IONIC LIQUIDS AS SOLVENTS FOR CHEMICAL TRANSFORMATIONS: A KINETIC INVESTIGATION

DISSERTATION

Submitted in partial fulfillment of the requirements provided for the award of Degree of

Master of Philosophy

In

CHEMISTRY

By

Mudasir Ahmad Rather

Under the supervision of

Dr. G. M. Rather

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KASHMIR
Srinagar – 190006, J&K, India

2012

Dedicated to my noble parents

ACKNOWLEDGEMENTS

Praise be to Allah for his continued blessings. Praise be to Allah for blessing me with noble parents whose love and meliflous affection made this whole journey wonderful and successful. Words are meaningless to express my unaccountable feelings to them for their belief in me, unequivocal support, kind understanding, patience and preservance and above all in making me what I am today. I wish them all the happiness and adventure that they have ensured that I had the opportunity to experience. ***I owe them more than anything else in the world.***

It is a matter of great privilege for me to work under the able and highly academic guidance of Dr. G. M. Rather, Associate Professor, Department of Chemistry, University of Kashmir who irreversibly cooperated with me and always gave me ample freedom. His energetic smile, optimistic attitude, critical jugdements and never ending enthusiasm made the realization of this dissertation possible.

Praise be to Allah for blessing me with an opportunity to meet an exceptional man Dr. Mohsin Ahmad Bhat, Assistant Professor, Department of Chemistry who nurtured my capabilities and above all his trust in my abilities kept me going and ultimately towards the attainment of this goal. His scholarly guidance, experienced words, meticulous practical training, disciplined and magnanimous nature, unlimited sincerity and affection towards students had always inspired me and I feel extremely fortunate to be his student. His devotion and dedication to work, passion for knowledge, inquisited mind and scientific attitude have made an everlasting impact on me and boosted my confidence. His exceptional guidance and invaluable comments during the period of the research and the writing of the study are very much appreciated. This research has been a remarkable adventure and I am indebted to him for making it a challenging and learning journey. Thank You Sir for being so patient and loving to me during the analysis of data. Thank You Sir for all your love and I am excited to spend everyday of my life thanking You over and over again. ***Really Sir You are the Real Mentor of the World of Research****.*

I would extend my special thanks Dr. Aijaz Ahmad Dar, Assistant Professor, Department of Chemistry, University of Kashmir for his wise counseling and kind concern.

My special thanks to present Head of Department of Chemistry for allowing me to work in the department. All other faculty members are also acknowledged for all the guidance and assistance they provided me whenever I approached them. I would also like to mention the non teaching staff especially Altaf Ahmad Mir for their assistance in every possible way.

I am very much thankful to my seniors Muzaffer Hussain Najar, Oyais Ahmad Chat and Raashid Baya for their continuous suggestions, encouragements, invaluable advice and moral support during my research work.

Special thanks to Rohi Jan, my research copartner for all the generosity and encouragement he has provided to me during the study.

I feel it my gratitude to appreciate and acknowledge my lab mates and of course good friends of mine- Sajad, Sarwar,Roohi Masrat, Suraya Jabeen,Uzma Khan,and Rais Ahmad Shah and especially Masrat Maswal for their kind concern, timely assistance, love, moral support and amicable cooperation in scientific and social fronts of life. Their infinite cooperation, hard work, sincerity and dedication to work are source of inspiration to me. I would also extend my special thanks to people from IIIM Srinagar Dr. Khursheed Ahmad Bhat, Dr. Bilal Ahmad, Showket Rasheed , Hafeezullah, Shabir Hussain and Shakeel Baya for their timely assistance and kind support.

A special and deep acknowledgement to my younger Sister, Rehana Nazir for her unwavering love and priceless prayers. Thanks to my cousine brothers Muzamil, Irfan, Aushaq Illahi, Tassaduq,

Inam, Majid and to also my cousine sisters Aroona, Mehnama, Rifat and Abiroo for their encouraging words, innocent love and utmost care during this whole period.

I would like to extend my deepest appreciation to all my friends Suhail, Fairoz, Aijaz, Showket, Masood,Iqbal, Waheed, Fozia, Usma and especially Younis for being there, whenever I was in need of them the most and for their love, support and encouragement.

Last but not the least I would like to thank CSIR and strongly acknowledge them for providing me the financial assistance.

This piece of work is a tribute to my beloved parents and to my teachers who have always been supportive, encouraging, motivating and guiding to me.

Overall it was remarkable and incredible experience of my life.

