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Corresponding States Theory for the Freezing of Ionic Liquids

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Corresponding states analyses for understanding the freezing temperatures of existing ionic liquids, and predicting freezing properties of ionic liquids yet to be discovered are described. "Room temperature" ionic liquids exist as such because they broadly obey a scaling relationship that describes all 1:1 electrolytes, including the alkali halides. In a zeroth-order treatment, the reduced freezing temperature (T_f^*) is simply expressed in units of a characteristic ion−ion pair potential energy containing a single size or length parameter (r_0): $T_f^* = k_B T_f r_0/e^2$, where k_B is Boltzmann's constant. All ionic liquids in the same conformal group have the same reduced freezing point (T_f^*). Organic ionic liquids have r_0 values roughly 3-times greater than those of alkali halides, which melt around 1000 K, hence their room temperature freezing points. Corresponding states analyses are reported for conformal groupings obtained for both the DME (distance of minimum energy) definition of r_0 and also the scaling obtained from the sum of the isolated cation and anion polarizability trace radii (PTR). We discuss the inclusion of first-order effects of nonconformable perturbations, such as the polarizability anisotropy and ion-size assymmetry. Scaling concepts promise to be a valuable tool for predicting freezing points of ionic liquids.

1. Introduction

Since the organic ionic liquids were discovered in the early 1980s,[1] the reason for their existence at low temperatures has not been well-understood by all. Unlike most other classes of atomic or molecular liquids, because of the dominance of the Coulombic potential, the characteristic cohesive energy of ionic liquids decreases as the ionic size increases.[2] Although the alkali halide melt at around 1000K, with melting points generally found to correlate with crystal density, or lattice parameter, but they are not high-melting point solids in a statistical mechanical sense. Rather, they can be seen as liquids having quite low freezing points given the large attractive characteristic electrostatic pair potential energy;[2] organic ionic liquid exhibit freezing temperatures that also vary approximately inversely with unlike interionic distance. Recent experimental studies[3] have confirmed an empirical correlation of freezing temperature with density for the room temperature ionic liquids.

Ionic liquids generally can be modeled with inverse-distance dependent long-range Coulombic potentials between like and unlike ions. If the short-range repulsion is represented by an inverse power, the pair potentials can be written in a general reduced form

$$\phi_{ij}/\varepsilon = [1/(n-1)](\sigma_{ij}r_0/r_{ij})^n + Z_iZ_j[n/(1-n)](r_0/r_{ij}) \tag{1}$$

where ε is the minimum energy in unlike pair potential at the minimum distance r_0. Z_i and Z_j are the ionic valencies. A size ratio σ_{ii}/σ_{jj} defines σ_{ij} when $\sigma_{ii} + \sigma_{jj} = 2$ by definition. For a symmetric salt, $\sigma_{ii} = \sigma_{jj} = 1$. All ionic liquids for which this model for the Hamiltonian is representative, will obey a molecular-reduced law of corresponding states, and the same phase diagram etc.
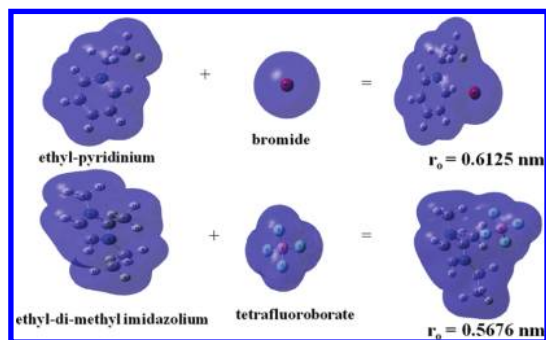
Figure 1 shows a set of model $n − 1$ pair potentials for a spherically symmetric 1:1 ionic liquid with ion−ion repulsions $n = 8$ and attractions in the Coulomb model that attaches one unit electron charge to the center of each ion ($Z_i = Z_j = 1$). In Figure 1, the set of 3 pair potentials of a typical ionic salt are plotted in reduced units of the characteristic distance to the first minimum in the unlike ion−ion pair potential, and a characteristic energy at the minimum. The pair potentials shown are for an asymmetric salts with size ratio $\sigma_j/\sigma_i = 2$, such as sodium chloride. In this form of the potential a fixed repulsive exponent n will comprise a conformal corresponding states group for which the minimum energy ε is related to the characteristic energy e^2/r_0, where e is the electron charge, by $\varepsilon = [(n − 1)/n]e^2/r_0$.

