THE MOLARITIES OF IONIC LIQUID SPECIES — DENSITIES ARE NOT BORING

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ABSTRACT

In the course of studying ionic liquids, it is customary to obtain density data, either for simple practical needs or for use with other physical measurements such as the determination of solute concentrations. Interest in molar volumes and their inverse, molar concentrations, has been minimal. We have assembled density data for a wide range of ionic liquids, including molten single and mixed alkali metal salts and ambient temperature chloroaluminate liquids. It is simple to calculate the molarities of the ions present in most cases. We observe a range from ~35 M for Li⁺ and Cl⁻ in liquid LiCl to ~1.5 M for the ions of a particular phosphonium salt with values of 3 — 6 M for a selection of chloroaluminate liquids. Within chloroaluminate systems, the anion concentrations are determined (a) by the AlCl₃ mole fraction but also (b) by the density which varies with the cation. Thus if the anion is a reactant, its reactivity should depend on the complete constitution of the liquid. Liquid water has a molarity of ~55 but aqueous solutions can be prepared containing concentrations of ions within the 1.5 to 35 M span. In the ionic liquids, have we simply substituted space for water compared to the aqueous solutions? Molecular orbital calculations were performed for constituent ions of liquids to estimate close-packed volumes. For simple salts these values can be compared to the lattice parameters from X-ray studies of solids. In all cases, ionic liquids appear to contain substantial (~40%) free volume. This approach offers the possibility of designing an ionic liquid of appropriate density and species concentrations, although non-ionic interactions such as H-bonding need to be accounted for in certain systems.

RESULTS AND DISCUSSION

For the purposes of this paper, we shall consider ionic liquids to be liquids in which the predominant species are ions. Thus we include most molten simple inorganic salts, the wide variety of organic salts liquid at or near ambient temperatures and even molecular /ionic compound mixtures where the total ion concentrations exceed 50%. While the notion of restricting the term “ionic liquid” to the ambient temperature systems creates a new field of study without the intimidation of furnaces and rapid corrosion, it is purely arbitrary from a physicochemical viewpoint and can lead to unawareness of useful comparative data.
The measurement of densities is of course simple and both molar volumes and partial molar volumes have been used to support ideas of liquid structures and molecular interactions. However, most ionic liquid densities have simply been noted or used to determine the concentrations of solutes. When the ionic liquid is not just a solvent but a reactant then the ion concentrations come into play. This situation was noted in 1964 by Gruen for Cl⁻ in LiCl-KCl eutectic and arose in our work on haloaluminates. It seems appropriate therefore to examine the molarities of the solvent ions in a variety of ionic liquids and to put the ambient temperature systems in a more general perspective.

**Liquid Inorganic Salts**

Table I lists the densities and corresponding salt molarities of selected molten single inorganic salts and mixtures, which have seen frequent use as solvents. For the majority of these systems it has been shown by a number of measurements, particularly of electrical conductivity, that complete ionization occurs and thus the densities measure the actual not just the maximum possible ion concentrations. Not surprisingly, LiCl is ~35 M in both Li⁺ and Cl⁻ while the well-known LiCl-KCl eutectic is ~27 M in Cl⁻ and 27 M in (K⁺ + Li⁺) giving the same species concentration as liquid H₂O.

**Salts at or Near Ambient Temperatures**

The densities and corresponding salt molarities of a selection of liquids comprising organic cations and inorganic anions is presented in Table II. The size and shape of the organic cations clearly results in maximum ion concentrations mostly in the 3~6 M range with special situations such as pyridinium chloride at 9.86 M (1) and tri-(1-hexyl)tetradecylphosphonium chloride at 1.7M (2).

For haloaluminate systems it has become customary to refer to the composition of a RX-AlX₃ liquid by AlX₃ mole fraction n. If one changes R, then one likely changes the density and ion concentrations for a given n value and these changes are particularly sensitive to n at certain points in the composition range. Table III gives the ion concentrations of EmimCl-AlCl₃ mixtures, assuming the pertinent equilibria to be

\[ \text{Cl}^- + \text{AlCl}_3 \leftrightarrow \text{AlCl}_4^- \]  \hspace{1cm} [1]

\[ \text{AlCl}_4^- + \text{AlCl}_3 \leftrightarrow \text{Al}_2\text{Cl}_7^- \]  \hspace{1cm} [2]

and that these equilibria lie far to the right (The equilibrium constant K = [Al₂Cl₇⁻][Cl⁻] /[[AlCl₄]² has been shown to be ~ 10⁻¹⁷ for Emim chloroaluminates and ~ 10⁻⁷ for the sodium system). The Al₂Cl₇⁻ concentration is seen to be particularly sensitive to n near n=0.67 which corresponds to the composition in the liquid of EmimAl₂Cl₇ (The phase diagram of several such systems indicate that the Al₂Cl₇⁻ salts are not congruently compounds but rather one obtains eutectics corresponding to the Al₂Cl₇⁻ stoichiometry.) In reactions involving Al₂Cl₇⁻, such as alkane cracking and processes brought about by Brensted superacids, at least some of the cation’s influence at a fixed n can be ascribed to differences in Al₂Cl₇⁻ molarity.

