1456 *J. Phys. Chem. A* **2007,** *111,* 1456−1461

Rapid and Accurate Estimation of Densities of Room-Temperature Ionic Liquids and Salts

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Received: September 22, 2006; In Final Form: January 3, 2007

Volume parameters for room-temperature ionic liquids (RTILs) and salts were developed. For 59 of the most common imidazolium, pyridinium, pyrrolidinium, tetralkylammonium, and phosphonium-based RTILs, the mean absolute deviation (MAD) of the densities is 0.007 g cm^{-3}; for 35 imidazolium-based room-temperature salts, the MAD is 0.020 g cm^{-3}; and for 150 energetic salts, the MAD is 0.035 g cm^{-3}. The experimental density (Y) for an alkylated imidazolium or pyridinium-based room-temperature ionic liquid is approximately proportional to its calculated density (X) in the solid state: $Y = 0.948X - 0.110$ (correlation coefficient: $R^2 = 0.998$, for BF_4^-, PF_6^-, NTf_2^--containing ionic liquids); $Y = 0.934X - 0.070$ (correlation coefficient: $R^2 = 0.999$, for OTf $^-$, $CF_3CO_2^-$, $N(CN)_2^-$-containing ionic liquids).

Introduction

Density is one of the basic and important physical properties of any material. This property is particularly important for energetic compounds. High density is desirable for energetic materials since more energy will then be packed per unit volume. Moreover, density is a critical factor that, according to a semiempirical equation suggested by Kamlet and Jacobs,[1] affects detonation performance, namely, detonation pressure (P) is dependent on the square of the density, and the detonation velocity (D) is proportional to the density:[2]

$$P\ (\mathrm{GPa}) = k\rho^2\varphi;\ D\ (\mathrm{mm}\ \mu\mathrm{s}^{-1}) = A\varphi^{1/2}(1 + B\rho)$$

Most recently, many efforts have been focused on energetic ionic liquids/salts,[3] since ionic energetic materials often possess advantages over molecular compounds such as low vapor pressure and high density. A typical example is 1,2,4-triazolium perchlorate which exhibits a density of 1.95 g cm^{-3}.[4] Density is also critically needed for the estimation of lattice energy (ΔH_L)[5] of an ionic species which then can be utilized to calculate the heat of formation ($\Delta_f H_{298}°$). On the basis of the Born−Haber cycle, $\Delta_f H_{298}°$ can be simplified as

$$\Delta_f H_{298}°\ (\mathrm{salt}) = \Delta_f H_{298}°\ (\mathrm{cation}) + \Delta_f H_{298}°\ (\mathrm{anion}) - \Delta H_L$$

For 1:1, polyatomic and nonlinear salts:[5]

$$\Delta H_L\ (\mathrm{kJ\ mol^{-1}}) = 1981.2\ (W/\rho)^{1/3} + 108.8$$

where W is the molar weight of the energetic salt (g mol^{-1}); ρ is the density.

The heats of formation of cation and anion [$\Delta_f H_{298}°$ (cation) and $\Delta_f H_{298}°$ (anion)] can be calculated using the electronic structure method or can be roughly estimated by a group additivity method. Thus, when the density can be predicted in a facile way, it is much easier to predict the properties such as heat of formation, detonation pressure, detonation velocity, and so on, which would facilitate screening of high-density energetic materials for civilian and military applications, since the nonprofitable candidates can be excluded at a very early stage.

Accurate density estimation can be achieved by several ways, for example, (1) group additivity where the volume parameters of different kinds of groups or atoms have been developed, for example, by Exner,[6] Stine,[7] Tarver,[8] Ammon,[9] and so forth; (2) average atom volume (AAV);[10] and (3) high-level ab intio calculations.[11] The former two methods mainly aim at estimation of densities of neutral molecules, no ionic species were specifically included, and while the third method theoretically can compute any molecule, for large molecules it is very expensive and time-consuming.

Jenkins has tabulated the volumes of a variety of mainly inorganic cations and anions to predict lattice energy,[12] where Goldschmidt radii (r_+) of alkali metal and alkali earth metal cations were used to define the corresponding effective volumes of cations, V_+, by taking them to be equal to $4/3\pi r_+^3$. The volume of an anion (V_-) was then estimated by subtracting the calculated cation volume from the molecular volume (V) of the salt, assuming that V is the linear sum of the cation and anion volumes. Therefore, for M_pX_q: $V = pV_+ + qV_-$, the density is estimated by $\rho = W/(0.6022V)$.

