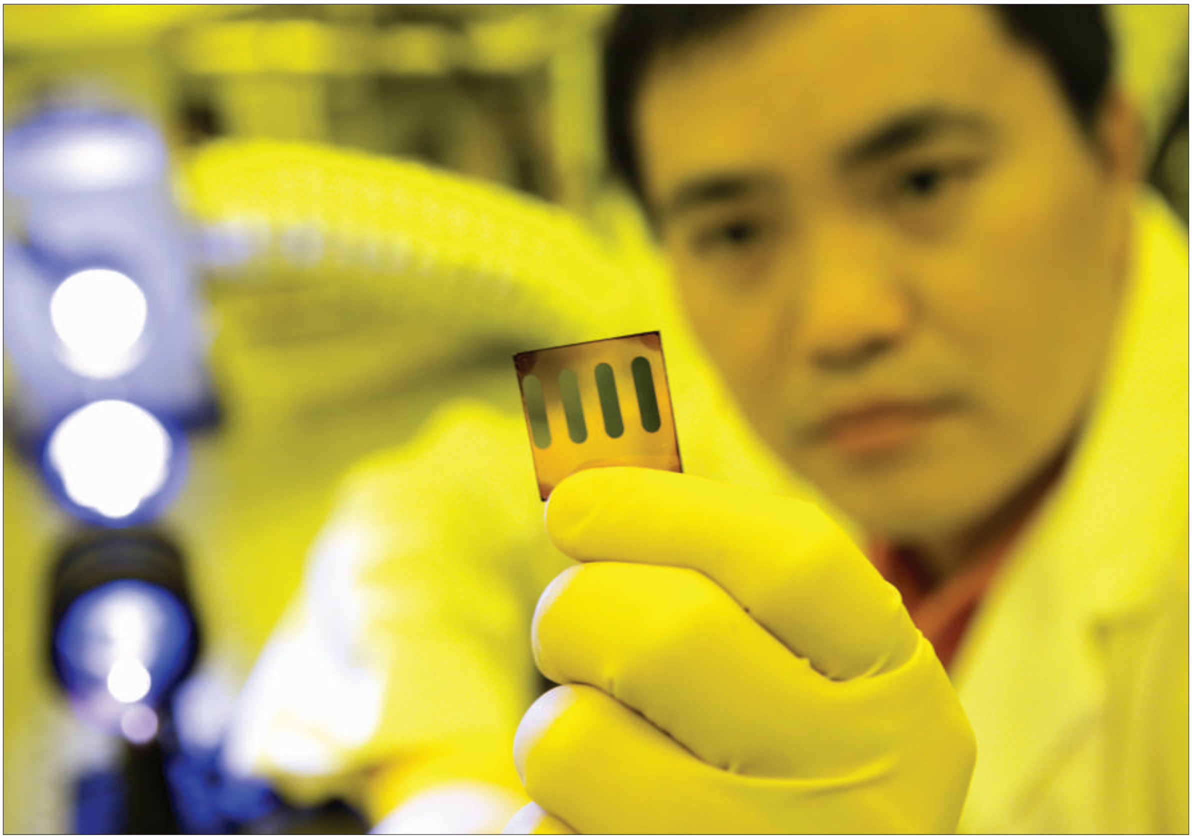

Singapore Journal of

Scientific Research

ISSN: 2010-006x

science alert

http://scialert.net/sjsr

Singapore Journal of Scientific Research 1 (3): 246-252, 2011
ISSN 2010-006x / DOI: 10.3923/sjsres.2011.246.252

Synthesizing of Ionic Liquids from Different Chemical Reactions

A.A. Shamsuri and K.A. Dzulkefly
Laboratory of Industrial Biotechnology, Institute of Bioscience, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia

Corresponding Author: A.A. Shamsuri, Laboratory of Industrial Biotechnology, Institute of Bioscience, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia

