Ionothermal synthesis—ionic liquids as functional solvents in the preparation of crystalline materials

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Received (in Cambridge, UK) 9th February 2009, Accepted 12th March 2009
First published as an Advance Article on the web 25th March 2009
DOI: 10.1039/b902611h

Ionothermal synthesis is the use of ionic liquids simultaneously as both the solvent and potential template or structure directing agent in the formation of solids. It directly parallels hydrothermal synthesis where the solvent is water. In this feature article I discuss the general features of ionothermal synthesis and how the properties of the synthesis differ from those of other synthetic methodologies. In particular, I will discuss the role of the ionic liquid anion in determining the structure of the synthesised solid, the role of mineralisers such as water and fluoride, and the targeted use of unstable ionic liquids to produce new inorganic and inorganic–organic hybrid materials.

1. Introduction

Over recent years ionic liquids (ILs) have received great attention in many fields.[1] Most of the studies have focused on the 'green' chemistry[2] potential of these compounds, with particular emphasis on the drive to replace organic solvents in homogeneous catalysis.[3] The particular property of ILs that makes them environmentally suitable for these purposes is their low vapour pressure,[4] which has significant advantages when replacing highly volatile organic solvents. However, there are many other uses of ionic liquids in diverse areas of technology ranging from electrolytes in batteries and fuel cells,[5] as electrodeposition solvents,[6] to the use of supported ionic liquid as catalysts.[7] In some reactions the ILs act only as inert solvents and in others the liquid plays a more active role in the reactions that take place.

The broadest definition of an ionic liquid is any material in the liquid state that consists predominantly of ionic species. Any ionic salt that can be made molten can therefore be classified as an 'ionic liquid', always assuming that the ionic components of the solid remain intact on melting. There are many examples in the literature of molten salts being used as the medium in which inorganic materials have been prepared.

Usually, these synthetic procedures take place at highly elevated temperatures, producing dense phase solids. For example, alkali metal hydroxide molten salts can be used as the molten phase, often contained in sealed inert (such as silver) vessels in the synthesis of many inorganic solids. In general such molten salt synthesis methods have been used as direct replacements for traditional solid state synthesis techniques.[8] However, the modern definition of ionic liquids tends to concentrate on those compounds that are liquid at relatively low temperatures and that contain organic components.[9] Room temperature ionic liquids (RTILs) are, as the name suggests, liquid at room temperature while near room temperature ionic liquids (nRTILs) are often defined as being liquid below a certain temperature, often 100 °C, although this varies depending on the application envisaged for the liquids. For ionothermal synthesis, nRTILs are often defined as being liquid below about 200 °C, the temperatures traditionally used in hydrothermal synthesis.[10] In modern usage the term ionic liquid is almost exclusively reserved for liquids that contain at least one organic ion. The organic components of ionic liquids tend to be large and often quite asymmetric which contribute to their low melting points by making efficient packing in the solid state more difficult.

Ionic liquids show a range of properties that make them suitable for use as media for the preparation of inorganic and inorganic–organic hybrid materials. They can be relatively polar solvents, ensuring reasonably good solubility of inorganic precursors.[11,12] Many (but not all) ILs have good thermal stability enabling them to be used at elevated temperatures.

Deep eutectic solvents (DESs) are a related class of ionic liquid, produced as a mixture of two or more compounds that has a lower melting point than either of its constituents.[13] Eutectic mixtures display unusual solvent properties that are very similar to those shown by the ionic liquids. High

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solubility can be observed (depending on the eutectic mixture used) for inorganic salts, salts that are sparingly soluble in water, aromatic acids, amino acids and several metal oxides.[14] Advantages of eutectic mixtures over other ionic liquids are their ease of preparation in a pure state and their relative non-reactivity with water. Many are biodegradable and the toxicology of the components maybe well characterized. Eutectic mixtures based on relatively available components such as urea and choline chloride are also far less costly than some other ionic liquids.

Fundamentally, there is of course no real difference between an ionic liquid and a molten salt, except perhaps that the organic nature of the components of an ionic liquid introduces much more scope for introducing functionality into the solvents. In the following feature article I will concentrate on the use of the nRTILs containing organic components as the media for materials synthesis, consistent with modern usage of the terminology. In particular I will concentrate on the synthesis of templated crystalline materials such as zeolites and metal organic frameworks where the IL cation acts to direct the structure of the resultant inorganic or inorganic–organic hybrid material.

2. Hydrothermal, solvothermal and ionothermal synthesis

Broadly speaking, the synthesis of crystalline solid state materials can be split into two main groups: those where the synthesis reaction takes place in the solid state and those which take place in solution. The solid state method usually requires rather high temperatures to overcome difficulties in transporting the reactants to the sites of the reaction. The high temperatures of solid state reactions also tend to provide routes to the thermodynamically more favoured phases in the systems of interest. Typically this method is used to prepare solid state oxides.

Transport in the liquid phase is obviously much easier than in solids, and syntheses require much lower temperatures (often less than 200 °C). The archetype of this type of preparative technique is hydrothermal synthesis, where the reaction solvent is water.[15] The most common method of accomplishing hydrothermal synthesis is to seal the reactants inside Teflon-lined autoclaves so that there is also significant autogenous hydrothermal pressure produced, often up to 15 bar. The lower temperatures required for hydrothermal synthesis often lead to kinetic control of the products formed, and it is much easier to prepare metastable phases using this approach than it is using traditional solid state approaches. The important reaction and crystallisation processes in hydrothermal synthesis do not necessarily take place in solution (although of course they can) but can occur at the surfaces of gels present in the mixtures.

Solvothermal synthetic methods refer to the general class of using a solvent in the synthesis of materials. Of course water is by far the most important solvent, hence the special usage of the term hydrothermal to describe its use. However, there are many other possible solvents. Alcohols, hydrocarbons, pyridine and many other organic solvents have all been used with varying degrees of success.[16] As with water these molecular solvents produce significant autogenous pressure at elevated temperatures. The solvents used in solvothermal synthesis vary widely in their properties, from non-polar and hydrophobic to polar and hydrophilic.

The solvents used in hydrothermal and solvothermal synthesis differ fundamentally from ILs in that they are molecular in nature. The ionic nature of ILs imparts particular properties, including low vapour pressures[17] (and so very little, if any, autogenous pressure is produced at high temperature).