Inspired by this work, we report here a rapid and facile method of group addivity for estimation of density specifically for room-temperature ionic liquids (RTILs) and salts.

Discussion

One paper has reported the prediction of densities of RTILs on the basis of surface tension;[13] however, this is not a straightforward method since it is based on a second physical property. For comparison, we believe that group addivity is the most convenient method of choice for this purpose. To derive the volume parameters for density estimation, the Cambridge Structure Database (CSD, ConQuest Version 1.8, 2006) was analyzed. The majority of ionic liquids/salts are based on imidazolium, triazolium, tetrazolium, and tetraalkylammonium cations with anions, such as BF_4^-, PF_6^-, (bis(trifluoromethanesulfonyl)amide (Tf_2N^-), CF_3SO_3 (OTf $^-$), NO_3^-, ClO_4^-, $N(NO_2)_2^-$, and so forth. Therefore, combining the known volumes of 1,3-dihydro-imidazolium, 1,4-dihydro-1,2,4-triazolium, and 1,5-dihydro-tetrazolium cations with the volumes of

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10.1021/jp066202k CCC: $37.00

TABLE 1: Volume Parameters of Groups and Fragments for Salts[a]

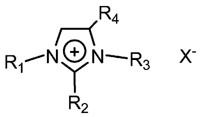
species	volume (Å^3)	species	volume (Å^3)
		Neutral	
imidazole	84	1,2,4-triazole	79
tetrazole	75	*s*-triazine	90
1,2,4,5-tetrazine	87	pyrimidine	100
cubane	135	furazan	77
benzene	110	pyridine	105
		cations	
1,3-2H-imidazolium (+)[b]	79	1,4-2H-1,2,4-triazolium (+)	73
1,4-2H-tetrazolium (+)	66	N-H-pyridinium (+)[b]	95
guanidinium (+)	69	triaminoguanidinium (+)	105
Me_4N^{+}[b]	113	Me_4P^{+}[b]	133
HMTA-H(+)[c]	155	NH_4^{+}[d,e]	21
NH_2NH_3 (+)	30	azetidinium (+)	76
		Anions	
imidazolate (−)	93	1,2,4-triazolate (−)	87
1-tetrazolate (−)	80	$(NO_2)_3C$ (−)	141
picrate (−)	218	NTO (−)[f]	123
NO_3^{-}[d]	64	ClO_4^{-}[d]	82
$N(NO_2)_2^{-}$	98	N_3^{-}	60
NO_2^{-}[d]	55	CN^{-}[d]	50
CF_3CO_2 (−)	108	CH_3SO_3 (−)	99
TfO^{-}[g]	129	PF_6^{-}	107
BF_4^{-}[d]	73	Tf_2N^{-}[b]	230
Br^{-}[d]	56	Cl^{-}[d]	47
		Groups	
H (bonded to N)	7	H (bonded to C)	5
CH_3[b]	30	NO_2	36
NH_2[h]	20	N_3	41
NF_2	37	CF_2	37.5
CN	30	OH	15
CH_2 (acyclic)[b]	24	CH_2 (five- or six-membered ring)	22
CH_2 (eight-membered ring)	21	C═O (not in a ring)	24
−N═N−	26	N	10
NH	15	F	12.5

[a] Typical deviation of cation or anion is 5−20 Å.^{3} [b] For ionic liquids: 1,3-dimethylimidazolium: 154; *N*-methylpyridinium: 146; Me_4N^+: 136; Me_4P^+: 163; 1,1-dimethylpyrrolidinium: 169; Tf_2N^-: 248; CH_2: 28; CH_3: 35; H 7 Å.^{3} [c] HMTA, hexamethylenetetramine. [d] Reference 12. [e] $V(NH_4^+) = 15$ Å^3 for inorganic salts. [f] NTO: 3-nitro-1,2,4-triazol-5-one. [g] Reference 11b. [h] For very strong hydrogen bonds, $V(NH_2) = 12$ Å,^{3} see text.

other functional groups, it is very convenient to derive the molecular volume of the various substituted imidazolium, triazolium, or tetrazolium ionic liquids and salts.