ABSTRACT

Ionic liquids believed as novel chemical agents and widely regarded as a greener alternative to many commonly used solvents because they are designable, recyclable and non-volatile. Based on it, ionic liquids have been studied for a wide range of synthetic applications, they have attracted considerable interest for use as non-volatile solvent based electrolytes in the areas of organic synthesis, catalysis, electrochemistry, solar cells, fuel cells, etc., due to they possess many benefits than volatile organic solvent. Several studies indicate the successful of using simple chemical reactions to synthesize ILs for large-scale processes. Recently, five types of ionic liquids are attracted much attention specifically alkylation ionic liquids, metathesis ionic liquids, protic ionic liquids, eutectic ionic liquids and protic eutectic ionic liquids. For that reason, this study describes precursor, preparation and application of these ionic liquids.

Key words: Alkylation, metathesis, protic, eutectic, protic eutectic ionic liquids

INTRODUCTION

The term Ionic Liquids (ILs) has been used to describe salts that melt below 100°C. ILs are electrolytes forming liquids that consist of cations and anions. ILs extremely low vapour pressure being non-volatile, high stability, highly polar, wide liquid-range, miscible with certain organic solvents and/or water and good solubility of organic and inorganic materials, chemically inert as well. They are reusable, non-inflammable, thermally stable (high thermal stability and liquid range up to about 300°C), can be designed and tunable solvency (Holbrey and Seddon, 1999; Ngo *et al.*, 2000; Shamsuri and Abdullah, 2010a; Welton, 1999). ILs are usually characterized by a wide-range electrochemical window of stability, a reasonable ionic conductivity (similar to most non-aqueous electrolytes). ILs are promising environmentally benign, numerous of reaction media which are expected to provide an attractive alternative to conventional Volatile Organic Solvents (VOSs) in current synthetic organic chemistry since their growing use does not lead to air pollution (Yamada *et al.*, 2007) with excellent solvent properties as fluoroalcohols due to the capability to form hydrogen bonding (Shamsuri *et al.*, 2009).

ILs have been hailed as the alternative to the VOSs in chemistry due to their green properties. VOSs nature consists of relatively small molecules so, they have weak intermolecular forces between them, making them highly volatile and they are also flammable and often toxic. Unlike VOSs, ILs do not vaporize into the air, effectively eliminating one of the major routes of environmental contamination (Wasserscheid and Keim, 2000), making its operations safer and environmentally acceptable. Additionally, ILs have recently classified into five types namely alkylation ILs, metathesis ILs, protic ILs, eutectic ILs and protic eutectic ILs. Nevertheless, during present investigations we have found that the compilation of five types of ILs was never been reported before and comparatively scarce to discuss. Therefore, this study focuses on the types of ILs in order to gain an in-depth understanding of the reactions and their applications.

Preparation of ILs

Alkylation ILs: The 1-alkyhimidazoles and pyridine compounds have proven to be good precursors for the preparation of alkylation ILs (Wassersheid and Welton, 2003). The chemical structure of common alkylation ILs precursors specifically 1-methylimidazole and pyridine compounds is given in Fig. 1.

Preparation of alkylation ILs by means of 1-methylimidazole has been shown in Fig. 2. The reaction particularly alkylation is prepared by reacting 1-methylimidazole with butyl halide in the presence of acetonitrile as a catalyst (Dupont *et al.*, 2004).

ILs are simple charged species that are not simply spheres but have shape and chemical functionality that impose subtle changes in the physical properties. Coulombic interactions are the dominant force between the ions, including dipole, hydrogen-bonding and dispersive forces are also important for the interactions between constituents in the ILs (Tokuda *et al.*, 2004, 2005) however, these forces are weak enough to keep them in the form of liquid at low temperature. Alkylation ILs are micro-biphasic systems composed of polar and non-polar domains (Santos *et al.*, 2007) with special solubility characteristics (Plechkova and Seddon, 2008). Alkylation ILs are potential candidates used to dissolve a wide range of organic and inorganic compounds for example, 1-allyl-3-methylimidazolium chloride could be dissolved cellulose up to 39 wt.% without derivatization (Wu *et al.*, 2004),1-butyl-3-methylimidazolium chloride has been shown to dissolve proteins (Biswas *et al.*, 2006) and 3-(1-methylimidazolium-3-yl) propane-1-sulfonate has been used for dissolution of bamboo biomass (Muhammad *et al.*, 2010).

