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Ionic Liquids : Environment-Friendly Solvents and Catalysts for the Future

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Abstract : Ionic liquids are receiving much attention as environment-friendly mediums for the organic reactions. Improvements in the rates of reaction and selectivity have been realized in many cases when ionic liquids were used in the places of the conventional solvents. Their application to esterification reaction resulted in high yields without removal of the water formed in the reaction. The esters form separate liquid phase in the reaction which are separated easily by decantation. It was demonstrated that high melting points of the ammonium salts did not prevent their use as ionic liquids in the esterification reaction.

Keywords : Ionic Liquids, Environment-Friendly, Solvents, Catalysts

Currently, ionic liquids are receiving a lot of attention as they holds promise to provide better alternative to the molecular solvents which are used traditionally to perform most of the chemicals reactions (Earle and Seddon, 2000). Ionic liquids are purely ionic, salt-like materials which have per definition melting points below 100 °C. Ionic liquids are composed of organic cations and mostly inorganic anions. Some common cations and anions employed in the ionic liquids are listed in the Figure 1. The number of molecular solvents currently employed as the reaction mediums are limited to

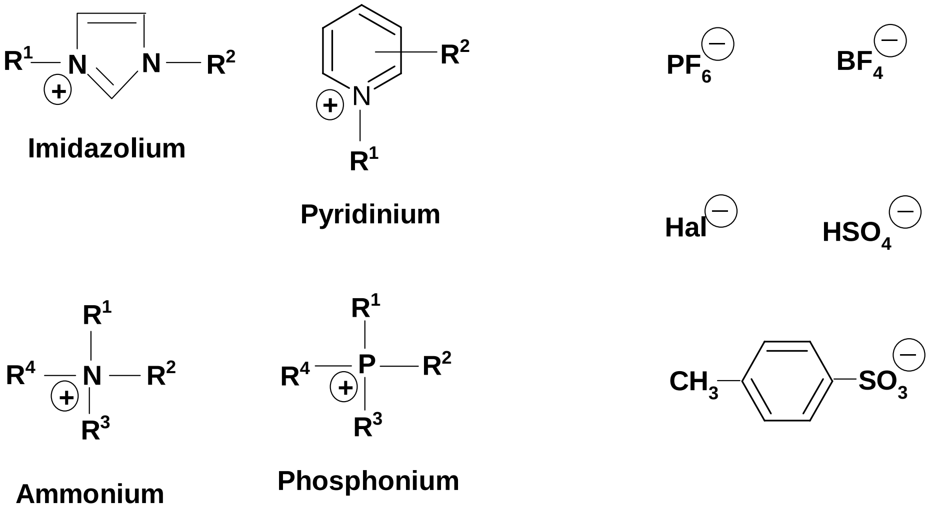

Fig. 1 : Common cations and anions used in the ionic liquids

approximately 200. However, millions of ionic liquids can be synthesized by variation of the alkyl substituents in the cations and making combinations with the variety of anions. Thus, the domain of ionic liquid is much larger than that of the molecular solvents.

There is a tremendous scope for manipulation of the properties of ionic liquids by variation of the structure to generate task-specific catalysts (Sheldon, 2001) or designer solvents. The properties of the ionic liquids that can be tailored are solubility and solvation properties, liquid temperature range, viscosity, density and surface tension.

Large volumes of volatile organic chemicals are discharged into atmosphere due to the use of the traditional molecular solvents in the chemical industries. The ionic liquid being practically non-volatile offers an environment-friendly substitute for the volatile molecular solvents. Ionic liquids have a great potential to revolutionize the way the solvents are utilized in the processes such as extraction, catalysis, separation, and polymer processes.

The ionic liquids possess amazing solubility behaviour. They can dissolve a wide range of organic, inorganic and polymeric materials to a high degree of concentration. It also includes non-polar covalent gases such as hydrogen, carbon dioxide, carbon monoxide, and oxygen. High solubility of gases makes them attractive solvents for catalytic hydrogenation, hydroformylation, carbonylation, and oxidation reactions. Higher solubility implies smaller reactor volume, lower investments and higher productivity.