3. Ionothermal zeolite synthesis

Many ILs used today often have chemical structures that are very similar to the structures of commonly used structure directing agents (sometimes also known as templates) in the hydrothermal synthesis of zeolites and other porous materials.[18] This realisation led to the first attempts to prepare zeotype frameworks using ILs as both the solvent and the template provider at the same time.[10] The potential advantage of this approach is that the competition between the solvent and template for interaction with any growing solid is removed when both solvent and template are the same species (Fig. 1). In principle this may lead to improved templating of the growing zeolite crystal structure. The first work in this area,

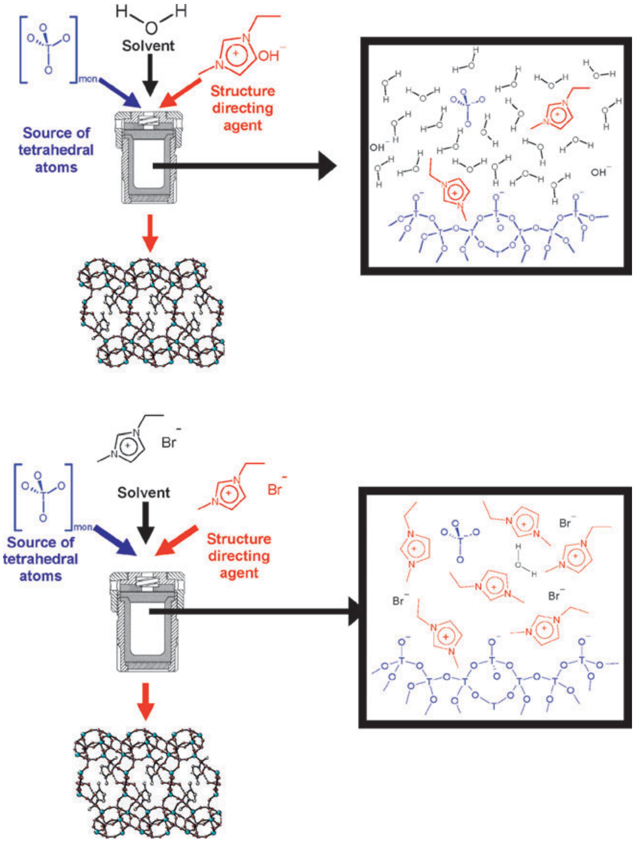

Fig. 1 Schematic representations of the synthesis of a tetrahedral (zeotype) framework under hydrothermal (top) and ionothermal (bottom) conditions. Note that in this depiction the solvent and the structure directing agent are the same species in the ionothermal synthesis and that species, such as water, can also be present in small amounts.

published in 2004, used 1-ethyl-3-methylimidazolium bromide and urea/choline chloride deep eutectic solvents to prepare several different materials depending on the conditions.[10]

Since the first breakthroughs in this area there have been many further attempts to prepare zeotype materials. The ionothermal synthesis of aluminophosphate zeolites has been by far the most successful. Many common ionic liquids are suitable solvents for the preparation of these materials, with both known[19–22] and previously unknown[23] structure types, as well as related low dimensional materials,[24,25] being synthesised successfully. It is interesting to note that more than simply preparing the base aluminophosphate structure, the ionothermal method is also suitable for incorporating the dopant metal atoms that give the frameworks their chemical activity. Silicon (to make so-called SAPOs)[26] and many different tetrahedral metals (Co, Mg *etc.*) can all be incorporated into the ionothermally-prepared aluminophosphate zeolites, and aspects such as their catalytic activity[27] and the use of additional templates[28] show some very promising results.

Silicon-based zeolites have, however, been much more of a challenge for ionothermal synthesis although there has been more success in the synthesis of mesostructured silica using ILs.[29] The problem with zeolite synthesis is primarily the solubility of silica staring materials in the commonly used ILs, which is not sufficiently good to allow silicate and aluminosilicate materials to be prepared. Before 2009 there was only one report of a silica polymorph being prepared from an ionic liquid[30] and one report of the synthesis of a sodalite.[31] Successful synthesis of zeolites requires the preparation of ionic liquids more suited to silicate dissolution. Recently in our laboratory we have been successful in preparing ionic liquids comprising mixed halide and hydroxide anions that are suitable solvents for the preparation of purely siliceous and aluminosilicate zeolites. The presence of hydroxide increases the solubility of the silicate starting materials and allows the zeolites to crystallise on a suitable timescale.[32]

4. Ionothermal synthesis of metal organic frameworks and coordination polymers

Similar to the synthesis of zeolites, ILs can be used as the solvent and the template to prepare many other types of solid. One of the most interesting and important classes of material that has been recently developed is that of metal organic frameworks (also known as coordination polymers).[33,34] These materials offer great promise for many different applications, but particularly in gas storage.[35–38] Normally these materials are prepared using solvothermal reactions, with organic solvents such as alcohols and dimethyl formamide. Ionothermal synthesis has been used extensively over the past few years to prepare these types of solid, and there are now many examples in the literature.[39–48]

Unlike zeolites, however, the lower thermal stability of coordination polymers leads to several issues regarding removal of ionic templates from the materials to leave porous materials. Often removing the IL cation is not possible without collapsing the structure. However, it is possible to prepare porous materials using deep eutectic solvents, and Bu *et al.* have recently proven this very elegantly.[49]

A great many of the materials prepared ionothermally are relatively low dimensional solids, and this is clearly a very productive method for the preparation of such materials. It is very clear that in these systems changing the chemistry of the solvent to ionothermal leads to great possibilities in this area.

5. The ionothermal synthesis of other types of material

While our lab concentrates on the ionothermal synthesis of zeolites and metal organic frameworks, there is of course no reason why ionothermal synthesis cannot be used to prepare other types of materials. Indeed, laboratories around the world have used ionic liquids to prepare many different types of solid, from nanoparticles of different types,[50–54] to semiconductors,[55] inorganic[56–59] and organic solids.[60] For space reasons I will not go into too much detail on this work as there are one or two excellent reviews[61,62] already available, but this is clearly an area where there is much scope to extend ionothermal synthesis in the future.