Metathesis ILs: The 1-butyl-3-methylimidazolium chloride ILs is the perfect precursor for the preparation of metathesis ILs (Dupont *et al.*, 2004). Metathesis ILs could be prepared by ion exchange reaction between 1-butyl-3-methylimidazolium chloride and potassium salt as shown in Fig. 3.

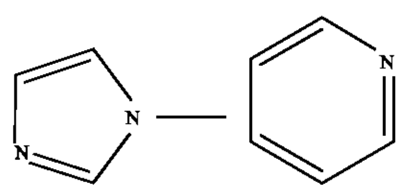

Fig. 1: Example of alkylation ILs precursors

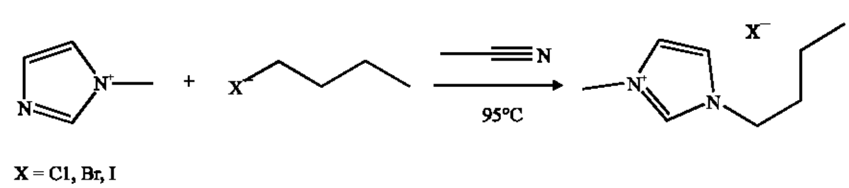

Fig. 2: 1-Methylimidazole reacts with butyl halide to produce alkylation ILs

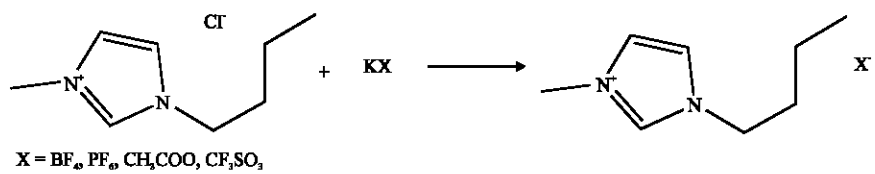

Fig. 3: 1-Butyl-3-methylimidazolium chloride reacts with potassium salt to produce metathesis ILs

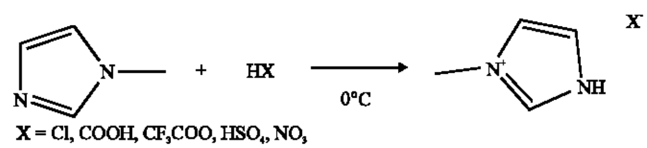

Fig. 4: 1-Methylimidazole reacts with acid to produce protic ILs

Based on the structure, the ionic exchange reaction taking place when 1-butyl-3-methylimidazolium ions replace potassium ions and bind to the negatively charged of anion salt. The potassium salt plays the role as an ion exchanger in ion exchange reaction and this reaction has the advantage such as high reaction rate (Rahmani and Mahvi, 2005). The physical and chemical properties of metathesis ILs are similar to the alkylation ILs but the range of structure of metathesis ILs is likely to be different than alkylation ILs that composed of small anions. Metathesis reaction is usually employed to produce hydrophobic and non-water soluble ILs such as 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium hexafluorophosphate. It is also used to produce room temperature IL such as trihexyl (tetradecyl) phosphonium bis (trifluoromethylsulfonyl) imide (Hayyan *et al*., 2010) since extinction of strong ion coupling in the compound may suggest the large size of anions compared to the alkylation ILs anions. Hydrophobic, solubility and other properties could be created by changing the anion of metathesis ILs.