Mudasir Ahmad Rather

Dr. Ghulam Mohammad Rather
Ph. D
Associate Professor

University of Kashmir
Srinagar-190006
J&K, India

DEPARTMENT OF CHEMISTRY

CERTIFICATE FROM SUPERVISOR

This is to certify that the work presented in this dissertation entitled “*IONIC LIQUIDS AS SOLVENTS FOR CHEMICAL TRANSFORMATIONS: A KINETIC INVESTIGATION*” is original and has been carried out by **Mr. Mudasir Ahmad Rather** under my supervision. This piece of work is suitable for submission for the award of M.Phil Degree in Chemistry. It is further certified that the work has not been submitted in part or full for award of any degree in this or any other University.

(Dr. G. M. Rather)
Supervisor

DECLARATION

I hereby declare that the work incorporated in the present dissertation was carried out by me in the Department of Chemistry, University of Kashmir, Srinagar 190006. The entire work or any part of it has never been submitted before for any prize or degree anywhere.

(Mudasir Ahmad Rather)

CONTENTS

LIST OF FIGURES

LIST OF TABLES

List of Schemes

Chapter 1

General Introduction

The development of cleaner technologies is a major emphasis in green chemistry. Among the several features of Green Chemistry, the reduction/replacement of volatile organic components (VOC) from the reaction medium is of greatest concern as these have been heavily implicated in causing changes to the climate on the global level like formation of smog as well as being identified as a source of ozone depletion (1). Because of these deleterious effects of VOC, search for neoteric non-volatile and less polluting solvents that are greener towards environment is on demand. Ionic liquids offer a class of solvents that have been used as reaction media for various chemical transformations over conventional solvents because of their eco-green nature. Ionic liquids are organic salts with melting point below 100^0C (2) while room temperature ionic liquids (RTILS) are salts having melting temperature at or around 25^0C and consists of ions where couloumbic forces are dominant in addition to hydrogen bonding, $\pi - \pi \, and \, n - \pi$ interactions, van-der Waals interactions and dispersive forces which play an important role for these to act as reaction solvents. Owing to the highly attractive and advantageous characteristic features of ionic liquids like low vapour pressure, low toxicity, wide range of solubility and miscibility, wide electrochemical window, high thermal and chemical stabilities, high recycling potential etc. have attracted chemists for exploiting them in diverse research area viz., in catalysis, chemical synthesis, reaction media, separations and extractions, biochemistry and other fields of fundamental as well as applied research (3,4,5,6,7).

1.1. History

The roots of ionic liquids go back to one hundred years and are firmly planted in traditional high temperature molten salts. These molten salts were used as reaction solvents due to highly interesting properties like wide liquidus range, wide electrochemical window, thermal and chemical stability, greater electrical conductivity and non-volatility. Moreover the availability of these salts on cheaper rates has compelled chemists to use them as solvents.