6. Ambient pressure ionothermal synthesis

Perhaps the most striking feature of ILs is their very low vapour pressure. This means that, unlike molecular solvents such as water, the ILs can be heated to relatively high temperatures without the production of autogenous pressure. High temperature reactions therefore do not have to be completed inside pressure vessels such as Teflon-lined steel autoclaves but can be undertaken in simple containers such as round bottomed flasks. The absence of autogenous pressure at high temperature also makes microwave heating a safer prospect as hot spots in the liquid should not cause excessive increases in pressure with their associated risk of explosion, assuming of course that the IL is stable and does not breakdown into smaller components during heating.[63,64] Fig. 2 shows the measured pressure during the synthesis of an aluminophosphate molecular sieve (SIZ-4) using a microwave heating experiment.[65] The top panel is the pure ionic liquid solvent, and it is clear that no autogenous pressure is produced. The bottom panel, however, shows that even when only modest amounts of water are added to the system significant pressures are evolved.

One of the most interesting potential uses of ambient pressure synthesis of zeolite coatings is for anti-corrosion applications. Yan[66] has shown that ionothermally-prepared zeolite films (Fig. 3) make excellent anti-corrosion coatings for several different types of alloys.[67] Given that current coatings technology is based on the use of environmentally-unfriendly chromium there is interest in finding more acceptable alternatives. Sealed zeolites are one such option. However, hydrothermal synthesis of zeolites inside sealed vessels is impractical for large, oddly shaped and cut pieces of metal. Yan contends that ambient pressure ionothermal synthesis eliminates the need for unwieldy sealed vessels, and given the excellent coatings that can be prepared using this approach it offers an interesting and potentially important alternative technology.

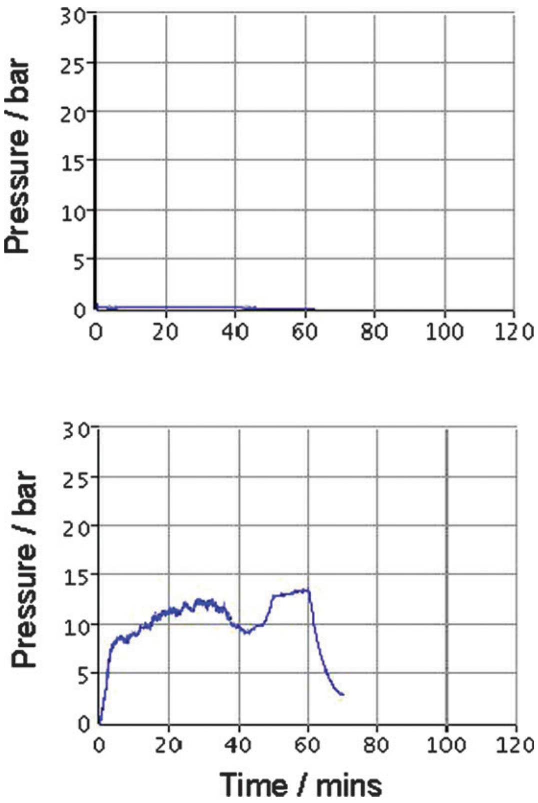

Fig. 2 The evolution of pressure (in bar) in the microwave synthesis of aluminophosphate SIZ-4 from (top) a pure ionic liquid solvent with no water added and (bottom) the same solvent system with 0.018 ml of water added. The maximum temperature is 200 °C and the duration of heating is 60 min. There is almost no pressure evolution in the pure ionic liquid.

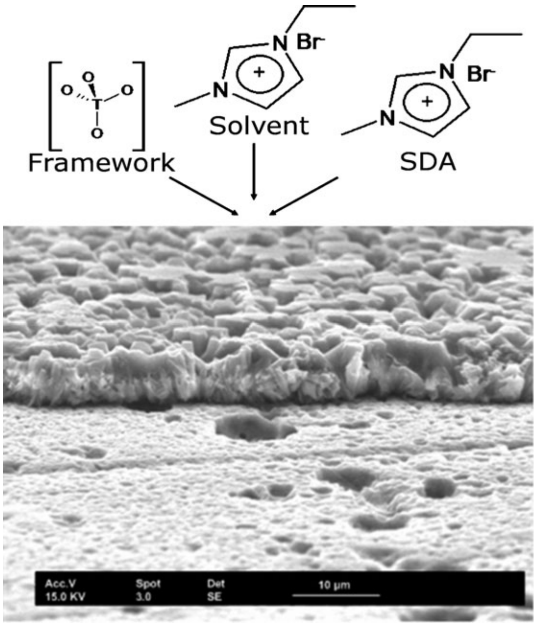

Fig. 3 Ambient pressure ionothermal synthesis of zeolite coatings offers great potential in anti-corrosion technologies. This diagram shows a Si-SIZ-4 type zeolite coating (see ref. 67 for further details).

7. The role of the cation—templating, co-templating or no templating?

The original concept behind ionothermal synthesis (Fig. 1) was to simplify the templating process that occurs in traditional zeolite hydrothermal synthesis by making the solvent and the template the same species. The template molecules normally involved in zeolite synthesis are usually cationic since the resultant framework has a negative charge. The commonly used templating cations are very similar in chemistry to IL cations. It is not surprising therefore that the IL cations are often occluded into the final structures of the materials, in exactly the same way as in traditional zeolite synthesis.[10]

In an exactly analogous fashion, metal organic frameworks can also be synthesised using the IL as both the solvent and the template. Most solvothermally prepared MOFs have neutral frameworks, but when the template is a cation the framework must, for charge balance, have a negatively charged framework, in exactly the same way as zeolites. Of course, the overall goal of all templating based synthesis is to have control over the architecture of the final material by changing the size of the templating cation. It is well known, however, that apart from rough correlations with size of the cation the templating interaction is not really specific enough to yield very precise control over the reaction. Fig. 4 shows that the same general features hold for ionothermal synthesis. In this work changing the size of the IL cation does have some effect on the final structure—the larger cations form more open frameworks with the extra space needed to accommodate the large template. However, this is not particularly specific in this type of MOF synthesis, indicating that templating is more likely to be by simple 'space filling' rather than any more specific or directed template-framework interactions.[68]

In hydrothermal synthesis there is also the possibility of adding alternative cations to act as templates. Of course the situation is exactly analogous in ionothermal synthesis, and added templates offer equally great opportunities. Recently, Xing *et al.*[69] have shown that methylimidazolium (MIA), when added to an 1-ethyl-3-methylimidazolium (EMIM) bromide IL leads to a cooperative templating effect, occluding both MIA and EMIM in the same solid. The intriguing feature of this solid is that it looks, at least on first inspection, as if the material is made of two distinct layers (Fig. 5). The MIA is located close to one layer and the EMIM close to the other—perhaps indicating that each cation plays a specific role in directing the structure of each part of the material. It is, of course, impossible to say this for certain until the full mechanism of synthesis is elucidated, something that is very difficult in practice. However, further circumstantial evidence for this may be the fact that the previously prepared EMIM-templated materials SIZ-1 and SIZ-4 have closely related structures to the EMIM-'templated' layer in this material.