Protic ILs: Several researchers have been reported an alternative method to produce ILs through acidic reactions using strong acids as protonator. Proton transfer from a Bronsted acid to a Bronsted base can also form ILs (Yoshizawa *et al*., 2003). It was reported that the protonation of 1-alkylimidazoles by strong acids provide salts which act as ILs and recognized as protic ILs (Picquet *et al*., 2003). Some inorganic or organic acids could be reacted directly with N-alkylimidazoles to form a new class of protic ILs which bear an acidic proton on nitrogen of the imidazolium ring. The advantage of protic ILs is the high yield that can be obtained economically with this method. Synthesis of protic ILs has been shown in Fig. 4, the protonation of the nitrogen constituent by strong acid is to neutralize the compound and it creates positive and negative ions (Picquet *et al*., 2003). In addition, melting points of protic ILs are low owing to the larger size of asymmetry nitrogen cations that providing greater degrees of freedom.

Protic ILs provide good proton conductivity compared to the inorganic media because of their higher ion mobility. In fact, some protic ILs has been shown to be more conductive than aqueous electrolytes at room temperature (Xu and Angell, 2003). Protic ILs have the additional advantage which the proton activity can be adjusted by the choice of Bronsted base and Bronsted acid used

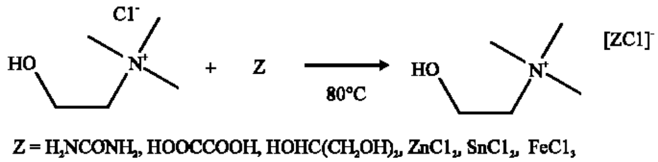

Fig. 5: Choline chloride reacts with complexing agent to produce eutectic ILs

in their formation (Byrne and Angell, 2008). Protic ILs are currently under intense study in a variety of applications, including fuel cells, where their ability to transport protons between electrodes has been an important discovery (Belieres *et al*., 2006). They have also been used as acidic catalysts for the esterification (Fraga-Dubreuil *et al*., 2002) due to the strong acids have high proton activity.

Eutectic ILs: Another ILs that is receiving interest is eutectic ILs (usually known as deep eutectic solvents), composed of a mixture forming a eutectic with a melting point much lower than either of the individual components (Abbott *et al*., 2001, 2003, 2004). Best of all, they are easy to make simply take the two solids, mix them together with gentle heating, until they melt and when they cool they remain liquid. The approach to make eutectic ILs is to start with a simple quaternary ammonium halide. In this case, choline chloride (2-hydroxyethyl-trimethylammonium chloride), has currently received widespread attention as a precursor for preparation of eutectic ILs (Abbott *et al*., 2003) due to low cost and easy availability (choline chloride is widely used as a feed supplement for livestock) (Hassan *et al*., 2005; Jahanian and Rahmani, 2008; Waldroup and Fritts, 2005). The use of choline chloride (Fig. 5) is interesting because this quaternary ammonium salt forms a liquid with complexing agent in a same phase, making eutectic ILs.

Choline chloride formed hydrogen bonds with hydrogen bond donors (including amides, carboxylic acids, alcohols) or metal chlorides, created a homogeneous liquid with a significant decrease in the melting point (Abbott *et al*., 2006). In the eutectic ILs phase, it consists of nitrogen cations and anions complex, in these structures, the weak interactions of the nitrogen cations with the anions complex and the large radius ratios, make possible break away of cation from anion relation and cation motion quantities can turn out to be greater. In nitrogen cations and anions, complex species the increased stabilization of the liquid state also reduced the kinetics of the crystallization process and in this system leads to the possibility of lowering melting points given low temperature ILs (Abbott *et al*., 2005).

These eutectic ILs have some superior characters in the preparation procedure exhibited as following; firstly, the preparation procedure of these eutectic mixtures is very simple, only needs to mix two different compounds mechanically and requires no medium; secondly, 100% reaction mass efficiency and zero emission in the synthesis are achieved and which is relatively environmentally benign. Additionally, substance density and energy density in the preparation process is the lower (Constable *et al*., 2002; Curzons *et al*., 2001). Abbott *et al*. (2005) showed that eutectic ILs could be employed in electropolishing, electroplating and metal oxide processing. They have also shown that choline chloride and either urea or ethylene glycol (as hydrogen bond donors) based eutectic ILs could be used in the electrodeposition of zinc, tin and zinc-tin alloys (Abbott *et al*., 2007).