Ionic liquids are highly polar yet non-coordinating solvents. They have strong rate enhancing effect on reactions involving cationic intermediates. They make attractive media for reactions, catalysis and separation as they have negligible vapour pressure and no odour. They do not evaporate even under vacuum and do not combust even when exposed to an open flame. Ionic liquids have good thermal stability, wide liquid temperature range (up to 300 ^{o}C), and high ionic conductivity which allows tremendous kinetic control over the reaction. Ionic liquids can specifically dissolve polar organic compounds and thus can be used for the separation of sulfur compounds from hydrocarbon fuels. An important application of ionic liquids is in homogeneous catalysis. In traditional homogeneous catalytic reactions, the product is separated from the catalyst by processes such as distillation which are costly. When the reactions are performed in ionic liquids the catalyst remains in the ionic liquid phase where the reaction occurs and the product forms a separate phase which can be isolated by decantation.

Fischer esterification using ionic liquids

Esterification of carboxylic acid with alcohol is an equilibrium reaction performed in the presence of a Brønsted acid catalyst. The equilibrium is shifted to the product side by continuously removing the water formed in the reaction to get high conversions. The ester is separated from the product by distillation which consumes energy. The use of Brønsted acidic ionic liquid in this reaction serves two purposes: It acts as a catalyst for the reaction and also provides a medium which effectively solvates the water formed such that it may not be available for the reverse reaction. In addition, the ionic liquid and the ester form separate phases and the ester can be separated by simple decantation. The use of ionic liquid in this reaction was limited to the salts with melting point below 100 ^{o}C as per the definition of ionic liquid. However, we found that simple salts, pyridinium methanesulfonate (m.p. 185 ^{o}C) and pyridinium *p*-toluenesulfonate (m.p. 121 ^{o}C) with high melting points can also be used as ionic liquid mediums in this reaction. The ionic liquid initially dissolves in the mixture of the reactants (acetic acid and 1-butanol) but forms a separate liquid layer once it absorbs the water formed in the reaction. The reactions gave high yields of the esters from various aliphatic acids and alcohols. Thus, we have shown, for the first time that high melting points of the salts do not prevent their use as ionic liquids in the esterification reaction (Ganeshpure and Das, 2007).

The majority of the ionic liquids reported for Fischer esterification are derivatives of imidazole which are synthesized in two or more steps using expensive materials. We have demonstrated that the simple triethylammonium salts also act as ionic liquid mediums and catalysts for the esterification reaction (Ganeshpure *et al.*, 2007). These salts are conveniently prepared in one step from easily available materials. The reactions were performed using carboxylic acid (20 mmol), alcohol (24 mmol) and ionic liquid (1 gm) at 90 ^{o}C for 4 h. The esters were obtained as separate layers and isolated by decantation. The reaction was generalized using a variety of carboxylic acids and alcohols to give the esters in nearly quantitative yield. The ionic liquids could be recycled in the reaction at least three times without loss of the activity.

We have prepared a series of alkylammonium salts and used them in the esterification of acetic acid with 1-octanol with a view to study the structure-activity relationship (Ganeshpure *et al.,* 2008). It was observed that the acidity of the anion significantly influenced the activity of the ionic liquids. For a given cation the yield of the ester decreased in the following order: $HSO_4^- > H_2PO_4^- > BF_4^-$. For a given anion the activity of the ionic liquid decreased with increase in the size of the cation. For example, $EtNH_3^+ > Et_2NH_2^+ > Et_3NH^+$. Increase in the size of the cation decreases its ability to solvate the water formed in the reaction. Moreover, increase in the size of the cation increases the solubility of ester in the ionic liquid resulting in no phase separation and lower yield of the ester.

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