Up to now the cation in the IL has acted only as a template in the synthesis. However, like any other solvent, including water, there is also the possibility of bonding interactions with the frameworks. Most of the ILs that are based on dialkylated imidazolium cations have no obvious sites through which to coordinate to the metal sites in the way that water does. However, some ILs, under specific conditions, can breakdown

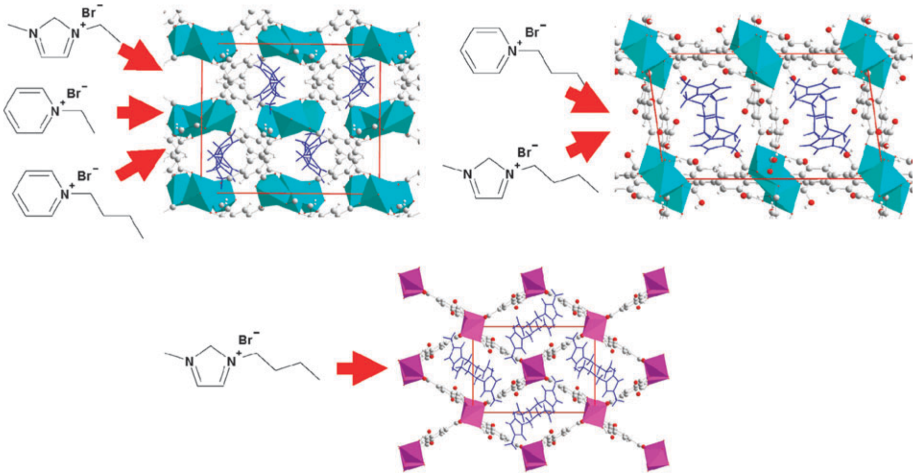

Fig. 4 The effect of changing the size of the IL cation on the resulting metal organic framework structure. The materials prepared in this study are Ni (blue) or cobalt (purple) terephthalate MOFs.

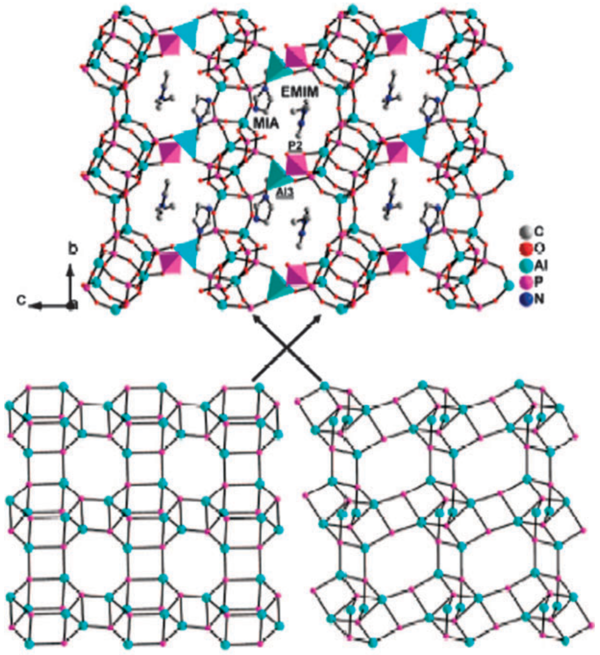

Fig. 5 The dual templating role of the IL cation (EMIM) and an added template (MIA) in the formation of an aluminophosphate zeolite-related material. Figure reproduced by kind permission from ref. 69.

to leave the monoalkylated imidazole species that can coordinate to metals.[70] As in hydrothermal synthesis, controlling how the solvent interacts with the framework materials is therefore important in determining the exact nature of the final material. A similar example where the solvent can coordinate to the metal in a metal organic framework comes when using choline chloride/urea-based deep eutectic solvent ILs. Normally, this type of solvent is regarded as relatively unstable, especially the urea portion which can break up and deliver smaller templates into the reaction. However, under conditions where the urea is stable it is possible to keep this intact, and in the case of ionothermally-prepared lanthanum-based MOFs the urea coordinates to the metal.[71]

In addition to the templating cations, ILs also contain an anion, and these turn out to be extremely important in controlling the properties of the solvents (see section 8). The anions can, in certain circumstances, also be occluded in the structure as a template, most often in combination with the IL cation. Bu *et al.* recently showed that in a series of MOFs (called ALF-n) the IL displayed several different types of behaviour, including templating by only the cation and templating by both the cation and anion simultaneously, illustrating the multiple functions that ILs can play even in the same systems.[48]

Finally, of course, the ILs can play the role as solvent only and not be occluded in the final structure at all. For species like aluminophosphate zeolites and MOFs, where the chemistry of the cation is similar to that of commonly used templates, one would expect them to be occluded in the final structure. However, there are certain situations where this does not happen. Perhaps the most striking of these is when a very hydrophobic ionic liquid is used. In the case of aluminophosphate and MOF synthesis, the more hydrophobic the IL used the less likely the IL cation is to be occluded.[24] Of course as the chemistry of the system is changed (*e.g.* by trying to make different types of inorganic material) the balance between the solvent and templating actions of ILs also changes.