Protic eutectic ILs: The combination of protonation and complexation reactions has been utilized in our previous studies to produce ILs named protic eutectic ILs (Shamsuri and Abdullah, 2010b).

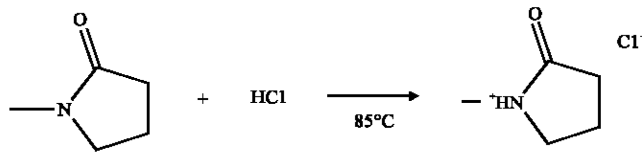

Fig. 6: Protonation of 1-methylpyrrolidin-2-one by hydrochloric acid to produce 1-methyl-2-oxopyrrolidinium chloride

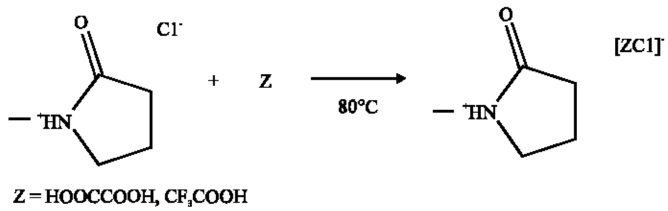

Fig. 7: 1-Methyl-2-oxopyrrolidinium chloride reacts with complexing agent to produce protic eutectic ILs

They have similar properties to the protic and eutectic ILs that have been made using a wide variety of quaternary ammonium cations, most notably imidazolium and choline cations. Protonation of nitrogen based organic compounds have altered their insoluble properties into salts that is a common way to make them water and acid-soluble substances. The protonation of nitrogen based organic compound by hydrochloric acid to produce hydrochloride salt has been shown in Fig. 6.

The idea to produce protic eutectic ILs was exploited by using hydrochloric acid as proton-rich electrolytes for proton carrying medium and also complexing agent as hydrogen bond donors. Protic eutectic ILs were prepared through environmentally friendly simple techniques, inexpensive and efficient congruent to the protic and eutectic ILs. During present study, we have found that the protic eutectic ILs were successfully produced by means of aminobenzaldehyde, hydroxymethyl amine and cyclic amide precursors giving low-viscosity ILs (Shamsuri and Abdullah, 2010b). When a complexing agent was added to the hydrochloride salt (Fig. 7) the melting point rapidly reallocated to the lower temperature. This complexation reaction actually, is driven by relatively strong hydrogen bonding interactions between the chloride ions and the hydrogen constituents of complexing agent (Shamsuri, 2011). Protic eutectic ILs are air and water stable and have high ionic conductivity that needed for electrochemical applications and they have also become alternative to the acidic reaction medium or acidic catalyst.

CONCLUSION

ILs believed as novel chemical agents and widely regarded as a greener alternative to many commonly used solvents, because they are designable, recyclable and non-volatile. Based on it, ILs have been studied for a wide range of synthetic applications, they have attracted considerable interest for use as non-volatile solvent based electrolytes due to they possess many benefits than VOSs. Several studies indicate the successful of using simple chemical reactions to synthesize ILs for large-scale processes. Five types of ILs have been described specifically alkylation ILs, metathesis ILs, protic ILs, eutectic ILs and protic eutectic ILs. However, almost limitless varieties of ILs are still to be discovered for production of ILs with a wide range of possible applications.

ACKNOWLEDGMENTS

The author is thankful to Professor Dr. Dzulkefly Kuang Abdullah for his valuable discussions on ionic liquids and to the Laboratory of Industrial Biotechnology, Institute of Bioscience, Universiti Putra Malaysia for providing the materials and facilities.

REFERENCES

Abbott, A.P., G. Capper, D.L. Davies, H.L. Munro, R.K. Rasheed and V. Tambyrajah, 2001. Preparation of novel, moisture-stable, Lewis-acidic ionic liquids containing quaternary ammonium salts with functional side chains. Chem. Commun., 19: 2010-2011.