Although there is an asymmetry in all ionic liquids to some degree, this does not vitiate the scaling properties. When the thermodynamic properties of ionic liquids are expressed in reduced units of the characteristic distance (r_0) and a universal characteristic energy (e^2/r_0) all ionic liquids for which pair
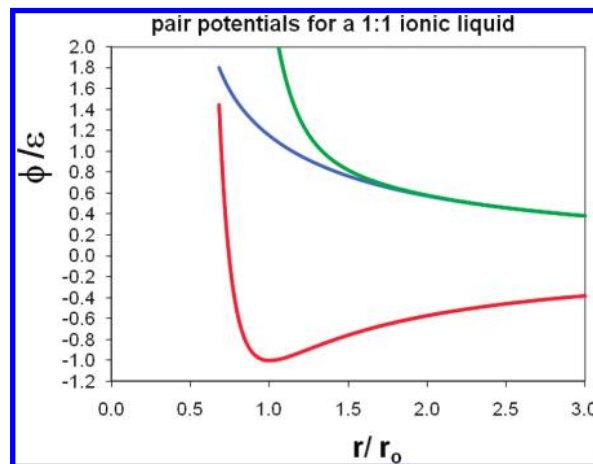
Figure 1. Typical Coulombic ion−ion pair potentials with inverse-power repulsions for an ionic liquid: $n = 8$ and $\sigma_{ii}/\sigma_{jj} = 2$; red ϕ_{ij} cation−anion; green ϕ_{ii}; and blue ϕ_{jj} like-ion.

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Figure 2. Electron density contours for ion pairs in two ionic liquids obtained from quantum mechanical optimization computations using GAUSSIAN; determination of the center-of-mass minimum pair potential length parameter r_0.

potentials such as eq 1 are representative, have similar reduced thermodynamic state functions, such as enthalpy or entropy. This is because (e^2/r_0) is of the order 50 times $k_B T_f$ (where k_B is Boltzmann's constant) and like ions do not approach close for the asymmetry to have any vitiating effect on the scaling. It further follows that ionic liquids which conform should all have the same reduced freezing point, since crystal and liquid phases alike obey the scaling law for free energies at freezing.

To a zero-order of perturbation,[2] all alkali halides for example have the same reduced melting point approximately, $T_f^* \sim 0.0145 \ e^2/k_B r_0$ Deviations from this general result for subgroups of alkali halides that fall within conformal groups, could be accounted for by nonconformal perturbations. Lithium halides, for example, with anion−anion interactions in the crystal phase and polarization effects in the liquid phase more predominant, conform within the group to $T_f^* \approx 0.010 \ e^2/k_B r_0$ Organic ionic liquids, with much larger ions than the alkali halides, have low freezing points in a simple spherical ion model and will have pair potential that resemble eq 1 and hence similar corresponding states scaling properties. All ionic liquids in the same conformal group, will have the same reduced freezing point (T_f^*). Organic ionic liquids have r_0 values roughly 3-times lower than those of alkali halides which melt around 1000 K, hence their room temperature freezing points. The objective of the preliminary computations we report here is to enquire to what extent the freezing points of organic ionic liquids can be quantitatively predicted ab initio, that is, using this simple scaling law and quantum mechanical predictions of the characteristic distance r_0.

2. Quantum-Mechanical Computations

The distance scaling parameter r_0 can be predicted from quantum mechanical computations.[4] Initially, the molecular structures of both cation and anion of the ionic liquid are energetically optimized using molecular mechanics through the universal force field[5] (UFF). Further optimization is then carried out using density functional theory (DFT). The DFT functional used for optimization is the hybrid density functional (B3LYP) and the basis sets is 6-31++G** which include the polarization on hydrogen atom. Typical results for the iso-electron density contours are shown in Figure 2 for two of the ionic liquids considered here. The iso-electron density surface shown is defined as the 0.001contour (in Hartree units). The scaling distance r_0 for each ionic liquid ion pair is then defined as the distance between the centers of mass of anion and cation at the global energy minimum and determined as such from the quantum mechanical computations.