8. The role of the anion—structure induction

As we have seen above, the common organic cations in ILs are chemically very similar to zeolite templates. However, ILs also contain an anion, and the nature of the anion plays an extremely important part in controlling the nature of the IL. Fig. 6 demonstrates this dependence of property on anion very clearly. Two low melting ionic liquids that are solid at room temperature can be prepared from the same cation (EMIM) but with two different anions: bromide and triflimide (NTf_2). The two ILs have very different properties, especially when it comes to their interaction with water. Fig. 6 shows what happens when the two compounds are left out in the air for 20 min. EMIM NTf_2 is a relatively hydrophobic material and

Fig. 6 The effect of moist air on hydrophobic EMIM triflimide (sample A) and hydrophilic EMIM Br (sample B). After 20 min exposure to normal air at room temperature the EMIM Br has absorbed enough moisture from the atmosphere to turn from a solid into a liquid.

there is no change in its properties on exposure to the moisture in the air. EMIM Br on the other hand is highly hygroscopic and turns liquid on reaction with moisture in the air.

Clearly, this change in IL chemistry on alteration of the IL anion is bound to have a significant effect on the products of any reaction carried out in such solvents. One example of this is given in section 7, where in the synthesis of aluminophosphates EMIM Br solvents lead to incorporation of the EMIM cation to form zeotype materials[10] whereas the use of the EMIM NTf_2 IL leads to no occlusion of the IL cation.[24] More interesting however, and potentially extremely useful, is the possibility of mixing the two types of liquid to form solvents with different chemistries from the end member liquids. Fig. 7 illustrates this for the synthesis of cobalt benzenetricarboxylate MOFs.[72] The two end member ILs, EMIM Br and EMIM NTf_2 form two different types of material, while a 50 : 50 mixture of the two ILs, which are miscible, forms a third structure type. This type of result opens up the possibility of mixing ILs to form solvents whose chemistry is different from the end members, giving rise to much more control over the properties of the solvent. In a similar example, a mixed anion IL (50% bromide, 50% triflimide) leads to the formation of coordination polymers containing fluorinated ligands when ILs containing only one anion (either bromide or triflimide) did not produce any crystalline solid.[73]

It is clearly the nature of the anion that determines the final material in these examples. However, the anions themselves are not generally occluded into the structure, and so this is an induction effect rather than a templating of structure directing effect. It is perhaps not too surprising that changing the chemistry of the solvent will change the type of product in such a manner. In the example illustrated in Fig. 7 there is no obvious correspondence between the nature of the anions and the nature of the final material. However, in 2007 we published an example of an anion induction using a chiral anion as part of an IL to induce a chiral coordination polymer that contains only achiral building blocks[74] (Fig. 8). In this example a chiral ionic liquid prepared from the butylmethylimidazolium (BMIM) cation in combination with L-aspartate as the anion, when used to prepare a cobalt benzenetricarboxylate MOF produced a chiral structure, with all indications that the bulk solid produced was homochiral. Where some specific property of the IL anion manifests itself in the resulting material, despite the fact that it is not actually occluded, the potential for 'designer' structure induction becomes very attractive, and one would hope that such properties of ionothermal synthesis will be explored and exploited more thoroughly in the near future.

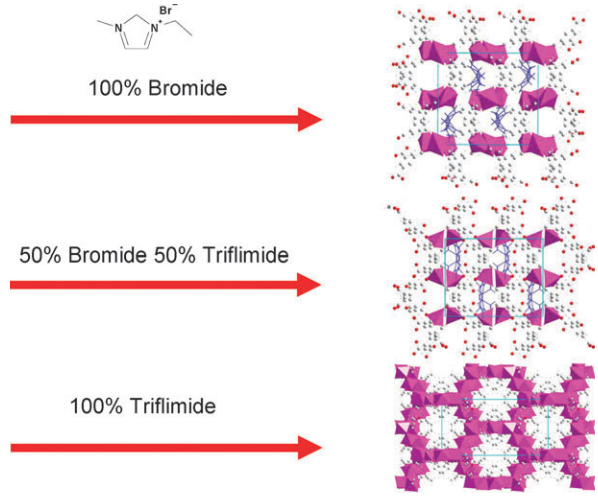

Fig. 7 The effect of the anion on the final structure of the material produced in an ionothermal synthesis. The top reaction shows uses EMIM Br as the solvent, and produces one particular cobalt-trimesic acid MOF. A 50 : 50 mixture of EMIM Br and EMIM triflimide produces a different MOF, while using only the EMIM triflimide produces yet another material. For further details see ref. 72.

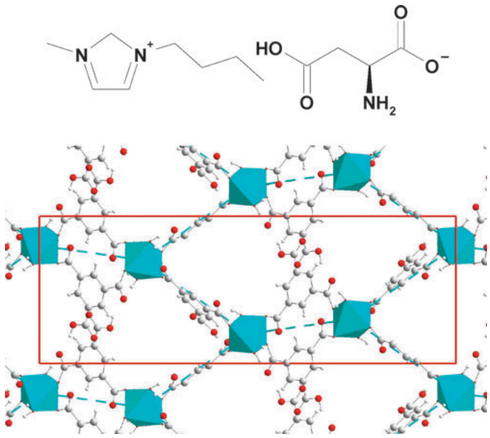

Fig. 8 The use of an ionic liquid with a chiral anion induces a chiral MOF structure. Use of an achiral anion produces achiral structures.

9. The role of water and other mineralisers

One of the very first questions asked about ionothermal synthesis was whether the ILs used were sufficient in their own right to promote the synthesis of zeolites and other inorganic materials, particularly those oxides where water might catalyse the condensation reactions needed to form the required bonds. One of the first things noted about ionothermal synthesis was that too much water was detrimental to the formation of zeolites. At low concentrations of water zeolites were the main products, but as more water was added to the IL solvents so that they were about equimolar in concentration only dense phases could be prepared. Wragg and Morris studied this effect in more detail and confirmed through several hundred high throughput reactions that larger amounts of water did indeed lead to dense phases.[65] The origin of this effect is still under investigation but it is known that the microstructure of water in ILs does change with concentration. At low concentrations the water is hydrogen bonded relatively strongly to the anion, and exists either as isolated water molecules or as very small clusters.[75] However, as the concentration of water increases larger clusters and eventually hydrogen bonded networks start to appear which change the properties of the liquid markedly. Eventually, of course, as more and more water is added it becomes the dominant chemical component (and therefore the solvent) and the system becomes hydrothermal rather than ionothermal.