Abbott, A.P., G. Capper, D.L. Davies, R.K. Rasheed and V. Tambyrajah, 2003. Novel solvent properties of choline chloride/urea mixtures. Chem. Commun., 7: 70-71.

Abbott, A.P., G. Capper, D.L. Davies and R.K. Rasheed, 2004. Ionic liquids based upon metal halide/substituted quaternary ammonium salt mixtures. Inorg. Chem., 43: 3447-3452.

Abbott, A.P., G. Capper, B.G. Swain and D.A. Wheeler, 2005. Electropolishing of stainless steel in an ionic liquid. Trans. Inst. Met. Finish., 83: 51-53.

Abbott, A.P., G. Capper, K.J. McKenzie and K.S. Ryder, 2006. Voltammetric and impedance studies of the electropolishing of type 316 stainless steel in a choline chloride based ionic liquid. Electrochimica Acta, 51: 4420-4425.

Abbott, A.P., G. Capper, K.J. McKenzie and K.S. Ryder, 2007. Electrodeposition of zinc-tin alloys from deep eutectic solvents based on choline chloride. J. Electroanal. Chem., 599: 288-294.

Belieres, J.P., D. Gervasio and C.A. Angell, 2006. Binary inorganic salt mixtures as high conductivity liquid electrolytes for >100 °C fuel cells. Chem. Commun., 46: 4799-4801.

Biswas, A., R.L. Shogren, D.G. Stevenson, J.L. Willett and P.K. Bhowmik, 2006. Ionic liquids as solvents for biopolymers: Acylation of starch and zein protein. Carbohyd. Polymers, 66: 546-550.

Byrne, N. and C.A. Angell, 2008. Protein unfolding, and the “Tuning In” of reversible intermediate states, in protic ionic liquid media. J. Mol. Biol., 378: 707-714.

Constable, D.J.C., A.D. Curzons and V.L. Cunningham, 2002. Metrics to green chemistry-which are the best. Green Chem., 4: 521-527.

Curzons, A.D., D.J.C. Constable, D.N. Mortimer and V.L. Cunningham, 2001. So you think your process is green, how do you know: Using principles of sustainability to determine what is green–a corporate perspective. Green Chem., 3: 1-6.

Dupont, J., C.S. Consorti, P.A.Z. Suarez and R.F. Souza, 2004. Preparation of 1-butyl-3-methyl imidazolium-based room temperature ionic liquids. Org. Synth. Coll., 10: 184-188.

Fraga-Dubreuil, J., K. Bourahla, M. Rahmouni, J.P. Bazureau and J. Hamelin, 2002. Catalysed esterifications in room temperature ionic liquids with acidic counteranion as recyclable reaction media. Catal. Commun., 3: 185-190.

Hassan, R.A., Y.A. Attia and E.H. El-Ganzory, 2005. Growth, carcass quality and blood serum constituents of slow growth chicks as affected by betaine Additions to diets containing 1. Different levels of choline. Int. J. Poult. Sci., 4: 840-850.

Hayyan, M., Farouq S. Mjalli, M.A. Hashim, Inas M. AlNashef, X.M. Tan and K.L. Chooi, 2010. Generation of superoxide ion in trihexyl (Tetradecyl) phosphonium bis (Trifluoromethylsulfonyl) imide room temperature ionic liquid. J. Applied Sci., 10: 1176-1180.

Holbrey, J.D. and K.R. Seddon, 1999. Ionic liquids. Clean Prod. Proc., 1: 233-236.

Jahanian, R. and H.R. Rahmani, 2008. The effect of dietary fat level on the response of broiler chicks to betaine and choline supplements. J. Boil. Sci., 8: 362-367.

Muhammad, N., Z. Man, M.A.B. Khalil and Y.A. Elsheikh, 2010. Dissolution of bamboo (*Gigantochloa scortechinii*) using ionic liquids. J. Applied Sci., 10: 1090-1096.

