Quantitative Structure-Property Relationships for Melting Points and Densities of Ionic Liquids

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14. ABSTRACT

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Abstract

Although innumerable different ionic liquids are possible, even basic physical-property data, such as the density and melting point, exist only for relatively few. Derivation of melting point QSPRs (Quantitative Structure-Property Relationships) for energetic ionic liquids would therefore greatly aid in the molecular design of new compounds. A new class of ionic liquids, based on 1-substituted-4-amino-1,2,4-triazolium bromide and nitrate salts, were recently synthesized and their melting points and densities measured. We optimized the molecular geometries of the cations of the ionic liquids using ab initio quantum chemical methods. Melting-point QSPRs were then derived from molecular orbital, thermodynamic, and electrostatic descriptors. Good correlations with the experimental data were found. The correlation coefficients for three-parameter melting-point QSPRs and for one-parameter density QSPRs exceed 0.9. Although some of the descriptors that appear in our QSPRs were designed to describe chemical reactions, we infer that they serve in this study to quantify interactions between the cation and anion.

Introduction

Hydrazine and its methylated derivatives are powerful reducing agents with a wide range of uses, including aerospace fuels.[1] The introduction of hydrazine, monomethyl hydrazine, and 1,1-dimethyl hydrazine grew out of a need for high-energy, noncryogenic, liquid fuels that can be used alone or mixed with other components. The toxicity of hydrazine fuels is a substantial operational concern to the U.S. Department of Defense as well as to the aerospace industry. The two most likely occupational exposure routes are inhalation and skin exposure.[2] We have previously reported quantitative structure-activity relationships for toxicity prediction of a series of high-energy compounds.[3]

Ionic liquids have melting points that fall below room temperature and have generated considerable interest as 'green' alternatives in current industrial applications because of their exceptional solvating ability and extremely low vapor pressures.[4,5,6,7,8] Energetic ionic liquids should be inherently less toxic than hydrazine-based fuels because the exposure routes are greatly diminished due to their low vapor pressures. Although approximately 10^{18} different ionic liquids are possible,[9] even basic physical-property data, such as the density and melting point, exist for relatively few. Derivation of melting-point QSPRs (Quantitative Structure-Property Relationships – models that relate chemical structure to physical properties) for energetic ionic liquids would therefore greatly aid in the molecular design of new families of energetic ionic liquids. QSPRs for the prediction of densities of energetic ionic liquids, which are correlated to their energy densities, would also be beneficial.

Melting points for organic molecules depend in general on the arrangement of atoms in the crystal lattice as well as on pairwise interactions. Difficulty in predicting melting points arises, in part, from the fact that these two properties are interdependent. Currently, the descriptors

available for derivation of melting-point QSPRs were not designed for the description of condensed media.[10] However, additional factors that affect the strength of a crystal lattice and, therefore, the melting point are molecular symmetry,[11] the molecule's conformational degrees of freedom[11] (both of which can be accounted for by descriptors obtained from gas-phase quantum mechanical calculations), and the molecular motion in crystals.[12]

Inorganic ionic compounds typically display high melting points due to strong electrostatic intermolecular forces. The intermolecular forces affecting the melting point of organic compounds are much weaker, e.g., hydrogen bonding and dipole-dipole interactions. The most accurate (RMS error = 0.5ºC) melting-point QSPR for organic compounds, which was derived for 24 unbranched alkanes, is composed entirely of topological indices.[13] However, the RMS error for the QSPR predicting the melting point of 56 normal and branched alkanes, which also used connectivity indices, is much larger (23.8ºC).[14] In a study of 303 normal and branched substituted alkanes, intermolecular forces provided descriptors for an 11-term QSPR with an RMS error of 16.4ºC.[15] In developing QSPRs for melting points of substituted benzenes, Katritzky, et al.,[16] found that a hydrogen-bonding descriptor together with other quantum chemical descriptors led to correlations much improved over QSPRs derived with only topological, geometrical, and other traditional descriptors.

Descriptors that characterize weak intermolecular interactions are expected to provide accurate melting-point QSPRs for ionic liquids because they are weakly coordinating. Melting-point QSARs derived by Katritzky and coworkers for ionic liquids and ionic-liquid analogues (based on pyridinium bromides[17] and on imidazolium and benzimidazolium bromides[9]) are composed of information content indices[18] – descriptors characterizing the cations' size and electrostatics – and the average nucleophilic reaction index, i.e., the propensity of the cations to react with

nucleophiles.[19] The resulting melting-point QSPRs have r^2 values ranging from 0.690–0.788, except for the QSPR derived for a subset of 18 substituted imidazolium bromides, which has an r^2 value of 0.943.[9,17]

Liquid-density QSPRs have been previously derived for alkanes in two studies.[20,21] In the first study, structural descriptors computed from molecular graphs were used to derive physical properties, including liquid density, for 134 alkanes.[20] Using the same dataset, better physical-property QSPRs were derived using descriptors based on graphs of atomic orbitals.[21] In neither study were physical interpretations of the liquid-density QSPRs attempted.