Following Jenkins' procedure described above, volumes of anions such as Tf_2N^-,[14a] picrate, trifluoroacetate, and $N(NO_2)_2^-$ [14b] were calculated, while BF_4^-, NO_3^-, ClO_4^-, NO_2^-, Br^-, and Cl^- were taken directly from the literature.[12] Jenkins recommended the values of 109 ± 8 and 56 ± 14 Å^3 for PF_6^- and N_3^-. These two values were refined as 107 and 60 Å,^{3} respectively (Table 1). For the volume parameters of functional groups, hydrogen bonded to nitrogen or carbon in the building blocks in Table 1 is arbitrarily set as 7 or 5 Å,^{3} respectively. This is to fit the fact that groups bonded to nitrogen normally have a smaller volume than those bonded to carbon by nearly 2 Å.^{3} Volume parameters for other functional groups were utilized as found in the literature or were refined. When the volume of anions and functional groups are available, it is easy to derive the average volume of the building blocks, such as 1,3-dihydro-imidazolium, 1,4-dihydro-1,2,4-triazolium, and so forth. For each species of neutral fragments, cations, and anions, 4−30 analogues were analyzed, and the average volumes are listed in Table 1. The typical average error in the estimated volume of a cation or anion is 10−20 Å.^{3} Ammonium salts normally show big deviations in densities. Its volume ($V(NH_4^+)$) was set previously at 21 Å,[3,12] but the average volume of seven inorganic salts including nitrate, perchlorate, and dinitroamide is about 15 Å^3. Therefore, we recommend 15 Å^3 as the volume of NH_4^+ for inorganic salts while 21 Å^3 for normal organic salts.

TABLE 2: Prediction of Densities of Imidazolium-Based RTILs[a]



entry	R_1	R_2	R_3	R_4	X	MW	density (g cm^{-3}) expt[a]	density (g cm^{-3}) this work
1	CH_3	H	C_2H_5	H	BF_4	197.97	1.279[b]	1.289
2	CH_3	H	C_2H_4OH	H	BF_4	213.97	1.33[c]	1.326
3	CH_3	H	*n*-C_4H_9	H	BF_4	226.02	1.208[d]	1.207
4	CH_3	H	*n*-C_6H_{13}	H	BF_4	254.08	1.148[e]	1.149
5	CH_3	H	*n*-C_8H_{17}	H	BF_4	282.13	1.109[e]	1.108
6	C_2H_5	H	*n*-C_6H_{13}	H	BF_4	268.1	1.128[e]	1.127
7	C_2H_5	H	*n*-C_8H_{17}	H	BF_4	296.16	1.088[e]	1.090
8	CH_3	H	*n*-C_4H_9	H	PF_6	284.18	1.37	1.367
9	CH_3	H	*n*-C_6H_{13}	H	PF_6	312.24	1.293[e]	1.293
10	CH_3	H	*n*-C_8H_{17}	H	PF_6	340.29	1.237[e]	1.236
11	C_2H_5	H	*n*-C_6H_{13}	H	PF_6	326.26	1.262[e]	1.263
12	C_2H_5	H	*n*-C_8H_{17}	H	PF_6	354.32	1.212[e]	1.213
13	CH_3	H	CH_3	H	NTf_2	377.28	1.559	1.558
14	CH_3	H	C_2H_5	H	NTf_2	391.31	1.518	1.511
15	C_2H_5	H	C_2H_5	H	NTf_2	405.34	1.452	1.470
16	CH_3	H	C_2H_5	CH_3	NTf_2	405.34	1.47	1.470
17	C_2H_5	H	C_2H_5	CH_3	NTf_2	419.36	1.432	1.433
18	CH_3	H	n-C_4H_9	H	NTf_2	419.36	1.429	1.433
19	CH_3	CH_3	C_2H_5	H	NTf_2	405.34	1.495	1.470
20	CH_3	H	2′-*i*-C_4H_9	H	NTf_2	419.36	1.428	1.433
21	CH_3	H	CH_2CF_3	H	NTf_2	445.28	1.656	1.654
22	CH_3	H	$C_2H_4OCH_3$	H	NTf_2	421.34	1.496	1.495
23	CH_3	H	*n*-C_6H_{13}	H	NTf_2	447.42	1.37[f]	1.371
24	C_2H_5	H	*n*-C_6H_{13}	H	NTf_2	461.44	1.343[e]	1.344
25	CH_3	H	*n*-C_8H_{17}	H	NTf_2	475.47	1.32[g]	1.320
26	CH_3	H	*n*-$C_{10}H_{21}$	H	NTf_2	503.53	1.271	1.279
27	CH_3	H	C_2H_5	H	OTf	260.23	1.390	1.389
28	C_2H_5	H	C_2H_5	H	OTf	274.26	1.330	1.343
29	CH_3	H	C_2H_5	CH_3	OTf	274.26	1.334	1.343
30	CH_3	H	*n*-C_4H_9	H	OTf	288.29	1.30	1.304
31	C_2H_5	H	*n*-C_4H_9	H	OTf	302.31	1.270	1.271
32	CH_3	H	*n*-C_6H_{13}	H	OTf	316.34	1.24[f]	1.242
33	CH_3	H	*n*-C_8H_{17}	H	OTf	344.39	1.12	1.194
34	CH_3	H	C_2H_5	H	CF_3CO_2	224.18	1.285	1.284
35	C_2H_5	H	C_2H_5	H	CF_3CO_2	238.21	1.250	1.244
36	CH_3	H	*n*-C_4H_9	H	CF_3CO_2	252.23	1.209	1.211
37	C_2H_5	H	*n*-C_4H_9	H	CF_3CO_2	266.26	1.183	1.182
38	CH_3	H	C_2H_5	H	$N(CN)_2$	177.21	1.08[h]	1.098
39	CH_3	H	*n*-C_4H_9	H	$N(CN)_2$	205.26	1.06[g]	1.052
40	CH_3	H	*n*-C_8H_{17}	H	$N(CN)_2$	261.36	1.0[g]	0.995
average density							1.299	1.302
mean absolute deviation (MAD)								0.006