The electric-field frequency (EFF) response is also computed in order to obtain values of the polarizability of both cation and anion. This EFF frequency can also be used to check if the optimized structure is at the global minima. Distance of minimum energy (DME) of cation−anion ion pair is optimized as a whole using the same functional and basis set. The numerical results for the distance between the centers-of-mass (CoM) at minimum energy from the GAUSSIAN computations for all the ionic liquids for the two classes we have considered are given in Table 1.

Pictures of the electron density contours, such as those in Figure 2, reveal a degree of asphericity associated with atomic structure of even the simplest of polyatomic ions. An interesting result, however, that emerges from quantum mechanical computations of electron density probability contours is that all molecules (and ions) are "quasi-spherical" at a sufficient distance. The question is "how far away does one need to go away for this to be a useful approximation?" It is a surprisingly short distance; the H_2 molecule-ion, for example, is almost spherical at just 3 Bohr orbits from center-of-mass. The modern molecular orbital treatment of molecular configurations ensures that when like-ions interact, they do so at such a distance that the spherically symmetric Coulombic potential suffices. Consequently, even complex organic ionic liquids can be expected to obey some aspects of the idealized corresponding states laws of spherically symmetric salts.

Here, we report analyses of the corresponding states predictions, and conformality for experimental freezing points, for two classes, or potential conformal groups, of ionic liquids, namely, (i) substituted pyridinium bromides and (ii) substituted imidazolium boron tetrafluorides. The only experimental data required for the present analyses are the freezing points of the ionic liquids; these have been obtained from the literature[6] and listed in Table 1.

3. Reduced Freezing Points: Scaling Laws

The DME (distance of minimum energy) reduced freezing temperature of an ionic liquid is related to the real experimental freezing temperature according to the corresponding states law[2]

$$T_f^* = k_B T_f r_0 / e^2 \qquad (2)$$

where T_f^* is the dimensionless reduced freezing temperature, k_B is Boltzmann's constant, T_f is the real experimental freezing temperature, r_0 is the distance of minimum energy in the anion−cation pair potential, and e is the electronic charge. We see that the reduced freezing temperature is the ratio of a characteristic kinetic energy of the liquid $k_B T_f$ to the characteristic potential energy of interaction e^2/r_0. According to corresponding states law, eq 2, all ionic liquids in a conformal group shall have the same reduced freezing temperature.

The first observation is that the scaling law eq 2 generally accounts for the differences in freezing temperatures between the two classes of ionic liquids Using the r_0 values in Table 1, we plot the reduced melting points of the organic ionic liquids as a function of absolute temperature for the experimental freezing temperatures. The alkali halides have r_0 values ranging from for 0.15 (LiF) to 0.33 nm (CsI); the range of r_0 obtained from the quantum computations for all the ionic liquids considered here is 0.61 (1E23DMIMD) to 0.79 nm (1B35DMPY). Hence, the factor of approximately 3 between average freezing temperatures of the two classes of ionic liquid (Figure 3).

The next observation is a tendency of the two classes to form separate conformal groups; the imidazolium salts seem to

Table 1. Basic Numerical Data for Characteristic Distance (r_0) Corresponding to the CoM Anion−Cation Distance at Minimum Total Energy, and Polarizability Parameters of the Ions in Ionic Liquids[a]

ion	r_0 (au)	T_f (K)	$10^3\ T_f^*$	xx	xy	yy	xz	yz	zz
Br[−b]				14.4	0.00	14.42	0.00	0.00	14.4
BF$_4$[−c]			14.2	0.00	14.20	0.00	0.00	14.2	
1B35DMPY[d]	4.1609	368	17.32	152.4	0.00	131.30	−12.14	0.00	81.6
1BPY[e]	3.1514	378	13.47	127.9	0.01	96.46	−13.49	0.03	64.1
1B3MPY[f]	3.3298	411	15.48	142.3	−4.32	111.38	−12.12	−4.86	73.3
1B4DMAPY[g]	4.1468	495	23.22	201.4	0.00	118.82	−16.31	0.00	85.1
1H3DMAPY[h]	3.5036	469	18.58	233.4	1.15	137.41	19.98	0.90	103.
1EPY[i]	3.0038	395	13.42	96.3	0.00	79.36	7.06	0.00	41.5
1MIMD[j]	3.8758	336	14.73	61.3	−0.03	53.49	0.00	0.00	26.0
1E3MIMD[k]	3.4228	287	11.11	92.9	0.40	70.78	−4.18	1.68	46.7
1E23DMIMD[l]	3.2411	367	13.45	99.7	1.02	88.23	3.89	−0.65	54.8
1B3MIMD[m]	4.0196	223	10.14	123.7	−2.19	88.01	−8.25	−2.98	68.0
1B23DMIMD[n]	4.1149	313	14.57	129.9	1.59	105.53	8.46	−1.53	76.0