A new class of energetic ionic liquids, based on 1-substituted-4-amino-1,2,4-triazolium bromides and nitrates (see Figure 1), was recently synthesized and their melting points measured (see Table 1).[22] Some of the data in Table 1 actually correspond to glass transitions because the glass forms much more readily than the crystal. In these cases, we employ glass transition temperatures in lieu of melting points because we are interested in the temperature at which the salt ceases to be a liquid. As reported by Drake, et al.,[22] these new ionic liquids are stable at room temperature and show no signs of decomposition after more than a year at ambient temperatures. The nitrate salts generally have lower melting points than the bromide salts. For the *n*-alkyl-substituted compounds, the melting points generally increase as the length of the alkyl group increases but this increase is not monotonic; compounds with an even number of substituent carbons generally display lower melting points that those with an odd number.[22] Densities of the bromide salts were also reported by Drake, et al.,[22] cf. Table 1. We endeavor in this paper to derive melting-point and density QSPRs for these new energetic ionic liquids and interpret them in terms of molecular interactions.

Methods

All *ab initio* quantum mechanical calculations were performed with Gaussian98, version A.9.[23] The optimal geometry for each cation (Table 1) was obtained using the restricted Hartree-Fock method (RHF) and the 6-31G** basis set (6-31G** is a split-valence basis set with polarization functions on all atoms). Vibrational frequencies were calculated for all cations using the same level of theory as the optimizations.

CODESSA version 2.61[24] was employed to derive correlations between each descriptor and the melting-point data, to derive the QSPRs, and to calculate the statistics for the QSPRs, including the correlation coefficient, r, the Fisher significance parameter, F, and q, the cross-validated correlation coefficient calculated using a leave-one-out method. CODESSA's best multilinear regression method and heuristic method were used to obtain three-parameter melting-point QSPRs. The heuristic method was used to obtain one-parameter density QSPRs. Both methods limit the collinearity of the selected descriptors and utilize statistical significance to derive QSPRs.

CODESSA categorizes descriptors as constitutional, topological, geometrical, electrostatic, quantum mechanical, and thermodynamic, although both electrostatic and thermodynamic descriptors are obtained from quantum mechanics calculations. Constitutional, topological, geometrical descriptors were seldom found to be among the best descriptors and rarely improved QSPRs that were derived without them. In this work, we therefore employed only electrostatic, quantum mechanical and thermodynamic descriptors to derive QSPRs. The descriptor pool consisted of about 250 descriptors. Unless specified otherwise, the partial atomic charges that were employed were calculated using the Natural Bond Orbital method,[25] as implemented in Gaussian'03.[23]

Results and Discussion

Even though they pertain to the gas-phase, optimal molecular geometries of the cations compare well to the crystal structures of the ethyl, *n*-propyl, *n*-hexyl, and *n*-heptyl bromide salts, which were the only bromide salt crystal structures published,[22] and to the isopropyl and methylcyclopropyl nitrate salts, which were the only two nitrate salt crystal structrures published.[22] As seen in Table 2, calculated bonds lengths are in good agreement to those found in the crystal structures. Although only bonds common to all cations are included in Table 2, experimental and theoretical bond lengths in the substituents are also in good agreement. A linear fit of the bond lengths in Table 2 has an r^2 value of 0.964. The average RMS deviation for the bond lengths in Table 2 is 0.0163 Å.

Good correlations with the experimental melting-poing data were found. The following QSPR was derived for the melting points (T_m) of the bromide salts:

$$T_m = -262. - 6.91 \times 10^5\ NRI_{NH2} + 47.4\ HACA2 - 136./E_{LUMO} \tag{1}$$

$N=13$, $r^2=0.914$, $F=31.9$, $s^2=26.6$, $q^2=0.784$

where NRI_{NH2} is the nucleophilic reactivity index[19] for the amine nitrogen (see Figure 1), HACA2 is the area-weighted surface charge of hydrogen-bond acceptor atoms,[26] and E_{LUMO} is the energy of the lowest unoccupied molecular orbital. Values for all melting-point descriptors are presented in Table 3. Correlations between descriptors appearing in Eqn. 1 are poor, as seen in Table 4a. Although NRI, which is essentially a Fukui function,[27] is implicitly designed to describe chemical reactions,[19] we infer that it serves here to quantify interactions between the

cation and anion. Similarly, reciprocal E_{LUMO}, as we have shown previously,[28] can be interpreted within the context of frontier molecular orbital theory[29] to describe the stabilization due to mixing of occupied MOs of a molecule with the LUMO of the cation. Therefore, reciprocal E_{LUMO} may also serve here to quantify interactions between the cation and anion. It is also plausible that the descriptors in Equation 1 account for interactions between cations. The RMS error in Equation 1 is about 5°C.