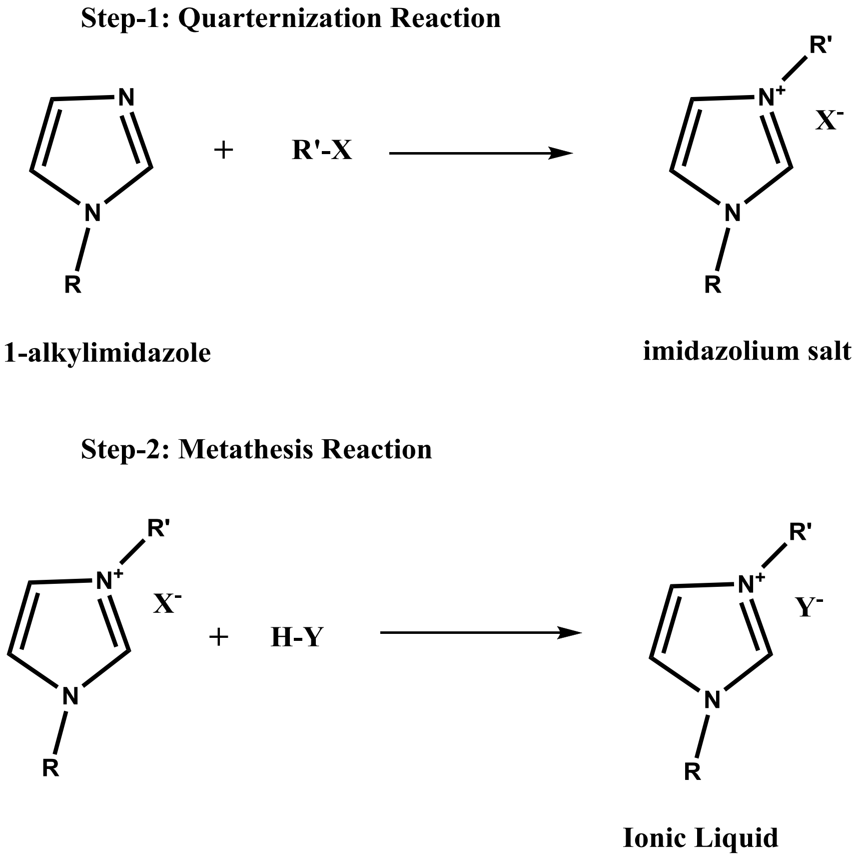
But the high operating temperature of the molten salts cause incompatibilities for reactions; besides at the industrial level these salts incur high energy costs to maintain their operating temperature, thus discouraging their use as reaction solvents. Thus search for newer type of solvents which could avoid the deleterious effects of molten salts finally lead to discovery of ionic liquids as non-aqueous solvents. It was in the mid 19th century Prof. Jerry Atwood of the University of Missouri made the first documented observation of the ionic liquid as a red oil which formed during Friedel-Crafts reaction of aromatic substrates with incipient electrophile chloromethane in presence of a Lewis acid catalyst like $AlCl_3$ (8). The red oil was later identified through spectroscopic techniques like NMR as a salt containing a cation presumed to be the reaction intermediate in the Friedel-Crafts reaction, named as sigma complex, and anion was heptachlorodialuminate (9). But actual discovery of the ionic liquids dates back to 1914 when scientists tried the synthesis of ethylammoniumnitrate (10), which was a liquid at room temperature containing a small amount of water (11). Later on in 1948 Hurley and Weir at the Rice Institute in Texas developed the first ionic liquid with chloroaluminate ions as bath solutions for electroplating the aluminium (12) and after that in 1970 groups of Osteryoung and Wilkes rediscovered them successfully by synthesising the room temperature chloroaluminate melts (13). The development of these room temperature ionic melts was focussed for electrochemical application purposes. Subsequently Seddon and Huxley groups used these chloroaluminate melts for electrochemical and spectroscopic investigation of transition metal complexes(14,15). Owing to their air and moisture instability and acidic nature, these ionic melts, could not be fully exploited as reaction media or in catalysis, synthesis etc. Thus search for moisture and air stable conducting liquids resulted in 2001 in the discovery of ionic liquids which were neutral, air and moisture stable and have been used for wide applications as solvents, catalysis, immobilising agents(16,17) etc. These modern day ionic liquids are referred to as second generation ionic liquids and include quaternary ammonium, phosphonium, imidazolium, pyrrolidinium cations with weakly coordinating anions like PF_6^-, Cl^-, Br^-, I^-,BF_4^-, ClO_4^-, CH_3COO^- etc.(18,19)

1.2. COMPOSITION

The general strategy of designing room temperature ionic liquids (RTILs) is to destabilize the crystalline phase of an ionic substance with respect to its melt. This is achieved by taking a combination of large size, diffuse charged and unsymmetrical ions. While the large size and diffuse charge in such combinations lead to weak columbic interactions, the low symmetry hampers their efficient packing in the crystal. In addition to molecular dissymmetry and charge delocalization, size mismatch of ions, side chain elongation and fluorination of hydrocarbon chain continue to be popular methods for inventing new RTILs. Usually a combination of large size unsymmetrical organic cation and a weakly coordinating inorganic/organic anion leads to a RTIL. The cations in RTILs are usually organic such as, quaternary ammonium cations, heterocyclic aromatic cations, pyrrolidinium cations, derivatives of natural products and some more esoteric cations and among anions hexafluorophosphate,tetrafluoroborate,trifluoromethanesulfonate,tris(trifluoromethylsulfonyl) methide, bis(trifluoromethylsulfonyl)imide, dicyanamide are common ones (3, 4, 7, 20, 21, 22, 23, 24, 25, 26). The enormous choice of cations and anions available and the strong dependence of physicochemical aspects of RTILs on the nature of constituents allows researchers to tailor the properties of RTILs as per the requirements. RTIL of desired physical properties can be synthesized by a careful selection of suitable cation-anion combination, with fine-tuning facilitated by subtle variations in molecular structure. This feature of RTILs has earned them the name of "*designer solvents*". Because of some potential advantages like high air and water stability, low toxicity, appreciable conductivity and structural organization, imidazolium based RTILs are more oftenly used especially for electrochemical applications (7, 27)