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Concentrated Electrolytes with Polar Solvents

Table IV presents the molarities of the molecules of the liquid hydrogen halides. While some dissociation of HF into $\text{H}_2\text{F}^+$ and $\text{HF}^-$ is known to occur, all of these systems are essentially molecular liquids.

When HF and HCl are dissolved in water, more and different ionization occurs, with the formation of $\text{H}_2\text{O}^+$ and halide ions. In the case of HF, the ionization is followed by ion pairing which means aqueous HF is not a strong acid; however, the ionization of HCl in water proceeds well. In Table V are shown the calculated molarities of solute and water for a selection of concentrated aqueous electrolytes. If complete ionization occurred, the $M_A$ values would indicate the molarities of cations and anions. We note that for the 4 systems chosen, water is the dominant component. Further, the total molarity of components in 49% aqueous HF, ionization regardless, exceeds that of each pure liquid.

If we compare the ion concentrations in the pure alkali salts, those in the ambient temperature organic salts and the potential values (where ionization is complete, the actual ones) for aqueous electrolytes, we notice that the higher values are obtained for the simple salts and the lower ones for the organic salts with the possibility of intermediate concentrations occurring in the aqueous electrolytes where at least half as many water molecules as ions are present. These comparisons are readily extended to solutions in other polar ionizing solvents. Two systems involving HF should be noted: (a) $\text{C}_2\text{H}_5\text{N}^+ \cdot 3 \text{HF}$ (3) and (b) $\text{EmimF} \cdot 2.3 \text{HF}$ (4). One might anticipate these liquids to consist of (a) $\text{C}_2\text{H}_5\text{NH}^+$ and $\text{H}_2\text{F}_3^+$ ions and (b) $\text{Emim}^+$ and a mixture of $\text{H}_2\text{F}_3^-$ and $\text{H}_3\text{F}_4^-$ ions. Alternatively, they may be thought of as concentrated salt solutions in liquid HF. From the densities the maximum cation (and anion) molarities are 4.24 M and 6.26 M respectively. While density data give us maximum possible ion concentrations, other measurements, primarily conductivities, have to be made to determine degrees of ionization or ion pairing.

Model Calculations: the Free Volume Question

The concept of free volume in liquids has proved useful in the past to explain transport properties, such as viscosity. The free volume is the difference between the molar volume of a liquid and the volume actually occupied by the ions or molecules. It makes sense that the strength of the intermolecular or ion-ion forces and the efficiency of packing will largely determine the free volume. The molar volume is easily calculated from the densities of all of the liquids mentioned above, plus many more. The more difficult quantity to obtain is the volume of the molecules or ions, since x-ray diffraction structures are obviously not available. Fortunately, the volumes the ions that comprise inorganic molten salts and the now popular semi-organic ionic liquids may be calculated by molecular orbital computation methods. Here we use the PM3 semi empirical method to calculate the volume contained inside the surface prescribed by the van der Waals radii. Tables VI and VII contain some examples of salts where the volumes are calculated from experimental densities and from the sum of the volumes of the ions: the free volume is reported as the difference. We actually have calculated the volumes of thirty cations and fourteen anions. We have compiled the densities of 58 single component semi-organic ionic liquids, eleven binary semi-organic liquids, plus a few
other multi-component curiosities. In addition, there is a plethora of densities of single component, binary and ternary inorganic molten salts reported in various handbooks and the series of compilations published by the NBS (now NIST). Only a few representative examples are presented here.

The free volumes of liquid salts having a constant anion and various sized cations are shown in Table VI. The right column lists the percent of the total volume (calculated from measured density) that is free volume. The percent free volume allows for easier comparison of the efficiency of packing in the liquids where the sizes of the cations vary over a large range. We see that the small inorganic molten salts cannot be readily compared with the semi-organic ionic liquids, because of the temperatures of the measured densities. The absolute free volumes of the inorganic melts are lower than the larger ionic liquids, but the percent free volumes are larger by about a factor of 3. This certainly arises from the thermal expansion at the high temperatures seen in the inorganic liquids. We expect the free volumes of the simple salts to be made up of the 26% left after close-packing of the spherical ions plus the observed 10-15% volumes of melting. In the semi-organic salt series of ionic liquids the fraction of the volume that is free volume is remarkably similar for the three liquids that have cation sizes that vary by almost a factor of five.