[a] The distance dimensions here are atomic units (au); polarizabilities (volumes) in au³. [b] Anion: bromide. [c] Anion: tetrafluoro boride. [d] Cation: 1-butyl 3,5-dimethyl pyridinium. [e] Cation: 1-butyl pyridinium. [f] Cation: 1-butyl 3-methyl pyridinium. [g] Cation: 1-butyl 4-dimethyl-amino pyridinium. [h] Cation: 1-hexyl 3-dimethyl-amino pyridinium. [i] Cation: 1-ethyl pyridinium. [j] Cation: 1-methyl imidazolium. [k] Cation: 1-ethyl 3-methyl imidazolium. [l] Cation: 1-ethyl 2,3-dimethyl imidazolium. [m] Cation: 1-butyl 3-methyl imidazolium. [n] Cation: 1-butyl 2,3-dimethyl imidazolium.
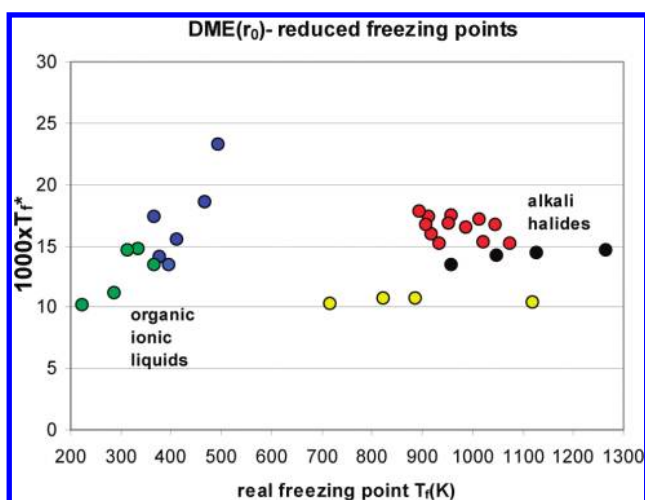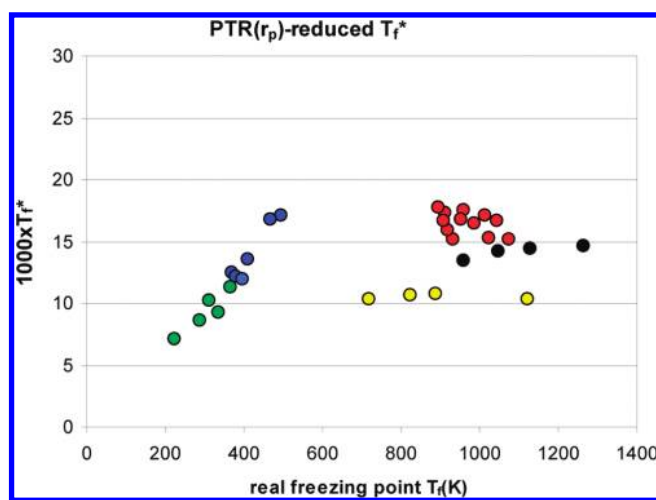

Figure 3. Distance of minimum energy (DME)-reduced freezing points of classes of ionic liquids compared with alkali halides; ethyl pyridinium bromides (green), imadazolium boron tetrafluorides (blue), Li halides (yellow), Cs halides (black), Na, K, and Rb halides (red).

