APPROACHES TO CRYSTALLIZATION FROM IONIC LIQUIDS: A STRATEGY FOR CONTROLLED FORMATION OF NEW SUPRAMOLECULAR ARCHITECTURES

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While the use of ILs as solvents for chemical reactions has been extensively reviewed and has been the subject of enormous publicity, work on developing an understanding of properties, and physical and structural data of ILs is less prolific. The most commonly studied IL systems contain ammonium, phosphonium, pyridinium, or imidazolium cations, with varying heteroatom functionality. Compared to conventional molecular organic solvents, ILs are much more complex, both chemically, and in terms of the wide range of interactions that can take place, and although some systematic studies of structure-property relationships have been attempted, there are no simple rubrics for comparison of the solvent and solvating properties of differing ILs.

One aspect of our research is the expansion of applications of ILs as crystallization solvents based on a core knowledge and understanding of the solvent parameters of ILs in order to realize goals of controlled crystallization, formation of unique materials, and modification of crystal habit or polymorphic states through solvent design. Since crystallization is the second most widely used separation method, it is important to explore crystallization of products from ILs as an important separations and purification process.

The apparent appeal of crystallization from an IL, with no losses of solvent through evaporation, must be immediately measured against the fact that many crystallization processes are evaporative, thus the challenges in crystallization are lack of vapor pressure (preventing evaporation) and apparent lack of thermal variation in solubility of many compounds (heating does not necessarily lead to increased solubility - but there is virtually no published data on this).

Crystallization approaches include (i) addition of a secondary non-solvent causing precipitation from IL solution at the change from an ionic liquid to concentrated salt solution (ii) evaporation of a secondary solvent with the IL acting as a supporting, nonvolatile nonsolvent phase, and (iii) reactive crystallization leading to controlled formation of insoluble products.

The variation in the solvent properties of different IL systems and the apparent ordering and structure in the liquid state leads to optimism that control over polymorph and crystallization can be afforded, and can lead to isolation of materials with discrete structural morphology, with direct relevance to pharmaceutical, inorganic chemistry, and the synthesis of new materials. For example, supramolecular silver(I)-pyrimidine cationic assemblies such as the 1:1 Ag(I)nitrate:pyrimidine architecture (Figure 1) that are conventionally prepared from acetonitrile can also be crystallized from non-volatile IL solutions.


The questions posed, and that will be addressed, are: (a) is crystallization from IL solutions of interest for bulk purification of products? (b) Can crystallization processes and crystal growth events be better understood by investigating IL systems? (c) Can non-traditional crystallization methods be used to produce new materials or crystal forms?

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