[a] Reference 18 unless otherwise stated. [b] Reference 19a, 1.24 g cm^{-3} in ref 18, 1.34 g cm^{-3} in ref 19b. [c] Reference 20. [d] Reference 13, 1.17 g cm^{-3} in ref 18. [e] Reference 21. [f] Reference 19b. [g] Reference 22. [h] Reference 23.

More anion and cation volumes can be derived from the present species. For example, $N(CN)_2^-$ can be deduced as 86 Å^3 from $N(NO_2)_2^-$ (98 Å^3), NO_2 (36 Å^3), and CN(30 Å^3), and other energetic anions such as 5-nitrotetrazolate, 3,5-dinitro-1,2,4-triazolate, 2,4,5-trinitroimidazolate, azotetrazolate, and so forth also can be estimated to be 111, 149, 186, and 176 Å,^{3} respectively. From Me_4N^+ (113 Å^3) and CH_2, Et_4N^+, Bu_4N^+, and 1,1-dimethyl-pyrrolidinium, can be derived as 209, 401, and 147 Å,^{3} respectively.

As listed in Table 1, all of these volume parameters are whole numbers while decimal fractions were omitted except for a very

TABLE 3: Prediction of Densities of Pyridinium, Pyrrolidinium, Tetralkylammonium, and Phosphonium-Based RTILs

entry	cation	anion	MW	density (g cm^{-3}) lit[a]	density (g cm^{-3}) this work
1	*N*-butylpyridinium	BF_4	223.02	1.22	1.222
2	*N*-butyl-4-methyl-pyridinium	BF_4	237.05	1.18	1.189
3	*N*-hexylpyridinium	BF_4	251.07	1.16	1.161
4	*N*-butyl-3-methylpyridinium	OTf	299.31	1.28	1.284
5	*N*-methyl-3-butyl-pyridinium	OTf	299.31	1.28	1.284
6	*N*-butyl-3-methylpyridinium	$N(CN)_2$	216.28	1.05	1.044
7	*N*-(3-hydroxypropyl)pyridinium	Tf_2N	418.34	1.55	1.517
8	1-butyl-1-methylpyrrolidinium	Tf_2N	422.41	1.40	1.400
9	1-butyl-1-methylpyrrolidinium	OTf	291.33	1.25	1.266
10	1-butyl-1-methylpyrrolidinium	$N(CN)_2$	208.30	1.02	1.020
11	1,1-dihexylpyrrolidinium	Tf_2N	520.60	1.25	1.240
12	1-methyl-1-octylpyrrolidinium	Tf_2N	478.52	1.29	1.296
13	1-(2-ethoxyethyl)-1-methylpyrrolidinium	Tf_2N	438.41	1.41	1.419
14	ethyl-dimethyl-propylammonium	Tf_2N	396.37	1.41	1.406
15	methyltrioctylammonium	Tf_2N	648.85	1.11	1.109
16	methyltrioctylammonium	CF_3CO_2	481.72	0.97	0.961
17	ethyl-dimethyl-N-2-ethoxyethylammonium	Tf_2N	412.37	1.43	1.429
18	trihexyltetradecylphosphonium	BF_4	570.66	0.94	0.929
19	trihexyltetradecylphosphonium	Tf_2N	764.00	1.07	1.062
average densities (g cm^{-3})				1.225	1.223
MAD (g cm^{-3})					0.007