Ngo, H.L., K. LeCompte, L. Hargens and A.B. McEwen, 2000. Thermal properties of imidazolium ionic liquids. Thermochim. Acta, 357-358: 97-102.

Picquet, M., I. Tkatchenko, I. Tommasi, P. Wasserscheid and J. Zimmermann, 2003. Ionic liquids, 3. Synthesis and utilisation of protic imidazolium salts in homogeneous catalysis. Adv. Synth. Catal., 345: 959-962.

Plechkova, N.V. and K.R. Seddon, 2008. Applications of ionic liquids in the chemical industry. Chem. Soc. Rev., 37: 123-150.

Rahmani, A.R. and A.H. Mahvi, 2005. Use of ion exchange for removal of ammonium: A biological regeneration of zeolite. Pak. J. Biol. Sci., 8: 30-33.

Santos, L.M.N.B.F., J.N.C. Lopes, J.A.P. Coutinho, J.M.S.S. Esperanca, L.R. Gomes, I.M. Marrucho and L.P.N. Rebelo, 2007. Ionic liquids: First direct determination of their cohesive energy. J. Am. Chem. Soc., 129: 284-285.

Shamsuri, A.A., R. Daik, I. Ahmad and M.H.H. Jumali, 2009. Nylon-6/liquid natural rubber blends prepared via emulsion dispersion. J. Polymer Res., 16: 381-387.

Shamsuri, A.A. and D.K. Abdullah, 2010a. Isolation and characterization of lignin from rubber wood in ionic liquid medium. Mod. Appl. Sci., 4: 19-27.

Shamsuri, A.A. and D.K. Abdullah, 2010b. Protonation and complexation approaches for production of protic eutectic ionic liquids. J. Phys. Sci., 21: 15-28.

Shamsuri, A.A., 2011. Complexation reaction using ammonium based chloride compounds for preparation of eutectic mixtures. Int. J. Chem., 3: 161-165.

Tokuda, H., K. Hayamizu, K. Ishii, M.A.B.H. Susan and M. Watanabe, 2004. Physicochemical properties and structures of room temperature ionic liquids. 1. Variation of anionic species. J. Phys. Chem. B, 108: 16593-16601.

Tokuda, H., K. Hayamizu, K. Ishii, M.A.B.H. Susan and M. Watanabe, 2005. Physicochemical properties and structures of room temperature ionic liquids. 2. Variation of alkyl chain length in imidazolium cation. J. Phys. Chem. B, 109: 6103-6110.

Waldroup, P.W. and C.A. Fritts, 2005. Evaluation of separate and combined effects of choline and betaine in diets for male broilers. Int. J. Poult. Sci., 4: 442-448.

Wasserscheid, P. and W. Keim, 2000. Ionic liquids-new solutions for transition metal catalysis. Angew. Chem. Int. Ed. Engl., 39: 3772-3789.

Wassersheid, P. and T. Welton, 2003. Ionic Liquids in Synthesis. 2nd Edn., Wiley-VCH, Weinheim, Germany.

Welton, T., 1999. Room-temperature ionic liquids. Solvents for synthesis and catalysis. Chem. Rev., 99: 2071-2084.

Wu, J., J. Zhang, H. Zhang, J. He, Q. Ren and M. Guo, 2004. Homogeneous acetylation of cellulose in a new ionic liquid. Biomacromolecules, 5: 266-268.

Xu, W. and C.A. Angell, 2003. Solvent-free electrolytes with aqueous solution-like conductivities. Science, 302: 422-425.

Yamada, C., K. Sasaki, S. Matsumura and K. Toshima, 2007. Aryl C-glycosylation using an ionic liquid containing a protic acid. Tetrahedron Lett., 48: 4223-4227.

Yoshizawa, M., W. Xu and C.A. Angell, 2003. Ionic liquids by proton transfer: Vapor pressure, conductivity and the relevance of ÄpKa from aqueous solutions. J. Am. Chem. Soc., 125: 15411-15419.