1.3. SYNTHESIS

Conventionally a two step procedure is used in the synthesis of RTILs (28, 29) as presented in Scheme 1.1. The first step is usually a quaternization reaction, wherein alkylation of heteroatom in an organic moiety is performed to produce salt of desired organic cation. In the second step the anion (usually a halide) of the salt synthesized in step first is substituted by the anion of choice through anion exchange reaction. A variety of synthetic procedures are available in the literature for the synthesis of RTILs and often the purity of final product happens to be a matter of concern about these procedures. Impurities even in the lowest concentration regime have drastic and undesired effects on the physicochemical characteristics of RTILs, especially those of electrochemical concern. Gordon and co-workers (30) recommended a three pronged approach viz., (i) purification of starting materials, (ii) control of conditions for quaternization and metathesis reactions and (iii) purification of the synthesized ionic liquids for research grade purity. The conventional synthesis and purification procedures for RTILs are time consuming and often give low yields. Low yields, waste generation, complicated workup procedures and non-green aspects of synthesis and purification processes for RTILs are current obstacles in the path of their generalized use. Hence many groups have extensively investigated these issues and subsequently non-conventional approaches like use of microwaves (31, 32) and ultrasound (33, 34, 35) have been tested for the synthesis and purification of RTILs. The use of these non-conventional methods was demonstrated to lead to better yield and purity, fast conversions and easy workup of synthetic and purification steps for RTILs. Various approaches for purification of RTILs have been a subject matter of many publications (36,37,38,39). Making the RTIL synthetic procedures greener, with maximum purity and stability of the synthesized product and designing new choices of cation-anion combinations, besides the structural modifications in the cation-anion skeleton to achieve desired properties in a low cost RTIL, continue to be an area of immense interest for synthetic chemists. Synthesis of RTILs from bio-renewable natural products is currently a new area of research in this regard (40, 41).



Step-1: Quarternization Reaction

1-alkylimidazole

imidazolium salt

Step-2: Metathesis Reaction

Ionic Liquid

Scheme 1.1. **General reaction scheme for synthesis of Ionic liquids**

1.4. STRUCTURAL ASPECT

Knowing and understanding the structure-property relationship of ionic liquids, helps us in designing of characteristic ionic liquids besides in optimising their physico-chemical properties. Physical studies like IR (43,44,45), Raman (46,47,48), Neutron scattering and X-Ray studies (49,50) suggested that ionic liquids possess structural organization which is outcome of the interplay of columbic forces, hydrogen bonding, vander-Wall’s interaction and many more (51,52,53). There are various factors responsible for low melting behaviour of these ionic liquids, large size of ions resulting in diffused charge layer thereby resulting in lowering of lattice energy (42) and also the highly asymmetrical nature of constituents i.e. cations and anions, preventing the efficient packing and strong charge ordering between its components resulting in wide liquidus range and low melting nature (54). Recent studies on the structure of imidazolium based ionic liquids revealed the formation of extended network of cations and anions connected together through hydrogen bonding, with one imidazolium cation surrounded by three anions and vice versa, shown in figure 1.1.

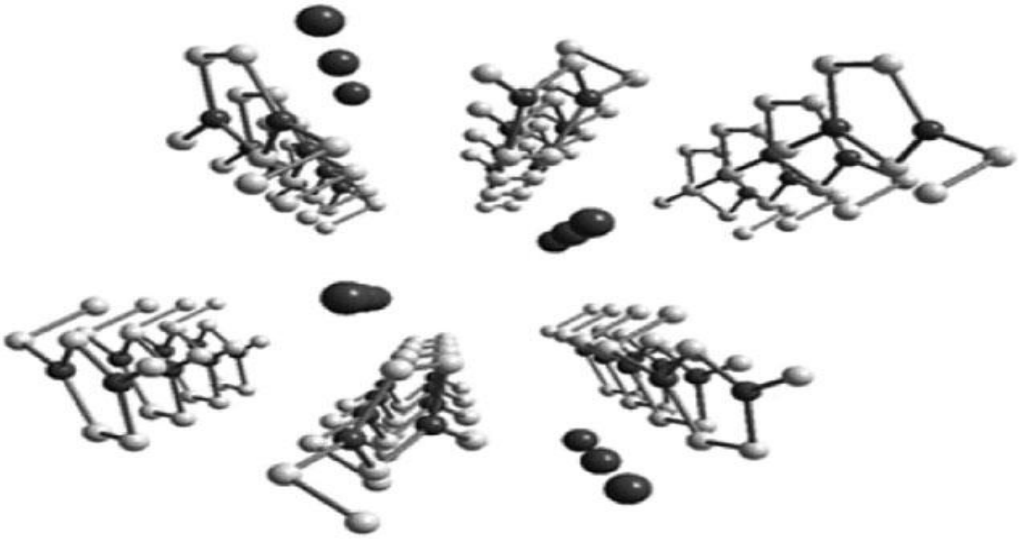


Fig. 1.1. A 3-D simplified schematic view of the arrangements of 1,3-dialkylimidazolium cations showing the channels in which the ‘‘spherical’’anions are accommodated