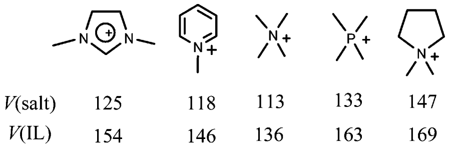
[a] Reference 19b.

few species. In this way, it is easier and much more convenient to estimate the density, but this does not lead to a decrease in accuracy. As shown in the Supporting Information, the nitrobenzene and nitrocubane derivatives are typical examples, and the mean absolute deviation (MAD) is competitive with a previous study by Tarver[6] and Ammon.[7] For 27 nitrobenzene derivatives, our method has the same MAD of 0.020 g cm^{-3} as obtained by Tarver.[6] For 10 cubane derivatives, the MAD of our method is 0.024 g cm^{-3}, which is slightly superior to 0.025 g cm^{-3} obtained using Ammon's parameters.[9a]

Imidazolium-based RTILs have been widely used as solvents for organic synthesis owing to their excellent physical properties, such as low viscosities and high thermal and aqueous stability,[15] and their densities are more readily available in the literature than those of other ionic liquids. Therefore, we utilized imidazolium-based ionic liquid/salts to calibrate our volume parameters. The linear dependence of the alkyl chain length on the densities of RTILs was previously reported.[13b] We found that each additional methylene group in an RTIL accounts for a volume change of 28 Å^3 regardless of the anion. A solid substance is denser than when it is in a liquid state. This phenomenon is also observed for RTILs/salts. It is quite common for some ionic liquids to supercool but subsequently to solidify on standing. A typical example is 1,3-dimethylimidazolium bis(trifluoromethylsulfonyl)amide where its liquid density was reported to be 1.559 g cm^{-3} (Table 2, entry 13)[16] while its density in the condensed state is 1.768 g cm^{-3} (Table 3, entry 10).[17] Therefore, the volume of 1,3-dimethylimidazolium, at 125 Å^3 for salts, should be calibrated to 154 Å^3 for RTILs and Tf_2N^- and also expanded from 230 Å^3 for room-temperature salts to 248 Å^3 for RTILs, since this anion is more prone to be organic in nature; thus, it also tends to have more "free space" in the liquid state. However, the volumes of anions such as BF_4^-, PF_6^-, $CF_3SO_3^-$, or $CF_3CO_2^-$ are taken to be constant in both states.

In general, RTILs are denser than water except for $N(CN)_2^-$-based ionic liquids. For 40 of the most common, imidazolium-based RTILs with anions of BF_4^-, PF_6^-, Tf_2N^-, $CF_3SO_3^-$, $CF_3CO_2^-$, or $N(CN)_2^-$, which have been widely investigated, the predicted densities agree excellently with experimental values (Table 2). The MAD was as low as 0.006 g cm^{-3}. The anion is the dominant factor in determining the density of ionic liquids. Generally, the order of increasing density for ionic liquids with a common cation is $N(CN)_2^- < BF_4^- < CF_3CO_2^- < CF_3SO_3^- < PF_6^- < Tf_2N^-$. The higher densities of Tf_2N^--containing ionic liquids arise mainly from the much higher mass of this anion, for example, although PF_6^- is denser than Tf_2N^- in the liquid state, (2.25 vs 1.88 g cm^{-3}), its lower mass (146 vs 280) led to the relative lower densities of the respective ionic liquids. The densities for alkylated pyridinium, pyrrolidinium, tetralkylammonium, and phosphonium-based RTILs were estimated in a similar way. The volumes of the building blocks, for example, *N*-methylpyridinium, Me_4N^+, Me_4P^+, and 1,1-dimethylpyrrolidinium, in the liquid state were roughly estimated as 146, 136, 163, and 169 Å,[3] respectively, which show similar volume expansion as 1,3-dimethylimidazolium caused by phase change from solid to liquid, and the incremental contribution of 28 Å^3 by each additional methylene group seems to be a general rule. The low MAD of 0.007 g cm^{-3} was also observed for the 19 RTILs (Table 3).