The strong binding of isolated water molecules in ILs leads to another interesting effect that can be used in ionothermal synthesis—so called water deactivation. At low concentrations of water this strong hydrogen bonding leads to water being less reactive than similar amounts in other solvents. This effect is so strong that highly hydrolytically sensitive compounds such as PCl_3 can be stored for relatively long periods, whereas they react quickly, and often violently, in other 'wet' solvents.[76] Such water deactivation is probably the reason why some of the materials prepared using ILs can have unusual features. For instance SIZ-13, a cobalt aluminophosphate material has a layered structure that is closely related to a zeolite, but has Co–Cl bonds. Normally such bonds are hydrolytically unstable and under hydrothermal conditions it is unlikely that this material would be stable.[19]

In zeolite (and other) synthetic procedures mineralisers, such as fluoride or hydroxide ions, added to the reaction mixtures in the correct quantities are often vital for crystallisation of the desired molecular sieve products. Fluoride in particular has recently been an extremely useful mineraliser for aluminophosphate,[77] and silicate[78,79] synthesis. In addition to helping solubilise the starting materials under the reaction conditions there is evidence that fluoride itself can play a structure directing role[80] and is intimately involved in template ordering in certain materials.[81,82] In ionothermal synthesis the addition of fluoride also seems to be important in determining the phase selectivity of the reaction.[10] It may also help to catalyse the bond forming reactions in zeolite synthesis, as suggested by Camblor and co-workers.[78] For instance, in the synthesis of aluminophosphates the addition of fluoride leads to the formation of SIZ-4 and SIZ-3, which are both fully connected frameworks, but SIZ-1, which is an interrupted structure with some unconnected P–OH bonds, without fluoride.

Tian and co-workers have recently completed an extremely nice kinetic study of the effect of both water and fluoride added to ionothermal systems in zeolite synthesis.[83] It is clear from their results that both small mounts of water, and particularly fluoride, increase the crystallisation rate. If the reactions are done carefully to exclude as much water as possible the crystallisation of the zeolites becomes very slow indeed, suggesting that for all practical purposes a small amount of water in the IL is vital if ionothermal synthesis is to be successful.

10. Unstable ionic liquids

In many publications one often sees mention of the high thermal and chemical stability of ILs. Bearing in mind of course that it is difficult to generalise across all the possible ILs this is true under many conditions. However, under ionothermal conditions some quite common ILs are unstable. Even some that are often relatively stable such as butylmethylimidazolium bromide can breakdown, especially in the presence of fluoride ions.[84] One possible reaction is the transalkylation reaction that swaps the alkyl groups, leading to the formation of dimethylimidazolium cations, which then templates a zeolite structure.[84]

Deep eutectic solvent ILs based on choline chloride/urea mixtures are also unstable under ionothermal conditions. The urea portion of the IL breaks up to release ammonium ions into the mixture, which then templates the SIZ-2 aluminophosphate material. This type of instability in the ILs is actually extremely repeatable. Deep eutectic ILs made from functionalised ureas all breakdown in the same way to produce the expected functionalised ammonium or diammonium cations that then go on to template many different structures.[85] Such reproducibility in the reactions of these ILs opens up interesting possibilities for the delivery of small amounts of template to the reaction mixture, as opposed to having the whole IL made up of the template.

11. Scope for the future

Normally, ionic liquids are classed as 'green' chemicals because they are most often used to replace volatile organic solvents. However, when preparing the materials I have discussed in this feature article, and in particular all inorganic framework solids such as the zeolites, the ILs are more often than not replacing water. In these situations ionothermal synthesis cannot be called a 'green' technology compared to that which it replaces. When replacing organic solvents in, for example, the synthesis of metal organic frameworks there is more justification for using the 'green' tag. However, even in these syntheses the success of the methodology has to rely on the ILs introducing new chemistry into the system that is not possible using other systems. Fortunately, over recent years ionothermal synthesis has been recognised as a highly flexible methodology that does indeed bring new chemistry to the system. Features such as water deactivation and chiral induction offer many possibilities for the preparation of materials that are unlikely or even impossible to make in other solvents.

One of the most interesting features of ILs for ionothermal synthesis is the sheer number of possible liquids available. There are an estimated 1 million binary ILs available,[1] compared with only a few hundred molecular solvents. The wide range of accessible properties of the liquids provides huge opportunities for matching the chemistry of the solvent system to that of the reactants. However, this also presents huge challenges—it is at the moment extremely difficult to predict *a priori* the properties of the solvent and how they will behave in combination with the reactants. Up to now only a few of the easily available ILs have been studied, leaving many potentially interesting solvents completely unexplored. One particularly interesting feature of ionothermal synthesis is the use of mixed ILs to tailor the solvent towards a particular reaction chemistry by mixing two different miscible ILs to produce a new solvent with different properties (section 8). Once again the issue of predicting the properties of the mixed ILs is a problem. However, this type of approach is particularly suited to high throughput methodologies, because new solvents can be prepared simply by mixing two ILs in various amounts, and the 'brute force' approach afforded by high throughput instrumentation can at least identify areas of interest in the compositional fields.

The use of ILs in the synthesis of solids has, of course, not been limited to new hybrid and inorganic framework solids. Work in the nanomaterials area and increasingly in other areas, such as the organic solid state, has increased steadily over the past few years. However, there is still much scope to develop the synthesis methodology further. I hope that as we discover ever more about the interesting properties of ILs the field of ionothermal synthesis will develop into an even more useful addition to the armoury of synthetic materials chemists.