The following QSPR was derived for the T_m of the nitrate salts:

$$T_m = -284. - 214.\ HDCA1_Z - 3.94 \times 10^4\ NRI_{min,C} + 3.16 \times 10^3\ FHDCA \tag{2}$$

$N=13$, $r^2=0.933$, $F=41.5$, $s^2=198$, $q^2=0.872$

Both $HDCA1_Z$ and FHDCA are measures of the hydrogen-bond donating ability[26] of the cation and $NRI_{min,C}$ is the minimum NRI for a carbon atom. $HDCA1_Z$ is the sum of the hydrogen-bond donor surface area weighted by each donor's partial charge and FHDCA is HDCA1 divided by the total molecular surface area, i.e., the fractional HDCA1. Both $HDCA1_Z$ and FHDCA1 are interpreted as hydrogen-bond donating ability. Equation 2 is similar to Equation 1 in that two terms include a NRI and a hydrogen-bond descriptor. As in Equation 1, we infer that $NRI_{min,C}$ and the hydrogen-bond descriptors in Equation 2 serve here to quantify interactions between the cation and anion or between cations. See Table 3 for values for all melting-point descriptors. Correlations between descriptors in Equation 2 are poor, as seen in Table 4b. Although the correlation and cross-validated correlation coefficients for Equation 2 are better than those for Equation 1, the RMS error – about 14°C – is almost three times larger. Equations 1 and 2 are

also similar to melting-point QSARs derived for other ionic liquids in that they involve hydrogen-bond descriptors and NRI.[9,17]

Ten excellent, single-descriptor QSPRs were derived for the densities of the bromide salts and are displayed in Table 5. Most descriptors include either various measures of hydrogen-bonding capability or have to do with the partial atomic charge distribution and are interpreted as characterizing the interactions between ions. Another descriptor, the average electrophilic reactivity index for a carbon atom, is similar in origin to the previously discussed NRI[19] and although it, too, was designed to characterize a chemical reaction, it serves here to quantify intereactions between ions. Another descriptor – a principal moment of inertia normalized by the number of atoms in each cation – is a measure of the molecular shape. Each descriptor predicts very accurately the liquid densities of the thirteen bromide salts and quantifies very well the interactions between ions while in the liquid state.

Conclusions

We have presented QSPRs for the melting points and liquid densities of a new class of energetic ionic liquids that can be used in the design of additional 1-substituted-4-amino-1,2,4-triazolium bromide and nitrate salts.. Although the descriptors used were originally intended to quantify chemical reactions, we believe that they serve here to describe the interactions between ions. Statistics, while certainly more than adequate, can be improved by designing descriptors especially for ionic liquids.

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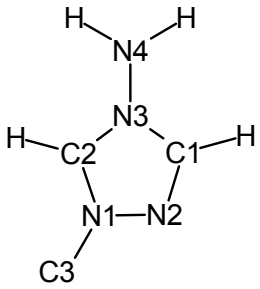
Table 1: Melting Points and Densities of Ionic Liquids

Substituent	Bromide Salt		Nitrate Salt
	T_m	ρ	T_m
methyl	92ºC	1.98 g/cm^3	-54ºC (g)
ethyl	67	1.69	-55 (g)
n-propyl	63	1.56	33
isopropyl	92	1.60	66
2-propenyl	62	1.59	-50 (g)
n-butyl	48	1.46	-50 (g)
methylcyclopropyl	73	1.58	56
n-pentyl	54	1.37	29
n-hexyl	76	1.34	0
n-heptyl	94	1.30	35
n-octyl	80	1.27	34
n-nonyl	81	1.26	53
n-decyl	90	1.23	51

Data denoted with (g) correspond to glass transition temperatures, as explained in the text.