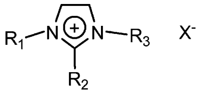
CHART 1: Volumes (Å^3) of the Building Blocks for Salts and RTILs



However, for room-temperature salts, the incremental contribution by each acyclic CH_2 group to the volume was nearly 24 Å.[3] For 35 imidazolium-based room-temperature salts, the MAD was found to be 0.020 g cm^{-3}, a little higher than that for RTILs. Even when a long alkyl chain such as *n*-$C_{18}H_{37}$ or one cocrystallized molecule of water is present in the unit cells, our estimation is also perfectly consistent with single-crystal values. When Hofmann's average atom volumes (AAV)[10] are used, very good results are obtained for some salts, but our present volume parameter proves to be more accurate (Table 4), especially in estimation of the densities of $^-NTf_2$ and Br^- ionic salts.

Since the present volume parameters can accurately estimate the density for both salts (Table 4) and RTILs (Table 2 and Table 3), which was exemplified by 1,3-dimethylimidazolium bis(trifluoromethylsulfonyl)amide as discussed above, we also

TABLE 4: Prediction of Densities of Imidazolium Salts

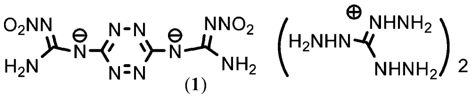


entry	R_1	R_2	R_3	X	MW	density X-ray^{lit}	this work	AAV
1	CH_3	H	CH_3	PF_6	242.10	1.698[c]	1.732	1.709
2	CH_3	H	C_2H_5	PF_6	256.12	1.662[d]	1.661	1.641
3	CH_3	CH_3	n-C_4H_9	PF_6	298.21	1.511[e]	1.505	1.495
4	CH_3	H	$-(CH_2)_3CN$	PF_6	295.16	1.642[f]	1.613	1.613
5	CH_3	CH_3	$-(CH_2)_3CN$	PF_6	309.19	1.578[f]	1.561	1.566
6	CH_3	H	$-C_{10}$-Im-CH_3	PF_6[a]	594.40	1.537[g]	1.533	1.513
7	CH_3	H	$-C_6O_2$-Im-CH_3	PF_6[a]	570.29	1.627[g]	1.647	1.635
8	CH3	H	n-$C_{14}H_{29}$	PF_6	424.45	1.279[h]	1.296	1.287
9	CH3	H	n-$C_{12}H_{25}$	PF_6	396.40	1.316[i]	1.327	1.318
10	CH_3	H	CH_3	NTf_2	377.28	1.768[j]	1.765	1.836
11	C_2H_5	C_2H_5	C_2H_5	NTf_2	433.39	1.596[j]	1.592	1.646
12	C_2H_5	CH_3	$CH_2C_6H_5$	NTf_2	481.43	1.552[k]	1.589	1.622
13	CH_3	H	$CH(CH_3)CO_2Et$	NTf_2	463.37	1.644[l]	1.645	1.710
14	H	H	CH_3	OTf	246.21	1.663[m]	1.668	1.666
15	CH_3	CH_3	CH_3	OTf	274.26	1.550[n]	1.549	1.552
16	CH_3	CH_3	C_2H_5	OTf	288.29	1.488[n]	1.503	1.508
17	t-C_4H_9	H	t-C_4H_9	OTf	344.39	1.354[o]	1.371	1.383
18	CH_3	CH_3	n-C_4H_9	BF_4	254.08	1.280[e]	1.352	1.332
19	CH_3	H	CH_3	Cl	132.59	1.281[p]	1.280	1.338
20	CH_3	H	C_2H_5	Cl	146.62	1.202[p]	1.242	1.291
21	CH_3	CH_3	C_2H_5	Cl	160.64	1.223[p]	1.207	1.255
22	CH_3	H	n-C_4H_9	Cl	174.67	1.200[q]	1.189	1.226
23	CH_3	NH_2	CH_3	Cl	147.61	1.275[r]	1.311	1.351
24	CH_3	H	n-$C_{12}H_{25}$	Cl[b]	304.9	1.106[s]	1.099	1.124
25	CH_3	H	n-$C_{14}H_{19}$	Cl[b]	332.95	1.095[t]	1.086	1.109
26	CH_3	H	n-$C_{18}H_{37}$	Cl[b]	361.01	1.086[t]	1.068	1.098
27	H	H	CH_3	NO_3	145.12	1.471[m]	1.491	1.500
28	CH_3	H	C_2H_5	NO_3	173.17	1.279[u]	1.350	1.377
29	CH_3	H	C_2H_5	NO_2	157.17	1.265[u]	1.280	1.322
30	H	H	n-$C_{14}H_{29}$	NO_3	327.46	1.127[v]	1.138	1.149
31	CH_3	H	C_2H_5	Br	191.07	1.523[w]	1.547	1.624
32	CH_3	H	n-C_4H_9	Br	219.13	1.446[q]	1.438	1.495
33	CH3	H	$-(CH_2)_3ImCH_3$	Br[a]	366.1	1.655[x]	1.625	1.705
34	n-C_3H_7	H	n-C_3H_7	Br	233.15	1.32[y]	1.248	1.447
35	CH_3	CH_3	C_2H_5	Br[b]	223.10	1.456[z]	1.453	1.552
average density						1.422	1.427	1.457
mean absolute deviation (MAD)							0.020	0.041