Notes and references

1 R. D. Rogers and K. R. Seddon, *Science*, 2003, **302**, 792–793.
2 L. A. Blanchard, D. Hancu, E. J. Beckman and J. F. Brennecke, *Nature*, 1999, **399**, 28–29.
3 D. J. Cole-Hamilton, *Science*, 2003, **299**, 1702–1706.
4 M. J. Earle, J. Esperanca, M. A. Gilea, J. N. C. Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon and J. A. Widegren, *Nature*, 2006, **439**, 831–834.
5 S. L. Chou, J. Z. Wang, J. Z. Sun, D. Wexler, M. Forsyth, H. K. Liu, D. R. MacFarlane and S. X. Dou, *Chem. Mater.*, 2008, **20**, 7044–7051.
6 A. P. Abbott and K. J. McKenzie, *Phys. Chem. Chem. Phys.*, 2006, **8**, 4265–4279.
7 W. S. Miao and T. H. Chan, *Acc. Chem. Res.*, 2006, **39**, 897–908.
8 S. J. Mugavero, M. Bharathy, J. McAlum and H. C. zur Loye, *Solid State Sci.*, 2008, **10**, 370–376.
9 P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, Germany, 2003.
10 E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald and R. E. Morris, *Nature*, 2004, **430**, 1012–1016.
11 W. M. Reichert, J. D. Holbrey, K. B. Vigour, T. D. Morgan, G. A. Broker and R. D. Rogers, *Chem. Commun.*, 2006, 4767–4779.
12 P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K. Van Hecke, L. Van Meervelt, B. Kirchner and K. Binnemans, *J. Phys. Chem. B*, 2006, **110**, 20978–20992.
13 A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chem. Commun.*, 2003, 70–71.
14 A. P. Abbott, D. Boothby, G. Capper, D. L. Davies and R. K. Rasheed, *J. Am. Chem. Soc.*, 2004, **126**, 9142–9147.
15 C. S. Cundy and P. A. Cox, *Chem. Rev.*, 2003, **103**, 663–701.
16 R. E. Morris and S. J. Weigel, *Chem. Soc. Rev.*, 1997, **26**, 309–317.
17 H. M. Luo, G. A. Baker and S. Dai, *J. Phys. Chem. B*, 2008, **112**, 10077–10081.
18 R. F. Lobo, S. I. Zones and M. E. Davis, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1995, **21**, 47–48.
19 E. A. Drylie, D. S. Wragg, E. R. Parnham, P. S. Wheatley, A. M. Z. Slawin, J. E. Warren and R. E. Morris, *Angew. Chem., Int. Ed.*, 2007, **46**, 7839–7843.
20 L. Liu, Y. Kong, H. Xu, J. P. Li, J. X. Dong and Z. Lin, *Microporous Mesoporous Mater.*, 2008, **115**, 624–628.
21 L. J. Han, Y. B. Wang, C. X. Li, S. J. Zhang, X. M. Lu and M. J. Cao, *AIChE J.*, 2008, **54**, 280–288.
22 Y. Hu, Y. J. Liu, J. Y. Yu, Y. P. Xu, Z. J. Tian and L. W. Lin, *Wuji Huaxue Xuebao*, 2006, **22**, 753–756.
23 E. R. Parnham and R. E. Morris, *J. Am. Chem. Soc.*, 2006, **128**, 2204–2205.
24 E. R. Parnham and R. E. Morris, *J. Mater. Chem.*, 2006, **16**, 3682–3684.
25 E. R. Parnham, P. S. Wheatley and R. E. Morris, *Chem. Commun.*, 2006, 380–382.
26 Y. P. Xu, Z. J. Tian, Z. S. Xu, B. C. Wang, P. Li, S. J. Wang, Y. Hu, Y. C. Ma, K. L. Li, Y. J. Liu, J. Y. Yu and L. W. Lin, *Chin. J. Catal.*, 2005, **26**, 446–448.
27 L. Wang, Y. P. Xu, B. C. Wang, S. J. Wang, J. Y. Yu, Z. J. Tian and L. W. Lin, *Chem.–Eur. J.*, 2008, **14**, 10551–10555.
28 L. Wang, Y. P. Xu, Y. Wei, J. C. Duan, A. B. Chen, B. C. Wang, H. J. Ma, Z. J. Tian and L. W. Lin, *J. Am. Chem. Soc.*, 2006, **128**, 7432–7433.
29 T. W. Wang, H. Kaper, M. Antonietti and B. Smarsly, *Langmuir*, 2007, **23**, 1489–1495.
30 E. R. Parnham and R. E. Morris, *Acc. Chem. Res.*, 2007, **40**, 1005–1013.
31 Y. C. Ma, Y. P. Xu, S. J. Wang, B. C. Wang, Z. J. Tian, J. Y. Yu and L. W. Lin, *Chem. J. Chin. Univ.*, 2006, **27**, 739–741.
32 P. S. Wheatley and R. E. Morris, manuscript in preparation.
33 S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334–2375.
34 G. Ferey, *Chem. Soc. Rev.*, 2008, **37**, 191–214.
35 R. E. Morris and P. S. Wheatley, *Angew. Chem., Int. Ed.*, 2008, **47**, 4966–4981.
36 N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 2003, **300**, 1127–1129.
37 R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939–943.
38 B. Xiao, P. S. Wheatley, X. B. Zhao, A. J. Fletcher, S. Fox, A. G. Rossi, I. L. Megson, S. Bordiga, L. Regli, K. M. Thomas and R. E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 1203–1209.
39 S. M. Chen, J. Zhang and X. H. Bu, *Inorg. Chem.*, 2008, **47**, 5567–5569.
40 T. Hogben, R. E. Douthwaite, L. J. Gillie and A. C. Whitwood, *CrystEngComm*, 2006, **8**, 866–868.
41 W. J. Ji, Q. G. Zhai, M. C. Hu, S. N. Li, Y. C. Jiang and Y. Wang, *Inorg. Chem. Commun.*, 2008, **11**, 1455–1458.
42 J. H. Liao and W. C. Huang, *Inorg. Chem. Commun.*, 2006, **9**, 1227–1231.
43 J. H. Liao, P. C. Wu and Y. H. Bai, *Inorg. Chem. Commun.*, 2005, **8**, 390–392.
44 J. H. Liao, P. C. Wu and W. C. Huang, *Cryst. Growth Des.*, 2006, **6**, 1062–1063.
45 Z. J. Lin, Y. Li, A. M. Z. Slawin and R. E. Morris, *Dalton Trans.*, 2008, 3989–3994.
46 F. N. Shi, T. Trindade, J. Rocha and F. A. A. Paz, *Cryst. Growth Des.*, 2008, **8**, 3917–3920.
47 L. Xu, E. Y. Choi and Y. U. Kwon, *Inorg. Chem.*, 2007, **46**, 10670–10680.
48 J. Zhang, S. M. Chen and X. H. Bu, *Angew. Chem., Int. Ed.*, 2008, **47**, 5434–5437.
49 J. Zhang, T. Wu, S. M. Chen, P. Feng and X. H. Bu, *Angew. Chem., Int. Ed.*, 2009, DOI: 10.1002/anie.200900134.
50 Y. Gao, A. Voigt, M. Zhou and K. Sundmacher, *Eur. J. Inorg. Chem.*, 2008, 3769–3775.
51 H. Kaper, M. G. Willinger, I. Djerdj, S. Gross, M. Antonietti and B. M. Smarsly, *J. Mater. Chem.*, 2008, **18**, 5761–5769.