Ionic liquids with the 1-butyl-3-methylimidazolium cation, but with different anions are listed in Table VII. The anions vary in size by a factor of eight and the total concentration of ions by a factor of two. Except for the liquid with the chloride anion, for which there is much evidence of H-bonding, the percent free volumes are all rather similar. Of course, the actual molar volumes are much greater for the larger anions. This suggests that the efficiency of the packing of the ions is similar for all of the ionic liquids, and that the large dialkylimidazolium cation controls that packing efficiency. A large percentage of free volume (25-30%) compared to the alkali halides probably is a common denominator for the room temperature ionic liquids.
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### Table I. Densities and corresponding molarities of selected molten single inorganic salts and mixtures.

| Salts                  | Densities (Temp/K) | Molarities (mol/l) | Ref. |
|------------------------|--------------------|--------------------|------|
| LiCl                   | 1.495 (900)        | 35.268             | (5)  |
| NaCl                   | 1.555 (1076)       | 26.608             | (5)  |
| KCl                    | 1.524 (1050)       | 20.442             | (5)  |
| CsCl                   | 2.7681 (940)       | 16.442             | (5)  |
| NaNO₃                  | 1.8991 (600)       | 22.250             | (5)  |
| NaCl-AlCl₃(38.2:61.8)  | 1.644 (450)        | 5.996              | (6, p921) |
| KCl-LiCl (40.45:59.55) | 1.573 (860)        | 28.467             | (6, p1044) |
| KCl-NaCl(50:50)        | 1.503 (1100)       | 22.603             | (6, p1064) |
| Li₂CO₃-Na₂CO₃ (53.3:46.7) | 1.969 (900)   | 22.153             | (7)  |
| NaCN-KCN (53:47)       | 1.24 (600)         | 21.920             | (8)  |

### Table II. Densities and corresponding salt molarities of ambient temperature ionic liquids comprising organic cations and inorganic anions

| Inorganic: organic salt mixture | Densities(g/ml) (Temp °C) | Molarities (mol/l) | Ref. |
|--------------------------------|----------------------------|--------------------|------|
| HBr: Me₃SBr (1:1)              | 1.74 (25)                  | 7.312              | (9)  |
| AlBr₃:Me₃SBr (2:1)             | 2.38 (50)                  | 3.447              | (9)  |
| AlCl₃:Me₃SCl (2:1)             | 1.40 (25)                  | 3.691              | (10) |
| AlBr₃:EmimBr (2:1)             | 2.22 (25)                  | 3.064              | (11) |
| AlBr₃:EtPyBr (2:1)             | 2.20 (25)                  | 3.049              | (12) |
| AlCl₃:PyHCl (1.78:1)           | 1.47 (35)                  | 4.170              | (13) |
| AlCl₃:EmimCl (2:1)             | 1.39 (25)                  | 3.363              | (14) |
### Table III. Ion concentrations of EmimCl-AlCl$_3$ mixtures at 25°C (14)

| AlCl$_3$ fraction | Densities (g/ml) | $M_{Cl^-}$ (mol/l) | $M_{AICl^+}$ (mol/l) | $M_{AlCl^2-}$ (mol/l) | Molarities* (mol/l) |
|-------------------|------------------|-------------------|---------------------|----------------------|---------------------|
| 0.25              | 1.2075           | 4.24              | 2.12                | 0                    | 6.36                |
| 0.3333            | 1.2329           | 2.91              | 2.90                | 0                    | 5.81                |
| 0.3999            | 1.2560           | 1.79              | 3.57                | 0                    | 5.36                |
| 0.45              | 1.2742           | 0.91              | 4.09                | 0                    | 5.00                |
| 0.50              | 1.2941           | 0                 | 4.64                | 0                    | 4.64                |
| 0.5499            | 1.3209           | 0                 | 3.33                | 0.95                 | 4.28                |
| 0.6001            | 1.3488           | 0                 | 1.95                | 1.95                 | 3.90                |
| 0.6666            | 1.3888           | 0                 | 0                   | 3.37                 | 3.37                |

* Molarity of all ions.