Figure 4. Polarizability trace radius (PTR)-reduced freezing points of classes of ionic liquids compared with alkali halides, ethyl pyridinium bromides (green), imadazolium boron tetrafluorides (blue), Li halides (yellow), Cs halides (black), Na, K, and Rb halides (red).

conform with the majority of alkali halides, whereas the pyridinium salts tend to have lower reduced T^* closer to the lithium group at $T^* \approx 0.01$. The alkali halide that one might expect to conform most closely with the organic liquids is that with the largest cation and smallest anion, that is, CsF with $T^* = 0.0135$. This is shown in black in Figure 2. It is interesting to observe that all the organic salts with low asymmetry in the polarizability tensor, all conform closely with $T^* = 0.0135$.

In ref 2, it was found that the lithium halides tended to obey a law of corresponding states based upon the size of the anion, rather than the pair potential minimum. Accordingly, we have also calculated an alternative set of reduced freezing points from the polarizabilities of the cations that are also listed in Table 1. The polarizability is a well-defined and experimentally measurable property of ions. It has the dimensions of volume, and its cube root can be an effective definition of the ionic size radius. For the alkali halides, these are referred to as Pauling's ionic radii.[2] The characteristic distance for the purposes of scaling is the sum of the radii of trace of the polarizabilities of cation and anion. This may then be defined as

$$r_p = {}^+[(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})]^{1/3} + {}^-[(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})]^{1/3} \quad (3)$$

and the scaling law for the reduced freezing temperature is, by analogy with eq 2

$$T_f^* = k_B T_f r_p / e^2 \quad (4)$$

The results (Figure 4) for the PTR reduced freezing temperatures are much the same for the alkali halides, but show reduced scatter within the two groups of the organic liquids. Thus, this means that we can now begin to use this type of analysis to predict the freezing transition points of ionic liquids that have not yet been synthesized. The first observation is that the radii of both cation and anion separately, as obtained from the polarizability tensor, which is also an experimentally measurable property obtainable from refractive indices. In all cases studied, it is close to the minimum distance in the pair potential between cation and anion. Thus, just as ionic radii of the alkali halides are additive,[2] so it appears that the ionic radii of organic cations and inorganic anions also additive when they combine to form ionic molecules or an ionic liquid.

The polarizabilities calculated using GAUSSIAN can be used to obtain ionic radii using eq 3 and hence to predict freezing temperatures for many other classes of ionic liquids synthesized by combining different combinations of anion and cation types.

We can now analyze the data in Table 1 further and enquire whether the effect of anisotropy on the melting point is to increase or decrease T_f. In the case of both classes of liquid the most anisotropic cations have experimental melting temperatures lower that predicted by the simple scaling law. This appears be the same effect as the polarization of the halide ions in lithium halides resulting in this conformal group having lower freezing points than predicted for CsF, as can be seen in Figure 3. Now, we have two criteria for low-temperature freezing; first, both cation and anion as large as possible, second is high anisotropy in the polarizability of either or both anion and cation.

4. Discussion and Conclusions

An alternative empirical method of predicting freezing physical properties of unknown materials, perhaps that have not yet been synthesized, is to find correlations between molecular structure properties, possibly from quantum calculations such as those we report here, and freezing temperatures of ionic liquids that are already known. This is an approach that has been advocated and reviewed by Katritzky and coauthors[7] and tested further for certain classes of ionic liquids.[8,9] These authors used an empirical approach called "QSPR" or "Quantitative Structure Property Relationship" method. This procedure correlates thermodynamic properties of ionic liquids with features of the molecular structures that can be quantified. Eiche et al.[9] analyzed a training set of 126 N-pyridium bromides using the following 6-parameter equation with correlation parameters described below

$$T_f = A + B[\text{PNSA}_2] - C[\text{FNSA}_3] - D[\text{BIC}] + E[\text{RNCG}] - F[\text{RPCS}] \quad (5)$$

wehere PNSA_2 is partial charge weighted negative surface area, FNSA_3 is partial charge weighted fractional negative surface area, BIC is bonding information content, RNCG is relative negative charge, and RPCS is relative positive charge surface area.

When the predicted freezing temperatures using this equation are plotted against the experimental values, a mean R^2 correlation value of 0.79 is determined. The above descriptors are based upon electronic charge distribution and symmetry effects obtainable from data such as given in Figure 2.

