

Ionic liquids-Useful Reaction Green Solvents for the Future (A Review)

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Abstract— Ionic liquids, being composed entirely of ions, were once mainly of interest to electrochemists. Recently, however, it has become apparent that their lack of measurable vapor pressure characterizes them as green solvents, and that a wide range of chemical reactions can be performed in them. To date, most chemical reactions have been carried out in molecular solvents. For two millennia, most of our understanding of chemistry has been based upon the behavior of molecules in the solution phase in molecular solvents. However, at room temperature, thermodynamics and kinetics of reactions carried out in ionic liquids are different to those in conventional molecular solvents, then the chemistry is different and unpredictable at our current state of knowledge. However, in addition to the scope for exciting new discoveries with which they tease us, ionic liquids have no measurable vapor pressure, and hence can emit no volatile organic compounds (VOCs).

Keywords— green solvent; hydrogen donor; transfer hydrogenation; reduction reactions; metal catalysis, solvent properties, viscosity, chemical processes etc.

I. INTRODUCTION

The Ionic liquids (IL) represent fascinating new class of solvents with unusual physical and chemical properties; low melting salts (up to 100°C). The main driving force for research in this area is the need to find replacement for environmentally damaging solvents in a wide range of chemical processes. To date, most chemical reactions have been carried out in molecular solvents. For the past twenty years, most of our understanding of our chemistry has been based upon the behavior of molecules in the solution phase in molecular solvents. Recently a new class of solvents has emerged called as Ionic liquids.

An ionic liquid is an organic salt in which the ions are poorly coordinated, which results in these solvents being liquid below 100°C, or even at room temperature (room temperature ionic liquids, RTIL's). At least one ion has a delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice. Ionic liquids are composed entirely of ions. For example, molten sodium chloride is an ionic liquid. The term "ionic liquids" has replaced the older phrase "molten salts" (or "melts"), which suggests that they are high-temperature, corrosive, viscous media (like molten minerals). The reality is that ionic liquids can be liquid at temperatures as low as -96°C. Furthermore, room-temperature ionic liquids are frequently colourless, fluid, and easy to handle. In the patent and academic literature, the term "ionic liquids" now refers to liquids composed entirely of ions that are fluid around or below 100°C. Properties, such as melting point, viscosity, and solubility of starting materials and other solvents, are determined by the substituents on the organic component and by the counter ion. Ionic liquids have been termed "designer solvents". This means that their properties can be adjusted to suit the requirements of a particular process. Properties such

as melting point, viscosity, density, and hydrophobicity can be varied by simple changes to the structure of the ions. For example, the melting points of 1-alkyl-3-methylimidazolium tetrafluoroborates and hexafluorophosphates are a function of the length of the 1-alkyl group, and form liquid crystalline phases for alkyl chain lengths over 12 carbon atoms. Another important property that changes with structure is the miscibility of water in these ionic liquids. For example, 1-alkyl-3-methylimidazolium tetrafluoroborate salts are miscible with water at 25 °C where the alkyl chain length is less than 6, but at or above 6 carbon atoms, they form a separate phase when mixed with water. This behaviour can be of substantial benefit when carrying out solvent extractions or product separations, as the relative solubility's of the ionic and extraction phase can be adjusted to make the separation as easy as possible. In addition, ionic liquids have practically no vapour pressure which facilitates product separation by distillation. There are also indications that switching from a normal organic solvent to an ionic liquid can lead to novel and unusual chemical reactivity. This opens up a wide field for future investigations into this new class of solvents in catalytic applications. Research into ionic liquids is booming. The first industrial process involving ionic liquids was announced in March 2003, and the potential of ionic liquids for new chemical technologies is beginning to be recognized. Together with ionic liquids, these alternative solvent strategies (sometimes referred to as alternative reaction media or green solvents) provide a range of options to industrialists looking to minimize the environmental impact of their chemical processes. As discussed above, Ionic liquids are salts consisting of cations such as imidazolium, pyridinium, quaternary ammonium and quaternaryphosphonium, and anions such as halogen, triflate, trifluoroborate and hexafluorophosphate, which

exists in the liquid state at relatively low temperatures. Their characteristic features include almost no vapour pressure, non-inflammability, non-combustibility, high thermal stability, relatively low viscosity, wide temperature ranges for being liquids and ionic liquid conductivity.