This type of molecular arrangement generates channels in which the anions are generally accommodated as chains and depends on the anion geometry, internal arrangement along the imidazolium columns. This type of arrangement of cations and anions resulted in formation of hydrophobic and hydrophilic domains in the ionic liquid, thus exhibits a high degree of spatial heterogeneity which is due to the interplay between electrostatic interaction and van der Waals interaction. This nano-phase segregation of imidazolium based ionic liquids helps in solvation of large number of macromolecules, ions, molecules and stabilisation of nanomaterials to greater extent (55,56,57,58,59,60). The structural aspects of ionic liquids have been extensively investigated theoretically by simulations. Studies based on united atom model revealed the long range structure in case of imidazolium based ionic liquids (61,62). Moreover course grain model (63) showed the aggregation of side chains only while homogeneous distribution of head groups.

1.5. Physico-chemical properties

The studies involving physico-chemical properties of ionic liquids are limited in comparison to those of conventional solvents. Structure and composition of ionic liquids open up a new window for modifying their properties which can be exploited for various applications. It is because of the tunable physico-chemical properties of the ionic liquids that justifies the name as ‘Designer solvents’.

1.5.1. Polarity and solvation

Ionic liquids have been the object of intensive study owing to their application in reaction solvents, electrochemistry and material sciences (64). Also they have proved as solvents of choice for organic reactions and catalysis processes as they ensure enhancement in reactivity, selectivity and catalyst recovery (65). Moreover the broad variation in solubility and miscibility properties enables these solvents to dissolve diverse ionic and covalent compounds, thus are considered eco-green alternatives to conventional solvents. This ability to dissolve various compounds is an important feature of ionic liquids based on the polarity and coordination ability of their ions (66,67). As solvents, RTILs have been investigated for their polarity aspects making use of macroscopic properties (68,69,70) and empirical parameters (71,72). While dielectric constant measurements show RTILs as solvents of moderate polarity, use of solvatochrome probes establish that their polarity values match with solvents like acetonitrile and dimethyl formamide (73). An excellent review about the RTIL solvation ability and polarity in this regard has been published by Chiappe et al. (74). Measured polarity of RTILs is not always a direct measure of their hydrophilicity and in many cases RTILs of same polarity exhibit different hydrophilicities. Polarity of RTILs is known to correlate to the size and charge density of constiuent ions. Increase in ion size that leads to spreading of charge decreases the polarity of RTILs. RTILs can act both as hydrogen bond donors and acceptors; while the basicity depends on the anion, hydrogen bond acidity is more a property of the cation although affected by the anion present. Solvation dynamics in RTILs has been found to be multimodal occurring over a wide range of time scales, from femto to nanoseconds (75-77).

1.5.2. Melting point and decomposition temperature

Low melting and high decomposition temperatures of ionic liquids are the most remarkable feature which decides their often use as reaction media and in synthesis. The wide liquidus range of these solvents enables them to be used as reaction solvents, in catalysis and electrochemistry etc. over a wide temperature range. Also due to the high decomposition temperatures, the use of ionic liquids as thermal storage fluids and in solar thermal electric power systems is highly advantageous (78-82). The quite low melting point of ionic liquids is on account of a subtle balance between cation and anion symmetry, flexibility of alkyl chains in cations, diffused charge on the ions, increasing length of alkyl chain and increasing size of the anion (83,84). Physical studies like DSC/DTA showed that [BMIM][Cl] has a melting point of 314.1k. Investigations by Scurto et al (85,86) revealed that pressuring simple organic salts with compressed CO_2 can lead to remarkably high melting depressions especially in fluorinated anions because of the strong interaction of CO_2 with the anions (87). Also nano scale confinement (88) of ionic liquids is responsible for such decrease as studied by Kanakabu et al. Many theoretical studies have shown the relevance of melting and decomposition temperature of ionic liquids to its structure. Trohalaki and Pachter (89) and

