .

<sup>e</sup> From the van der Waals volumes of the ions divided by 0.6875, see the text following Eq. (2).

entries in Marcus et al. [12]. Some of the values for complex anions ( $\text{AlCl}_4^-$ ,  $\text{FeCl}_4^-$ ,  $\text{TaCl}_6^-$ ) are also from Jenkins et al. [9]. Many of the ionic volumes of organic cations have been adopted from the ‘scaled volumes’ of Beichel et al. [3], that do not differ much from those (presumably non-scaled) listed by Ye and Shreve [5] and by Slater et al. [6]. The  $v_-$  value of  $\text{CH}_3\text{CO}_2^-$  is from Almeida et al. [13], those of  $\text{BF}_4^-$ ,  $\text{CH}_3\text{SO}_3^-$ ,  $\text{CF}_3\text{CO}_2^-$  are from Ye and Shreve [5], and those of  $\text{PF}_6^-$ ,  $\text{N}(\text{CN})_2^-$ ,  $\text{CF}_3\text{SO}_3^-$ , and  $\text{NTF}_2^-$  (bis(trifluoromethylsulfonyl)amide) are from Slater et al. [6]. Other anion ionic values are from several sources: for FSA (difluoro-sulfonylamide),  $\text{N}(\text{FSO}_2)_2^-$  it is the average of the unit cell volumes per formula unit of crystalline  $\text{Na}^+$  and  $\text{K}^+$  salts [14] after subtraction of the cation volumes [9]. The  $v_-$  for  $\text{B}(\text{CN})_4^-$  is the average of the unit cell volumes per formula unit of two crystalline quaternary ammonium salts [15] after subtraction of the cation volumes (see below). The  $v_-$  for the tosylate anion ( $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ ) is from Bica et al. [7] and a large value for FAP ( $\text{PF}_3(\text{C}_2\text{F}_5)_3^-$ ) is from Liu et al. [16]. For the alkylsulfate esters the expression for  $v_-$  is derived from Bica et al. [7]. Note that for some of the anions discordant values have been reported, shown in the fourth and sixth columns of Table 1, some differing considerably from those in the second column but others only slightly, and these are not used further in this paper.



**Fig. 1.** A plot of the experimental molar volumes,  $V_{\text{exp}}$ , of 174 RTILs at 298.15 K against those calculated according to Eq. (2) from the ionic volumes listed in Table 1: ●  $C_n\text{mim}^+$  salts, ▲  $C_n\text{Py}^+$  salts, ▼  $R_4\text{N}^+$  salts, ◆  $C_n\text{MePyr}^+$  salts, ■  $R_4\text{P}^+$  salts, and ○ are outliers.

For many of the cations of RTILs there is a constant increment in the ionic volume per  $-\text{CH}_2-$  group in their alkyl chains. This view was challenged by Bogdanov and Kantlehner [18], according to whom the increment per methylene group diminishes linearly with the number  $n$  of such groups:  $\Delta v(\text{CH}_2)/\text{nm}^3 = 0.031 - 0.00146n$  for an optimal fit of the molar volumes and viscosities of some four dozen RTILs. This approach, however, has not been endorsed by others, who accepted the constancy of this increment that is applied in the present study. The entries marked ‘tw’ in Table 1 resulted from a linear regression of the relevant values from [3], rather than those for  $C_n\text{mim}^+$  and  $C_n\text{Py}^+$  ( $C_n = \text{H}(\text{CH}_2)_n$ ) from Slattery et al. [6], that have estimated uncertainties of 0.005–0.02  $\text{nm}^3$ . The values from Bica et al. [7] in the sixth column lead to too large values for the longer chain ions. The ionic volumes of the unsymmetrical tetraalkylphosphonium cations,  $C_n(C_m)_3\text{P}^+$ , were calculated in this work from the few values for individual lengths of the alkyl chains [3,5,6,10,19,20]. A few individual cationic volumes, not covered by these expressions are: 1-butyl-2,3-dimethylimidazolium ( $C_4\text{mmim}^+$ ) [17], 1-butyl-4-methylpyridinium ( $C_4(4M)\text{Py}^+$ ) [6], and 1-ethyl-1-methylpiperidinium ( $\text{EtMePip}^+$ ) [11].

## 2. Molar volume calculations

As mentioned above and demonstrated in Fig. 1, the calculation of the molar volumes of RTILs by means of Eq. (3) and the ionic volumes listed in Table 1 leads to too small values, about 87% of the experimental ones. Several schemes have been proposed to account for the difference between the sum of the cationic and anionic volumes in crystalline solids and the corresponding sums in liquid RTILs. This was done by Ye and Schreve [5] rather arbitrarily by the addition of  $0.025 \text{ nm}^3$  on the average to the ionic volumes of five cation series (1-alkyl-3-methylimidazolium, 1-alkylpyridinium, 1-alkyl-1-methylpyrrolidinium, quaternary ammonium and phosphonium) and one anion ( $\text{NTF}_2^-$ ) but not to other anions. Thus good predictions of the densities of RTILs (at non-specified temperatures):  $\rho = M/N_A(v_+ + v_-)$  could be achieved. A different empirical expression was applied by Slattery et al. [6] to the densities of RTILs with  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{N}(\text{CN})_2^-$ , and  $\text{NTF}_2^-$  anions:  $\rho(1)/(\text{g cm}^{-3}) = 1.4684[M/(\text{g mol}^{-1})]/[(v_+ + v_-)/\text{nm}^3]^{1.0026}$ , valid at 20–22 °C. Subsequently Preiss et al. [21] improved on this expression and allowed for the temperature dependence of the density, employing four

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