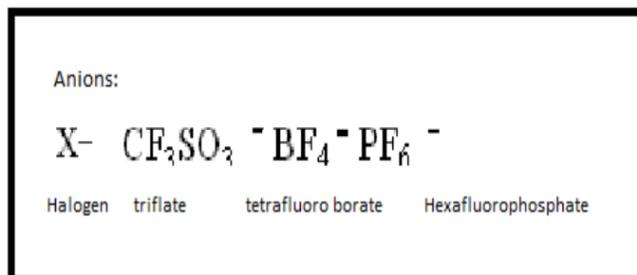
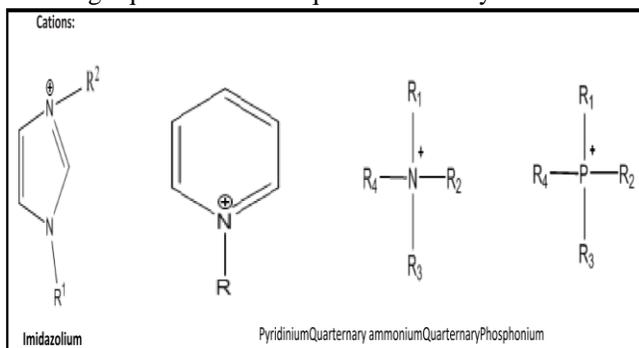


Figure 1

Ionic liquids are used in some reactions like Heck Reaction, Suzuki-Miyaura Coupling Reaction, Friedel-Crafts Reaction, Aldol Condensation.

II. HECK REACTION:

In Heck reaction using palladium catalysts, polar solvents such as DMF and acetonitrile are employed and aryl iodides are normally used as substrates. When less reactive aryl bromides or chlorides are employed, more active catalysts like phosphine ligands are added to retain the catalytic activity. By using, 1-butyl-3-methylimidazolium bromide (bmimBr) as solvent, aryl bromides react with styrene to produce stilbenes in high yields without adding a phosphine ligand⁵.

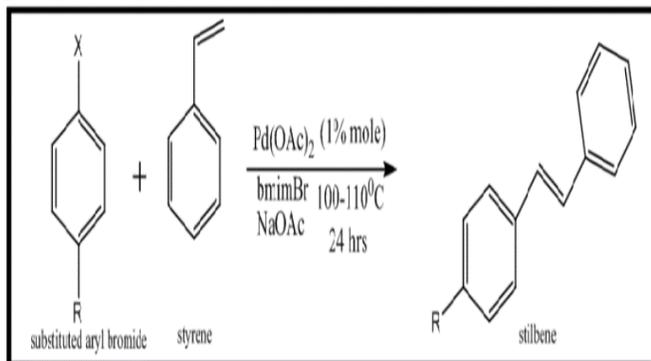


Figure 2

III. SUZUKI-MIYAJURA COUPLING REACTION:

In Suzuki-Miyaura coupling reaction where biaryls are produced from aryl halides and aryl boronic acids in the presence of Palladium catalyst and a base. The removal of the catalyst is often a problem. In the system where an ionic liquid is used as solvent, the product can be extracted with ether after the reaction is complete, with catalyst being retained in the ionic liquid. The ionic liquid and the catalyst can then be reused as they are.

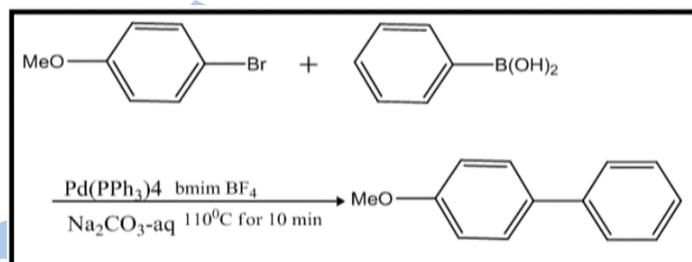


Figure 3

IV. WITTING REACTION:

It is a useful method for C-C double bond formation. However separation of the product and by-product, triphenylphosphine oxide is a classic problem. The separation and purification are usually carried out by crystallization or chromatography. When an ionic liquid is used as solvent, the product and phosphine oxide can be easily separated by combining an ether extraction and toluene extraction after the reaction is complete. In addition, it is possible to efficiently reuse the ionic liquid.