Varneck et al (90) predicted melting points of imidazolium ionic liquids using quantitative structure-property relation(QSPR) with almost a good accuracy. Neural network approach used by Carreva and Aires-de-Sousa for pyridinium bromide ions with moderate success and later on (91) recursive neural network (92) was used by Bini et al to same above type of ionic liquids with slight deviations. But very good agreement to experimental results in melting temperature determination of ionic liquids have been achieved using molecular dynamics simulations as studied by Naoto and co-workers (93). Thermo gravimetric analysis(TGA) have shown that the large thermal stability of ionic liquids is mainly due to nature of the anion. For example for 1-alkyl-3-methylimidazoliumtetrafluoroborate, the value is 676.15k for butyl chain and 633.15k for octadecyl chains and for common anions the order of onset values is $Tf_2N>BF_4>PF_6>$halides (94). Large onsets for decomposition temperatures were also reported for pyridinium or tetraalkylphosphonium based ionic liquids (95, 96). Moreover many theoretical studies have revealed cation and anion effects on decomposition temperatures with a good agreement to experimental studies (97).

1.5.3. Vapour pressure

Ionic liquids don’t exert measurable vapour pressure at ambient temperature, hence perceived as potential replacements for volatile organic counter parts. Therefore the low volatility of ionic liquids, which arises from strong couloumbic interactions between the constituent cations and anions, has become the hallmark property that singles them out for development of green chemistry. Investigations by Rebelo et al (98) noted that no reliable experimental data on the vapour pressure and their dependence on temperature existed for these ionic liquids and predicted that it should be possible to distil ionic liquids having $[NTf_2]^-$ anions and imidazolium cations containing long alkyl chain lengths at temperatures between their estimated boiling and decomposition temperatutes and subsequently carried out distillations of $[C_{10}mim][NTf_2]^-$ and $[C_{12}mim][NTf_2]^-$ at 70°C under reduced pressure. Later on studies by MacFarlane and co-workers on tetraalkylphosphonium and tetraalkylammonium based ionic liquids have revealed that these exhibited high degree of volatility (99). They also demonstrated that equi-molar binary mixtures of ionic liquids can be distilled. But in general, the vapour pressures of ionic liquids, notably the widely used imidazolium based one's with short cationic alkyl chains, are negligible at ambient temperatures and pressures. Thus many ionic liquids show little or no evidence of distillation below their thermal decomposition temperature.

1.5.4. Transport properties

Transport properties of ionic liquids viz. viscosity, electrical conductivity, thermal conductivity, self diffusion coefficient, are the most important and relevant one's for chemical process design and development (100). These properties can be tailored or designed by altering the constituents of ionic liquids for obtaining the desired ionic liquids which can be then used for areas of research especially in reaction media.

1.5.4.1. Viscosity

Viscosity is a measure of a liquid's resistance to flow. Liquids with lower viscosity flow more readily and vice versa. The commonly used physical unit for viscosity is centipoise(cP). In general ionic liquids are more viscous than molecular solvents, and at room temperature have viscosity lying in the range of 10-500cP (101). The large viscosity of ionic liquids could be disadvantageous for some industrial applications or their use in reaction solvents but on the other hand it would be favourable for using in lubrication purposes. Nevertheless, viscosity of ionic liquids can be tuned through adequate combination of cations and anions leading to optimum range of viscosities for various applications. The viscosity of ionic liquids generally increases with increasing size of cation and particularly with increasing alkyl chain lengths. Also ionic liquids with weakly coordinating anions like $[BF_4]^-$,$[PF_6]^-$ and $[NTf_2]^-$ have lower viscosities than those with strongly coordinating anions such as $[NO_3]^-$. For example the room temperature viscosities of $[C_6mim][\ [BF_4]^-$ and $[C_6mim][\ [NO_3]^-$ are 314 and 840cP respectively (102). Moreover, viscosities of ionic liquids expectedly decrease with increase in temperature. Impurities like water and halide ions have dramatic effect on the ionic liquid viscosities (103,104). Water can be absorbed by ionic liquids because of their hygroscopic nature and the halide ions typically occur in ionic liquids in metathesis step when the anion exchange of an organic halide with an inorganic salt occurs. These problems can be minimised by extraction of ionic liquid into an organic solvent and washing the solution with small amount of deionised water followed by drying in a rotary evaporator. Impact of pressure on viscosity of ionic liquids is seriously demanding because of relevance of viscosity for industrial purposes, and thus leads to development of various predictive models for its determination. Gardas and Coutinho developed a group contribution using Orrich-Erbar-type approach revealed a large deviation but large enough for advocating industrial purposes (105,106). The latter group contribution model based on the Vogel-Tammann-Fulcher equation (107)