52 L. L. Li, W. M. Zhang, Q. Yuan, Z. X. Li, C. J. Fang, L. D. Sun, L. J. Wan and C. H. Yan, *Cryst. Growth Des.*, 2008, **8**, 4165–4172.

53 M. Y. Li, W. S. Dong, C. L. Liu, Z. Liu and F. Q. Lin, *J. Cryst. Growth*, 2008, **310**, 4628–4634.

54 Z. X. Li, L. L. Li, Q. Yuan, W. Feng, J. Xu, L. D. Sun, W. G. Song and C. H. Yan, *J. Phys. Chem. C*, 2008, **112**, 18405–18411.

55 A. M. Guloy, R. Ramlau, Z. J. Tang, W. Schnelle, M. Baitinger and Y. Grin, *Nature*, 2006, **443**, 320–323.

56 E. R. Parnham, A. M. Z. Slawin and R. E. Morris, *J. Solid State Chem.*, 2007, **180**, 49–53.

57 Y. H. Liu, C. W. Lin, M. C. Chang, H. Shao and A. C. M. Yang, *J. Mater. Sci.*, 2008, **43**, 5005–5013.

58 H. S. Park, Y. C. Lee, B. G. Choi, W. H. Hong and J. W. Yang, *ChemSusChem*, 2008, **1**, 356–362.

59 A. Thirumurugan and C. N. R. Rao, *Cryst. Growth Des.*, 2008, **8**, 1640–1644.

60 P. Kuhn, M. Antonietti and A. Thomas, *Angew. Chem., Int. Ed.*, 2008, **47**, 3450–3453.

61 M. Antonietti, D. Kuang, B. Smarsly and Y. Zhou, *Angew. Chem., Int. Ed.*, 2004, **43**, 4988–4992.

62 A. Taubert and Z. Li, *Dalton Trans.*, 2007, 723–727.

63 Z. J. Lin, D. S. Wragg and R. E. Morris, *Chem. Commun.*, 2006, 2021–2023.

64 Y. P. Xu, Z. J. Tian, S. J. Wang, Y. Hu, L. Wang, B. C. Wang, Y. C. Ma, L. Hou, J. Y. Yu and L. W. Lin, *Angew. Chem., Int. Ed.*, 2006, **45**, 3965–3970.

65 D. S. Wragg, A. M. Z. Slawin and R. E. Morris, *Solid State Sci.*, 2009, **11**, 411–416.

66 R. Cai, M. W. Sun, Z. W. Chen, R. Munoz, C. O'Neill, D. E. Beving and Y. S. Yan, *Angew. Chem., Int. Ed.*, 2008, **47**, 525–528.

67 R. E. Morris, *Angew. Chem., Int. Ed.*, 2008, **47**, 442–444.

68 Z. Lin and R. E. Morris, unpublished work.

69 H. Z. Xing, J. Y. Li, W. F. Yan, P. Chen, Z. Jin, J. H. Yu, S. Dai and R. R. Xu, *Chem. Mater.*, 2008, **20**, 4179–4181.

70 P. J. Byrne, D. S. Wragg, J. E. Warren and R. E. Morris, *Dalton Trans.*, 2009, 795–799.

71 F. Himeur, D. S. Wragg, I. Stein and R. E. Morris, *Solid State Sci.*, submitted for publication.

72 Z. Lin, D. S. Wragg, J. E. Warren and R. E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 10334–10335.

73 Z. Hulvey, D. S. Wragg, Z. Lin, R. E. Morris and A. K. Cheetham, *Dalton Trans.*, 2009, 1131–1135.

74 Z. Lin, A. M. Z. Slawin and R. E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 4880–4881.

75 C. G. Hanke and R. M. Lynden-Bell, *J. Phys. Chem. B*, 2003, **107**, 10873–10878.

76 E. Amigues, C. Hardacre, G. Keane, M. Migaud and M. O'Neill, *Chem. Commun.*, 2006, 72–74.

77 R. E. Morris, A. Burton, L. M. Bull and S. I. Zones, *Chem. Mater.*, 2004, **16**, 2844–2851.

78 M. A. Camblor, L. A. Villaescusa and M. J. Diaz-Cabanas, *Top. Catal.*, 1999, **9**, 59–76.

79 S. I. Zones, R. J. Darton, R. Morris and S. J. Hwang, *J. Phys. Chem. B*, 2005, **109**, 652–661.

80 L. A. Villaescusa, P. Lightfoot and R. E. Morris, *Chem. Commun.*, 2002, 2220–2221.

81 I. Bull, L. A. Villaescusa, S. J. Teat, M. A. Camblor, P. A. Wright, P. Lightfoot and R. E. Morris, *J. Am. Chem. Soc.*, 2000, **122**, 7128–7129.

82 L. A. Villaescusa, P. S. Wheatley, I. Bull, P. Lightfoot and R. E. Morris, *J. Am. Chem. Soc.*, 2001, **123**, 8797–8805.

83 H. J. Ma, Z. J. Tian, R. S. Xu, B. C. Wang, Y. Wei, L. Wang, Y. P. Xu, W. P. Zhang and L. W. Lin, *J. Am. Chem. Soc.*, 2008, **130**, 8120–8121.

84 E. R. Parnham and R. E. Morris, *Chem. Mater.*, 2006, **18**, 4882–4887.

85 E. R. Parnham, E. A. Drylie, P. S. Wheatley, A. M. Z. Slawin and R. E. Morris, *Angew. Chem., Int. Ed.*, 2006, **45**, 4962–4966.