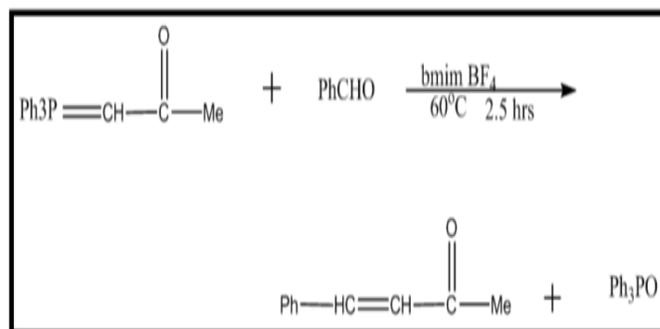


Figure 4

STILLE REACTION: Stille reaction is a useful reaction where an organotin compound and an electrophilic reagent are reacted to form a C-C bond under mild condition in the presence of palladium catalyst. In the reaction of vinyltributyltin and iodocyclohexenone in an ionic liquid, the product can be extracted with ether and the catalyst is retained in the ionic liquid. The ionic liquid and the catalyst can be reused as they are. This ionic liquid/catalyst phase is air and moisture stable and so can be used after a long storage without loss in activity.

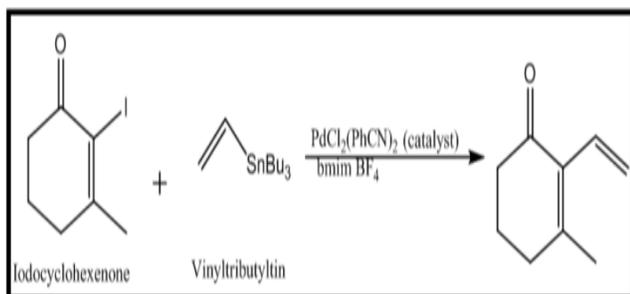


Figure 5

V. FRIDEL-CRAFTS REACTION:

In Friedel-Crafts reaction, benzoylation of anisoles is catalysed by copper triflate in bmimBF₄. Methoxybenzophenone is quantitatively obtained within 1hr, with p/o product ratio of 96/4[8]. The same reaction performed using Acetonitrile gave a lower conversion of 64% at 1hr with reduced p/o product ratio of 93/7.

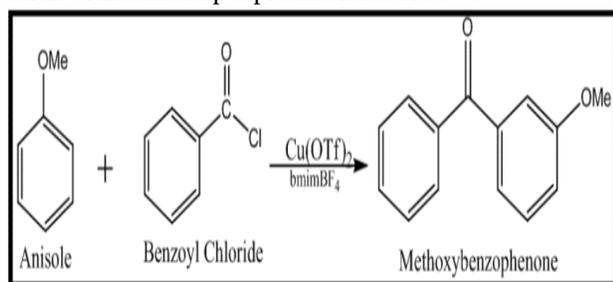


Figure 6

VI. REDUCTION:

Reduction of aldehydes using trialkylboranes is an important organic transformation reaction. But reduction using simple trialkylboranes generally requires reaction temperatures above 1500C. kalbaka et al have reported this reduction using trialkylborane in which bmimBF₄, eninBF₄ and 1-ethyl-3-methylimidazolium hexafluorophosphate (emimPF₆) are used as solvents¹³ for example when benzaldehyde was reduced by tributylborane in emimPF₆, the reaction proceeded rapidly at 1000C to give the product in high yield. Although long reaction time(48 hrs) is needed comparatively, the product can be obtained even at room temperature. In addition photoreduction has also been reported using ionic liquids.

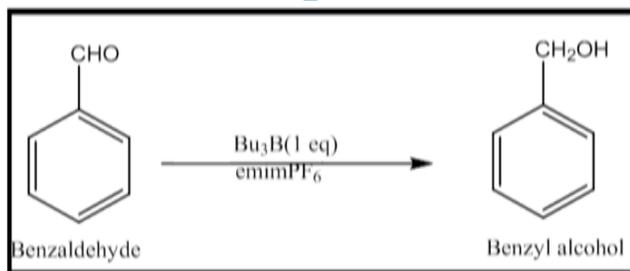


Figure 7

For extraction of Zn²⁺, Cd²⁺, Fe³⁺ and Cu²⁺ from aqueous solutions:

This work analyzed the extraction of metal ions from aqueous solutions using ionic liquids in the absence of chelating agents. For this purpose, hydrochloride solutions of Zn²⁺, Cd²⁺, Cu²⁺ and Fe³⁺ were used as model systems and ionic liquids based on 1-n-alkyl-3-methylimidazolium and tetraalkyl ammonium cations combined with several anions (hexafluorophosphate, bis{(trifluoromethyl)sulfonyl}imide, tetrafluoroborate, and chloride) were used as extraction agents. It was found that the ionic liquid methyltrioctylammonium chloride, [MTOA⁺][Cl⁻], allowed almost the nearly complete removal of Zn²⁺, Cd²⁺ and Fe³⁺ and an extraction percentage around 80 % for Cu²⁺, from the aqueous solutions. Furthermore, efficient selective separation of Zn²⁺ and Cd²⁺ from Fe³⁺ and Cu²⁺ was achieved using 1-methyl-3-octylimidazolium tetrafluoroborate, [omim⁺][BF₄⁻], since high extraction percentages were reached for Zn²⁺ and Cd²⁺ (%E > 90) while this parameter is very low for Fe³⁺ and Cu²⁺. These results indicate that the use of ionic liquids as an alternative to traditional extraction agents in liquid/liquid extraction of heavy metal ions is very promising.

VII. CONCLUSIONS:

The range of reactions in ionic liquids gives a flavour of what can be achieved in these neoteric solvent. Because the properties and behavior of the ionic liquid can be adjusted to suit an individual reaction type, they can truly be described as designer solvents. We have shown that, by choosing the correct ionic liquid, high product yields can be obtained, and a reduced amount of waste can be produced in a given reaction. Often the ionic liquid can be recycled, and this leads to a reduction of the costs of the processes. It must be emphasized that reactions in ionic liquids are not difficult to perform and usually require no special apparatus or methodologies. The reactions are often quicker and easier to carry out than in conventional organic solvents.

Also this work demonstrates the exciting potential of ionic liquids for use as extraction agents in green extraction processes, since it is possible to design a specific ionic liquid for each metal ion by changing either the anion or the cation in order to create more efficient processes.

VIII. REFERENCES

- [1]. M. Freemantle. Chem. Eng. News 76, (30th March) 32-37 (1998).
- [2]. T. Welton. Chem. Rev. 99, 2071-2083 (1999).
- [3]. J. Holbrey and K. R. Seddon. Clean Prod. Proc. 1, 223-236 (1999).
- [4]. K. R. Seddon. J. Chem. Tech. Biotech. 68, 351-356 (1997).
- [5]. P. Walden. Bull. Acad. Imper. Sci. (St. Petersburg) 1800 (1914).
- [6]. H. L. Chum, V. R. Koch, L. L. Miller, R. A. Osteryoung. J. Am. Chem. Soc. 97, 3264-3267

- (1975).
- [7]. J. S. Wilkes, J. A. Levisky, R. A. Wilson, C. L. Hussey. *Inorg. Chem.* 21, 1236–1264 (1982).
- [8]. K. R. Seddon. In *Molten Salt Forum: Proceedings of 5th International Conference on Molten Salt Chemistry and Technology*, Vol. 5–6, H. Wendt (Ed.), pp. 53–62 (1998).
- [9]. C. L. Hussey, T. B. Scheffler, J. S. Wilkes, A. A. Fannin, Jr. *J. Electrochem. Soc.* 133, 1389–1391 (1986).
- [10]. J. D. Holbrey and K. R. Seddon. *J. Chem. Soc., Dalton Trans.* 2133–2139 (1999).
- [11]. C. M. Gordon, J. D. Holbrey, A. R. Kennedy, K. R. Seddon. *J. Mater. Chem.* 8, 2627–2636 (1998).
- [12]. L. Dutta, A. Fleet, Y. Patell, K. R. Seddon, unpublished results.
- [13]. M. J. Earle and K. R. Seddon, unpublished results.
- [14]. Martyn J. Earle, and Kenneth R. Seddon, *Ionic liquids. Green solvents for the future*, *Pure Appl. Chem.*, Vol.72, No.7, pp. 1391-1398, 2000.
- [15]. Colin D. Hubbard, Peter Illner and Rudi van Eldik, *Understanding chemical reaction mechanisms in ionic liquids: Successes and Challenges*, *ChemSoc Rev.*, 2011, 40, 272-290.
- [16].

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