$$n = n_0 . \exp\left(\frac{B}{T - T_0}\right) \qquad (1)$$

where η_0, B and T_0 are constants, better explains the variations of η_0 with temperature. Besides, Hole theory (108) has been successfully used (109) to analyze the RTIL viscosity and its tuning through structural variations. It has been shown that viscosity of RTILs can be modeled by assuming that they behave like an ideal gas whose motion is restricted by the availability of sites for the ions to move into. Hence for an RTIL,

$$\eta = \frac{m\bar{c}/2.12\sigma}{P(r>R)} \qquad (2)$$

where η is the coefficient of viscosity, m is the geometric mean of the constituent

ion molecular mass,$\bar{c}$ is the average speed of the molecule (= 8kT/π.m)$^{1/2}$, σ the collision diameter (4πR^2) and P(r≥ R) is the probability of finding a hole of radius r, greater than the radius R, of the RTIL whose value can be evaluated through,

$$Pdr = \frac{16}{15\sqrt{\pi}} a^{7/2} r^6 e^{-ar^2} dr \qquad (3)$$

where a is given by

$$a = \frac{4\pi\gamma}{kT}$$

γ being the surface tension. Good correlation between the η calculated on the basis of Hole theory and that measured experimentally has been reported. As evident from the above treatment, RTIL viscosity can be decreased by decreasing the surface tension, increasing the free volume or by decreasing the ionic radius. This is the reason for low viscosity of RTILs with fluorinated anions. Various groups have extensively studied the impact of cation, anion, their size, symmetry and charge delocalization on the η values of RTILs in detail (110-113). Viscosity of RTILs has been demonstrated to be temperature sensitive (114,115) and cases obeys an Arrhenius type relationship, Guzman-Andrade (GA) law,

$$n = A. \exp\left(\frac{E_a}{RT}\right) \qquad (4)$$

where E_a is the activation energy for viscous flow

1.5.4.2. Conductivity and diffusion

Ionic liquids by definition exhibit ionic conductivity of the order of Siemens per metre(Sm^{-1}) or for low conductivities, milli siemens per centimetre(mScm^{-1}), which is a measure of the liquid's ability to conduct an electric current. The intrinsic ionic conductivity of ionic liquids depends on the availability of the ions to become charge carriers and on the ionic mobility. The ionic mobility can be reduced by ion-ion interaction that leads to the formation of ionpairs and ion aggregates which are neutral (116,117). Also the ionic mobility correlates well with the diffusion rates which in turn depends on the viscosity of the ionic liquids depicted in Vogel-Tamman-Fulcher equation (118). Studies involving diffusion and conductivity behaviour of ionic liquids is highly demanding for the effective use of these neoteric solvents for various applications like electrochemistry, reaction solvents, synthesis etc. These transport properties of ionic liquids, being dependent on their chemical structure, could be tuned through the modification of cations and anions to achieve the desired properties. Many attempts have been made in this regard and Stokes-Einstein and Nernst-Einstein equations (119) show relevance of ionic diffusivity on electrical conductivity of ionic liquids. Therefore electrical conductivity of ionic liquids lying in the range of 0.1-20mScm^{-1} (115).Besides influence of parameters like the diffusion rates, viscosity, chemical structure, ion aggregation and size and ionic mobility on ionic conductivity (111,112, 120-123), temperature also has profound effect on the conductivity as shown in Arrhenius type equation below

$$ln\sigma = ln\sigma_0 - \frac{E_a}{RT} \tag{5}$$

where E_a is the activation energy for the conduction and σ_0 is a constant.

1.5.5. Electrochemical potential window

The electrochemical potential window is the voltage range over which a material is neither oxidised nor reduced at an electrode and is therefore electrochemically inert. Ionic liquids have wide electrochemical window because of inherent robustness of its ions to redox reaction and which can be tuned by varying the composition of these solvents (5,7,115). It has been investigated that imidazolium based ionic liquids have this window in the range of 2.0-6.0V (7,115), the size of windows are influenced by presence of electro-active impurities such as halide ions and the choice of working electrode. It is because of these characteristic properties which make ionic liquids as potential electrolytes for batteries, solar cells, fuel cells and also as potential solvents for electrochemical investigations (5).