[a] Dicationic salts, see corresponding references. [b] With one cocrystallized molecule of water, $V(H_2O) = 25$ Å^3. [c] Reference 24. [d] Reference 25. [e] Reference 26. [f] Reference 27. [g] Reference 28. [h] Reference 29. [i] Reference 30. [j] Reference 17. [k] Reference 31. [l] Reference 32. [m] Reference 33. [n] Reference 34. [o] Reference 35. [p] Reference 36. [q] Reference 37. [r] Reference 38. [s] Reference 39. [t] Reference 40. [u] Reference 41. [v] Reference 42. [w] Reference 43. [x] Reference 44. [y] Reference 45. [z] Reference 46.

predict the solid densities of alkylated imidazolium and pyridinium-based ionic liquids listed in Table 2 and Table 3. We found that when RTILs became solid, the density changes were almost linear. As can be seen in Figure 1, the experimental densities (Y) of ionic liquids containing BF_4^-, PF_6^-, NTf_2^-, OTf^-, $CF_3CO_2^-$, or $^-N(CN)_2$ display a very good linear relationship with the corresponding predicted densities (X) in the solid state (Figure 1). Thus, the equation $Y = 0.948X - 0.110$ (for BF_4^-, PF_6^-, $-NTf_2^-$ containing ionic liquids) or $Y = 0.934X - 0.070$ (for $-OTf$, $CF_3CO_2^-$, $^-N(CN)_2$-containing ionic liquids) can be used to roughly predict the densities of RTILs that contain functional groups other than alkyl chains, from its predicted densities in the solid state.

Accurate prediction of density for energetic ionic salts is more intriguing and challenging. However, use of the present volume parameter method provides a rapid way to predict the density of complex ionic salts accurately, for example, Chavez et al. reported a tetrazine-based high energetic salt (**1**).[47]



(**1**)

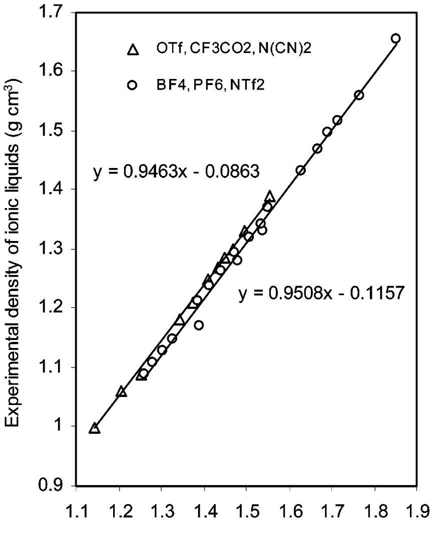


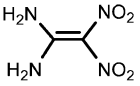
Figure 1. Densities of liquids vs densities of solids.

From Table 1, $V_{(\text{anion})} = 2[V(\text{N}^-) + V(\text{CN}) + V(\text{NO}_2) + V(\text{NH}_2)] + V(\text{tetrazine}) - 2V(\text{H, bonded to carbon}) = 301$ Å^3,

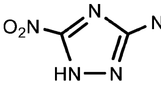
$V(\text{salt}) = V_- + 2V_+ = 511$ Å^3, thus density = 1.607 g cm^{-3}, which agrees exactly with the experimental value of 1.61 g cm^{-3} (gas pycnometer).[47]

Volume of Amino Group. When additional energetic materials were explored for density predictions, we found that the very strong hydrogen bonds between NH_2 and oxygen should be singled out for consideration, although no such attempt has been previously conducted. As demonstrated for substituted aniline derivatives (Supporting Information), if both carbons vicinal to the amino group have nitro groups, in most cases, the molecules have very strong intra- and intermolecular hydrogen bonds. A typical example is 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), owing to the presence of strong hydrogen bonds, it exhibits an unusually low solubility in common solvents and very high density 1.938 g cm^{-3}. Accordingly, the volume of the amino group must be adjusted from 20 Å^3 to 12 Å.[3] This is supported by 20 analogues that are available in the CSD with only a few exceptions. If only one vicinal carbon bears a nitro group, the volume of the amino group can be assigned 20 Å.[3] Although Tarver used the same value (15.663 cm^3 mol^{-1}) for the C−NH_2 group in a 25 nitrobenzene series, this parameter also has to be altered for some specific molecules, for example, hexaminobenzene with a density of 1.439 g cm^{-3} [48] and a deviation of +0.351 g cm^{-3} will be obtained using his parameters, while our method only has an error of −0.042 g cm^{-3}. We also find that Hofmann's average atom volume[10] underestimates the densities of nitroanilines with strong hydrogen bonds.