Four of the descriptors used by Eike et al.[9] are "charged partial surface area descriptors". Further information about these descriptors can be obtained from the review article of Katritzky et al.[7]

If we assume the melting points of the 11 ionic liquids investigated, six of which fall into the class of pyridinium salts in the training set used by Eike et al.,[9] to be unknown, without resort to parametrization, we can use a simple corresponding states law to predict the T_f values. It is simply assumed that all ionic liquids will obey the corresponding states scaling law, based on having the same reduced freezing temperature as cesium fluoride ($T_f^* = 0.0135$). This is selected as reference salt because it has the largest cation–anion ratio of the alkali halides. The CsF-scaling law is

$$T_f = 0.0135 e^2 / k_B r_0 \quad (6)$$

Using r_0 and T_f values from Table 1, we obtain the results for the present groups shown in Figure 5. This correlation is obtained, hitherto, without the use of any fitted parameters; it gives an R^2 value of 0.7462 (Figure 5), which compares very favorably with values of 0.790, 0.775, 0.716, and 0.766 obtained
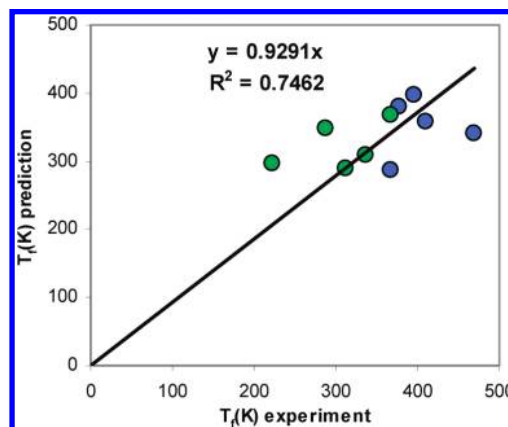
Figure 5. Correlation between predicted and experimental freezing points of organic ionic liquids; green circles denote ethyl-pyridinium bromides and blue circles imadazolium boron tetrafluorides.

for *N*-pyridium bromides and three classes of substituted ammonium bromides from Figures 3 to 7 in ref 9.

Figure 5 can be regarded as a starting point in predicting freezing points of ionic liquids. Inspection of the direction of the deviations (correlation slope = 0.9291 in Figure 5) for both classes studied here, suggest the zeroth order predicted values, using the CsF reference corresponding state, are on average 10% too low. Perhaps this is just what one would expect since the crystal phases of the alkali halides are all found to reduce further with the inclusion of ion-size asymmetry and anisotropy of the cation polarizability.[2]

There are three possible sources of the deviations of the outlying data points in Figures 3 and 4 from an "exact" conformality. One source could be a larger-than-expected uncertainty in some of the experimental melting points. Ionic liquids with a high asymmetry may have higher viscosities at freezing and barriers to nucleation leading to supercooling in the freezing point determination. It seems likely that experimental melting points may be underestimated in some cases. Also, there are approximations in the ultimate wave functions used to model the atomic structures at minimum energy in GAUSSIAN. Both these sources of uncertainty will become less as experimental melting point techniques improve and as the GAUSSIAN wave functions become increasingly realistic. Because of these uncertainties, however, we cannot assume with confidence that the whole source of the deviations from conformality, is the deviation of the real potential energy surfaces of the Hamiltonians from the simple model pair potentials in eq 1 on which the corresponding states analysis is based.

Finally, we note that the molecular-reduced principle of corresponding states can also be applied to explain not just thermodynamic properties but also transport properties such as viscosity or thermal conductivity of ionic liquids. An empirical obedience to phenomenological reduced laws for the alkali halides was observed more 30 years ago.[10] It would be interesting to see to what extent we can extend corresponding states scaling principles to transport properties of the organic ionic liquids. When the crystallization time-scale is long, many ionic liquids form glasses rather than crystallize, and whereas the freezing transition temperature is independent of mass, but decreases with ionic size, one expects just the opposite in the case of the glass transition temperature, which is determined by viscosity, and which therefore increases with ionic masses. With the crystallization transition temperatures decreasing with ionic size, and glass transition temperatures increasing with ionic

size, this raises the interesting question of a "crossover". Could the glass transition temperature for of an ionic liquid, comprising even larger organic ions, exceed the equilibrium crystallization temperature, we wonder? We can speculate that as the organic and inorganic complex ions increase even further is size, there is the possibility of organic ionic liquids may never crystallize.

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