Room Temperature Ionic Liquids

Ionic compounds are made of positively charged ions (cations) and negatively charged ions (anions). The strong, Coulombic forces of attraction between the opposite charges are called ionic bonds. Typically, a lot of energy is needed to break these strong ionic bonds to melt ionic solids, and they consequently have very high melting points (NaCl, table salt, has a melting point of 801 ºC; NaF, the fluoride ingredient in toothpaste, has a melting point of 993 ºC; MgO, used in the manufacture of cement, as an antacid, and in TV plasma screens, amongst many other applications, has a melting point of 2852 ºC). Ionic compounds in liquid form are therefore usually extremely hot.

Although less common, naturally occurring ionic compounds with low melting points do exist (potassium chlorate, $KClO_3$, used in the manufacture of safety matches, has a melting point of 356 ºC, and the fertilizer ammonium nitrate, NH_4NO_3, an explosive compound used in several high-profile terrorist attacks, including the Oklahoma City bombing, has an even lower melting point of 170 ºC). Even these low melting point ionic compounds are still solid at well above room temperatures. However, by understanding what makes ionic bonds stronger and what makes them weaker, scientists have been able to engineer ionic compounds with melting points so low that they have already melted and are in the liquid state at room temperature. The key to creating super-low melting point ionic compounds is super-weak ionic bonds that break below room temperature. To create these super-weak bonds requires an understanding of the nature of the Coulombic attraction between the ions in an ionic compound.

The force holding two ions together is proportional to the product of the charges on each ion divided by the square of the distance between the ions (this is the distance between the centers of the ions). This is written;

$$Force \propto \frac{Q_1 Q_2}{r^2}$$

This means that the smaller the ionic charges (Q_1 and Q_2), the weaker the force holding them together. It also means that the larger the separation (r, the distance between the centers of the two ions), the weaker the force holding them together. So, ionic bonds will be weakest when the charges are small (+1 and –1 is best) and the separation is large (the larger the ions, the further apart their centers are). This explains why MgO has one of the higher ionic melting points (ionic charges are +2 and –2, and the ions are small, so the distance between their centers is also small), and NH_4NO_3 has one of the lower ionic melting points (ionic charges are +1 and –1, and the ions are polyatomic, making them relatively large, so the distance between their centers is also large).

However, even the lowest melting point naturally occurring ionic compounds are solid at room temperature. If we want an ionic compound that is a liquid at room temperature (i.e. has a melting point below 25 ºC), we have to get creative. We can't do better than ionic charges of +1 and –1, but we *can* use (or create) polyatomic ions that are very large and bulky, keeping the ions well separated within the solid crystal structure. This is the key to creating a room temperature ionic liquid.

Examples of room temperature ionic liquids are; 1-butyl-3-methylimidazolium hexafluorophosphate (fig. 1) which melts at 6.5 ºC, and 1-butyl-3,5-dimethyl pyridinium bromide (fig. 2) which melts at –24 ºC. In both cases, the cation and anion have +1 and –1 charges respectively, and in both cases, the ions are large and bulky. Both ions in 1-butyl-3-methylimidazolium hexafluorophosphate are polyatomic, and the cation is actually derived from a rather large organic molecule, and although the anion in 1-butyl-3,5-dimethyl pyridinium bromide is a simple monatomic bromide, bromine is a fourth row element and therefore quite large. More importantly, the 1-butyl-3,5-dimethyl pyridinium cation is extremely large and bulky, preventing the bromide from getting close to the positive charge on the ion. In both these examples, the separation between the charges is so great in the solid crystal structure that the Coulombic forces are extremely weak and easily broken, even at temperatures below 25 ºC.

Fig. 1. 1-butyl-3-methylimidazolium hexafluorophosphate

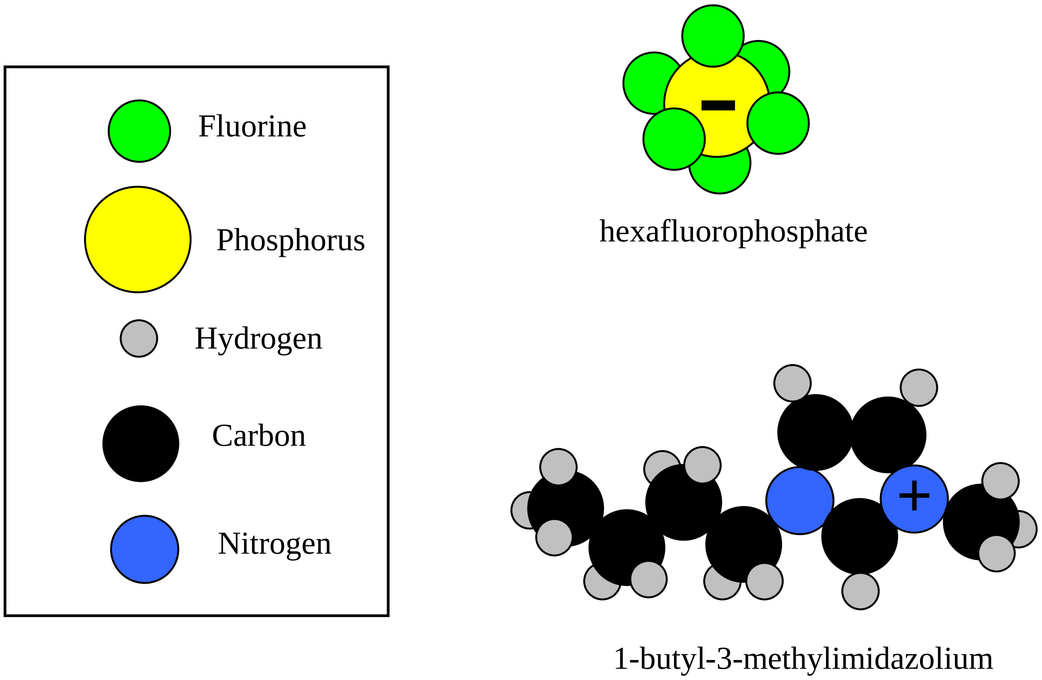

Fig. 2. 1-butyl-3,5-dimethyl pyridinium bromide