Table 2: Comparison of Selected Bond Lengths Found in Crystal Structures to Calculated Results



Bromide Salts

Bond	ethyl		propyl		isopropyl		hexyl		heptyl	
	Crystal	Calc.	Crystal	Calc.	Crystal	Calc.	Crystal	Calc.	Crystal	Calc.
	Å	Å	Å	Å	Å	Å	Å	Å	Å	Å
N1-N2	1.369	1.349	1.373	1.349	1.361	1.349	1.373	1.349	1.377	1.349
N1-C2	1.312	1.297	1.307	1.297	1.298	1.297	1.308	1.297	1.314	1.297
N1-C3	1.480	1.478	1.470	1.477	1.477	1.492	1.456	1.478	1.464	1.478
N2-C1	1.310	1.278	1.307	1.278	1.297	1.278	1.293	1.278	1.303	1.278
N3-N4	1.419	1.383	1.414	1.383	1.400	1.383	1.394	1.383	1.401	1.383
N3-C1	1.356	1.366	1.364	1.366	1.355	1.366	1.350	1.366	1.357	1.366
N3-C2	1.337	1.327	1.329	1.327	1.327	1.328	1.334	1.328	1.333	1.328

Table 2, continued

Nitrate Salts

isopropyl		methylcyclopropyl	
Crystal	Calc.	Crystal	Calc.
Å	Å	Å	Å
1.363	1.349	1.366	1.349
1.316	1.297	1.310	1.297
1.484	1.478	1.466	1.477
1.305	1.278	1.303	1.278
1.451	1.383	1.401	1.383
1.354	1.366	1.354	1.366
1.338	1.327	1.332	1.327

Table 3: Descriptor Values for Melting-Point QSPRs

Substituent	NRI_{NH2}	HACA2	E_{LUMO}	$HDCA1_Z$*	$NRI_{min,C}$	FHDCA
	au	Å^2	au			
methyl	1.73×10^{-6}	4.95	-0.876	0.0161	6.17×10^{-4}	0.208
ethyl	6.44×10^{-6}	4.29	-0.991	0.0144	1.04×10^{-3}	0.220
n-propyl	3.13×10^{-5}	4.35	-1.049	0.0120	9.19×10^{-4}	0.215
isopropyl	1.10×10^{-5}	4.17	-1.144	0.0117	1.27×10^{-3}	0.224
2-propenyl	1.83×10^{-5}	4.17	-0.999	0.0135	1.17×10^{-4}	0.203
n-butyl	7.11×10^{-5}	4.39	-1.09	0.0109	3.07×10^{-3}	0.215
methylcyclopropyl	6.17×10^{-6}	4.06	-1.11	0.0119	9.51×10^{-5}	0.215
n-pentyl	5.70×10^{-5}	4.48	-1.11	9.97×10^{-3}	1.21×10^{-3}	0.214
n-hexyl	2.61×10^{-5}	4.21	-1.12	9.37×10^{-3}	3.11×10^{-4}	0.214
n-heptyl	1.28×10^{-5}	4.46	-1.13	8.60×10^{-3}	1.16×10^{-4}	0.213
n-octyl	6.72×10^{-6}	4.15	-1.13	8.50×10^{-3}	5.30×10^{-5}	0.217
n-nonyl	3.75×10^{-6}	4.10	-1.14	7.97×10^{-3}	2.66×10^{-5}	0.217
n-decyl	2.19×10^{-6}	4.16	-1.14	7.61×10^{-3}	1.46×10^{-5}	0.216

*Zefirov's empirical atomic partial charges[30,31] are employed.

Table 4a: Correlation Matrix for Descriptors in Equation 1:

	NRI_{NH2}	HACA2	$1/E_{LUMO}$
NRI_{NH2}	1.00	–	–
HACA2	0.168	1.00	–
$1/E_{LUMO}$	-0.110	0.689	1.00

Table 4b: Correlation Matrix for Descriptors in Equation 2

	$HDCA1_{HA}$	$NRI_{min,C}$	FHDCA
$HDCA1_{HA}$	1.00	–	–
$NRI_{min,C}$	-0.359	1.00	–
FHDCA	-0.466	0.205	1.00

Table 5: Density QSPRs for 1-substituted-4-amino-1,2,4-triazolium bromides

Intercept	Coefficient	r^2	F	s^2	q^2	Descriptor
0.669	3.24	0.973	397.	0.00140	0.954	$FHDSA_Z$: Fractional hydrogen-bond donor surface area, i.e. hydrogen-bond donor surface area divided by the total molecular surface area.*
0.974	33.3	0.972	383.	0.00140	0.964	$ERI_{avg,C}$: Average electrophilic reactivity index for carbon atoms.[19]
0.756	2.819	0.964	295.	0.00180	0.929	FHDSA: Fractional hydrogen-bond donor surface area, i.e. hydrogen-bond donor surface area divided by the total molecular surface area
0.654	75.4	0.961	270.	0.00200	0.951	FHACA2: sum of the square root of the hydrogen-bond acceptors' surface areas weighted by the acceptors' partial charge. The sum is then divided by the total molecular surface area.
16.3	-16.0	0.960	262.	0.00200	0.922	V_H: Average valence of H atoms
27.0	-6.64	0.945	188.	0.00280	0.928	V_C: Average valence of C atoms
1.15	48.4	0.936	162.	0.00320	0.915	I_A/N: Principal moment of inertia about the first main axis divided by the number of atoms in the molecule.
2.06	-1.26	0.931	148.	0.00350	0.906	μ_{hc}:Total hybridization component of the molecular dipole, i.e., the dipole calculated from partial atomic charges subtracted from the dipole moment calculated quantum mechanically in Gaussian'03 as the first derivative of the energy with respect to an electric field.
0.744	29.3	0.924	134.	0.00380	0.901	$FHASA2_Z$: Fractional hydrogen-bond acceptor surface area, i.e., the sum of the hydrogen-bond acceptor surface areas divided by the total molecular surface area.*
0.727	-87.2	0.923	132.	0.00390	0.892	$FNSA3_Z$: Sum of the negatively charged molecular surface area weighted by the atomic partial charge. The total molecular surface area then divides the sum.*

*Zefirov's empirical atomic partial charges[30,31] are employed as weights ($FHASA2_Z$ and $FNSA3_Z$) or to determine which hydrogens are donors ($FHDSA_Z$).

Table 6: Descriptor Values for Density QSPRs

Substituent	$FHDSA_Z$	$ERI_{avg,C}$	FHDSA	FHACA2	V_H	V_C	I_A/N	μ_{hc}	$FHASA2_Z$	$FNSA3_Z$
	–	au	–	$\tilde{A}^{-1}$	–	–	au	au	–	–
methyl	0.390	0.0298	0.400	0.0174	0.898	3.78	0.0179	0.0819	0.0433	-0.0138
ethyl	0.334	0.0228	0.356	0.0134	0.909	3.81	0.0116	0.346	0.0304	-0.0105
n-propyl	0.269	0.0183	0.301	0.0123	0.917	3.83	9.14×10^{-3}	0.479	0.0279	-9.91×10^{-3}
isopropyl	0.279	0.0181	0.311	0.0120	0.915	3.83	6.78×10^{-3}	0.426	0.0258	-8.77×10^{-3}
2-propenyl	0.305	0.0184	0.305	0.0125	0.910	3.85	8.00×10^{-3}	0.347	0.0287	-0.0112
n-butyl	0.245	0.0152	0.239	0.0115	0.924	3.85	6.43×10^{-3}	0.500	0.0265	-8.68×10^{-3}
methyl-cyclopropyl	0.267	0.0152	0.284	0.0113	0.915	3.85	6.84×10^{-3}	0.285	0.0247	-9.20×10^{-3}
n-pentyl	0.225	0.0130	0.219	0.0106	0.928	3.86	5.48×10^{-3}	0.545	0.0246	-8.32×10^{-3}
n-hexyl	0.211	0.0114	0.207	9.12×10^{-3}	0.932	3.86	4.20×10^{-3}	0.557	0.0208	-7.41×10^{-3}
n-heptyl	0.195	0.0101	0.188	8.87×10^{-3}	0.934	3.87	3.71×10^{-3}	0.594	0.0208	-6.85×10^{-3}
n-octyl	0.189	9.10×10^{-3}	0.185	8.23×10^{-3}	0.936	3.88	3.01×10^{-3}	0.608	0.0186	-6.19×10^{-3}
n-nonyl	0.177	8.27×10^{-3}	0.174	7.62×10^{-3}	0.938	3.88	2.72×10^{-3}	0.640	0.0173	-5.70×10^{-3}
n-decyl	0.170	7.58×10^{-3}	0.166	7.25×10^{-3}	0.940	3.89	2.28×10^{-3}	0.655	0.0166	-5.57×10^{-3}

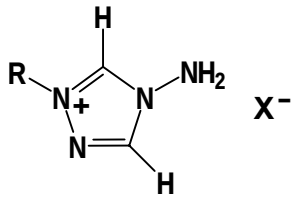


Figure1: Molecular structure of ionic liquids based on 1-substituted-4-amino-1,2,4-triazolium. X^- is either Br^- or NO_3^- and R is a series of aliphatics or other common organic group (seeTable 1).

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