### Table IV. Ion concentration in molecular solvents

| Solvents | Temperature (°C) | Densities (g/ml) | Molarities (mol/l) | Ref. |
|----------|------------------|------------------|--------------------|------|
| H$_2$O   | 25               | 1.00             | 55.56              |      |
| HF       | -80              | 1.2              | 60.0               | (15) |
| HF       | 25               | 0.9546           | 47.7               | (16) |
| HCl      | -114             | 1.187            | 32.6               | (15) |
| HBr      | -84              | 2.603            | 32.2               | (15) |
| HI       | -47              | 2.85             | 22.3               | (15) |

### Table V. Ion concentration in aqueous solvents (17)

| A         | H$_2$O | Density (g/ml) | $M_A$ | $M_{H_2O}$ | $\Sigma(M_A+M_{H_2O})$ |
|-----------|--------|----------------|-------|------------|------------------------|
| 37.2% HCl | 62.8%  | 1.19           | 12.1  | 41.5       | 53.5                   |
| 49.0% HF  | 51.0%  | 1.18           | 28.9  | 33.4       | 62.3                   |
| 70.0% HNO$_3$ | 30.0% | 1.42           | 15.9  | 23.7       | 39.6                   |
| 45.0% KOH | 55.0%  | 1.46           | 11.7  | 44.6       | 56.3                   |

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### Table VI. Free Volumes of Chloride Ionic Liquids

| Cation        | Density g/cm³ | Temp. °C | Formula mass g/mol | Salt Molarity mol/L | Calc. Cation Volume from (PM3) Å³ | Salt Volume from PM3 Å³ | Salt Volume from density Å³ | Free Volume Å³ | Percent Free Volume |
|---------------|---------------|----------|-------------------|---------------------|---------------------------------|--------------------------|-----------------------------|----------------|-------------------|
| Li⁺           | 1.495         | 1173     | 42.39             | 35.268              | 2.8                             | 25.24                    | 47.10                       | 21.86          | 46.41             |
| Na⁺           | 1.555         | 1349     | 58.44             | 26.608              | 8.04                            | 30.48                    | 62.43                       | 31.95          | 51.18             |
| K⁺            | 1.524         | 777      | 74.55             | 20.443              | 17.22                           | 39.66                    | 81.26                       | 41.60          | 51.19             |
| MeN\(_2\)\(\)N\(_2\)Et⁻ | 1.157       | 85       | 148.00            | 7.818               | 152.11                          | 174.55                   | 212.49                      | 37.94          | 17.85             |
| MeN\(_2\)\(\)N\(_2\)Bu⁻ | 1.095       | 60       | 174.67            | 6.269               | 197.74                          | 220.18                   | 264.98                      | 44.80          | 16.91             |
| \(\)P(C₆H₁₃)₂C₁₄H₂₉⁻ | 0.8819     | 25       | 518.00            | 1.703               | 744.28                          | 766.72                   | 975.69                      | 208.97         | 21.42             |

The volume of Cl⁻ calculated by PM3 is 22.44 Å³
Table VII. Free Volumes of 1-Butyl-3-methylimidazolium Ionic Liquids

| Anion          | Density g/cm\(^3\) | Temp. °C | Formula mass g/mol | Salt Molarity mol/L | Calc. Anion Volume from (PM3) Å\(^3\) | Salt Volume from PM3 Å\(^3\) | Salt Volume from density Å\(^3\) | Free Volume Å\(^3\) | Percent Free Volume |
|----------------|--------------------|----------|-------------------|---------------------|---------------------------------------|----------------------------|-------------------------------|-----------------|-------------------|
| Cl\(^-\)       | 1.095              | 60       | 174.67            | 6.269               | 22.44                                 | 220.18                     | 264.98                        | 44.80           | 16.91             |
| BF\(_4^-\)     | 1.1811             | 60       | 226.03            | 5.225               | 40.55                                 | 238.29                     | 317.89                        | 79.60           | 25.04             |
| CF\(_3\)COO\(^-\) | 1.209              | 21       | 252.24            | 4.793               | 55.7                                  | 253.44                     | 346.57                        | 93.13           | 26.87             |
| PF\(_6^-\)     | 1.3381             | 60       | 284.19            | 4.708               | 57.75                                 | 255.49                     | 352.80                        | 97.31           | 27.58             |
| CF\(_3\)SO\(_3^-\) | 1.2668             | 60       | 276.26            | 4.586               | 70.88                                 | 268.62                     | 362.25                        | 93.63           | 25.85             |
| AlCl\(_4^-\)   | 1.2113             | 60       | 308.00            | 3.933               | 108.73                                | 306.47                     | 422.38                        | 115.91          | 27.44             |
| (CF\(_3\)SO\(_2\))\(_2\)N\(^-\) | 1.429              | 19       | 419.39            | 3.407               | 133.66                                | 331.40                     | 487.52                        | 156.12          | 32.02             |
| Al\(_2\)Cl\(_7^-\) | 1.303              | 60       | 441.33            | 2.952               | 191.48                                | 389.22                     | 562.63                        | 173.41          | 30.82             |

Volume of bmim\(^+\) from PM3 is 197.74 Å\(^3\)