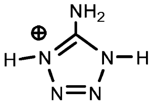
For other neutral and ionic energetic materials, the simultaneous presence of amino and NO_2, NO_3^-, or ClO_4^- sometimes also led to unusual high density, for example, for FOX-7 (**2**). Using the method of Ammon[9] or Hofmann,[10] the predicted density was only ∼1.76 g cm^{-3}, while its single-crystal density is 1.907 g cm^{-3} (170 K)[49] or 1.886 g cm^{-3} (295 K).[50] While using our tabulated volume parameter, and corrected for hydrogen bonds (−8 Å^3), a value of 1.863 g cm^{-3} is predicted, which is reasonably close to the CSD density of 1.886 g cm^{-3}. Similarly, volumes of 3-amino-5-nitro-triazole (ANTA, **3**),[51] salts of 5-amino-tetrazolium nitrate (**4**),[52] picrate (**5**),[53] and 3,4,5-triamino-1-hydro-1,2,4-triazolium nitrate (**6**), perchlorate (**7**), and dinitroamide (**8**)[54] also must be corrected for hydrogen bonds (−8 Å^3). Special caution should be taken in these estimations. In other words, the combination of the NH_2 group and NO_2 or NO_3^- or ClO_4^- in one molecule to form strong hydrogen bonds is an effective way to improve the density of energetic materials.



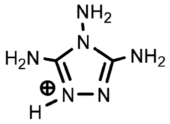
(**2**)



(**3**)



X= NO_3^-, (**4**)
picrate (**5**)



NO_3^-, (**6**)
ClO_4^- (**7**)
$^-N(NO_2)_2$ (**8**)

The volume of N^+ is about 0.23 Å^{3,4} which is negligible, and N^- is roughly estimated as 26 Å^3 from $V(^-N(NO_2)_2)$ and $V(NO_2)$. These two parameters can be used to roughly estimate the volumes of a new cation or anion which are not available in Table 1. For 150 energetic salts, mainly from Xue et al.,[55] Drake and co-workers,[4,54,56] Chavez and and co-workers,[47,57] Klapötke et al.,[58] and Katritzky et al.,[59] the MAD is 0.035 g cm^{-3}; 40.6% of the estimated densities were within absolute deviation of 0.0−0.02 g cm^{-3}, 29.3% were within 0.021−0.04 g cm^{-3}, 16.6% were within 0.041−0.06 g cm^{-3}, 8.8% were within 0.061−0.08 g cm^{-3}, 2.7% were within 0.081−0.100, and only 2.0% were within 0.1−0.15 g cm^{-3}, thus, nearly 90% of the estimated densities could be used in Kamlet−Jacobs calculations within acceptable errors.

In conclusion, we have developed a volume parameter for salts and RTILs, namely, for 59 of the most common imidazolium-based RTILs, the mean absolute deviation is 0.007 g cm^{-3}; for 35 imidazolium-based ionic salts, the MAD is 0.02 g cm^{-3}; and for 150 energetic ionic salts, the MAD is 0.035 g cm^{-3}.

Acknowledgment. The authors acknowledge the financial support of the AFOSR, (Grant F49620-03-1-0209), the NSF (Grant CHE0315275), and the ONR (Grant N00014-02-1-0600).

Supporting Information Available: Two tables that contain the predicted and experimental densities of nitrobenzenes and cubanes. An additional table of molecular structures for species discusses the paper. Two instructional examples are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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(2) Where $k = 1.58$, ρ(g cm^{-3}) = density, $\varphi = N[M(-\Delta_E H)]^{1/2}$, N = moles of gases per gram of explosives, M = average molar mass of formed gases (g mol^{-1}), $\Delta_E H$ = calculated enthalpy of detonation (cal g^{-1}), which is related to heat of formation ($\Delta_f H_{298}{}^0$) of explosive, $A = 1.01$, $B = 1.30$.

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