1.5.6. Surface tension

Interfacial properties of ionic liquids are very important for many industrial applications such as control of mass transfer efficiency for gas-liquid or liquid-liquid extraction operations or for multiphasic homogenous catalysis. Also these properties can control the reaction kinetics of chemical reactions, thus determining solvent's ability to act for such purposes. There are scarce reports about surface tension measurements available in the literature. The available data reported is based on imidazolium ionic liquids. So it is the need of hour to investigate fully the interfacial properties of these solvents for use in various applications. The first studies on surface tension have been published by Law and Watson (124) that revealed it decreases linearly with temperature and also showed that surface tension decreases with increasing alkyl chain lengths in imidazolium ionic liquids. Surface tension of ionic liquids is lower than those of water and molten inorganic salts have also been reported (125). Surface tension of ionic liquids is highly influenced by impurities especially hydrophilic one's (126). The effects of water content on the surface tension value are controversial and ambiguous. Some authors reported a decrease and further increase with increasing water content while others reported a linear increase with increasing water content which reveals the dependence of surface tension on the nature and type of ionic liquids (127). Many theoretical studies have been done in order to develop new predictive methods for surface tension determination. Gardas and Coutinho (128) developed QSP approach to predict surface tension of ionic liquids by using parachor (129) concept and correlation of surface tension with molar volume (130). Also molecular dynamic simulation of the surface tension showing decreasing trend with ion size asymmetry (131). Temperature effects have also been reported through these simulations by Hegger et al.(132).

1.5.7. Recycling

One of eco-friendly aspects of using ionic liquids as solvents is their high potential of recycling, which reduces not only hazardous waste but also their cost. Owing to these features ionic liquids have been used as biphasic catalysts, solvent media and in synthesis. The recycling power of ionic liquids was reported by Anderson and co-workers in rhodium catalysed hydroformylation (67) reaction in which the products formed a separate layer leaving the solid mixture of ionic solvent and catalyst, which was used again and again with reproducible results.

Aims and Objectives of the study

Solvent is the key component in chemical transformations by playing an active role in the kinetic aspects of the reaction. It controls the interaction between the reactants through intermolecular forces and heat transfer and forms a solvate shell around the solute. Those types of interactions are of paramount importance in achieving conversion and selectivity (133). As concern about the environmental impact of chemical transformation mounts, room temperature ionic liquids (RTILS) were being advocated as reaction media for their many remarkably advantageous features like low volatility, high thermal stability, high solvating potential, recycling nature (3,4, 134) etc. Moreover the highly structured nature and totally ionic nature of these RTILS have proven to enhance the reaction rates and stereo-selectivity (4, 134-136). The latter two are important features of RTILS that are yet to be explored fully from kinetic point of view. Chemical transformations like Diels-Alder reaction and Nucleophillic substitution reaction are expected to be good indicators of these two aspects of RTILS as solvents. Therefore a complete understanding of their role as solvents for chemical transformations will lead to good control over the design of ideal RTILS for set goals.

Diels-Alder reaction is one of the important reaction in organic synthesis and chemical industry (137, 138). The two concerns for chemists in Diels-Alder reaction are the rate enhancement and stereo-selectivity. Internal pressure, enforced hydrophobicity and hydrogen bonding capability are such parameters used to achieve the selected target (139). Therefore RTILS make the chemists convenient choice as solvents for kinetic investigation of above reaction owing to their structured nature. Many chemists like Seddon and co-workers (140), Tiwari et al (141, 142) etc have reported the rate enhancements of Diels-Alder reaction. Also Nematollahi et al have published his work related to electrochemically induced Diels-Alder reaction in RTILS (143). Similarly Nucleophillic Substitution reaction is of utmost practical use for transformations in medicinal and agricultural chemistry (144). But there are meagre reports related to kinetic investigation of nucleophillic substitution reaction in RTILS and also authors have failed to give the genuine explanations for these kinetic benefits (145,146). Therefore keeping in view the scarcity of literature related to kinetic investigations in RTILS and also little understanding of how these RTILS affect the reactivity in the above mentioned classes of reactions i.e., Diels-Alder reactions and Nucleophillic Substitution reaction, this piece of work was carried out in different kinds of N-Alkylimidazolium based RTILS like [BMIM][Cl], [BMIM][BF_4], [BMIM][PF_6] and [BMIM][CH_3COO] to see the solvent/salt effects on rate kinetics of above reactions.

References

1. Holbrey, J.D.; Seddon, K. R. *Ionic liquids. Clean products and process 1*.**1999**, 223-236.

2. Seddon, K. R. *Ionic liquids for clean technology. In; Molten salt forum proceedings of 5th international conference on molten salt chemistry and technology*. **1998**, vol. 5-6.

3. Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis, Wiley-VCH; Weinheim*, **2003**.

4. Welton, T. *Chem. Rev*. **1999**, *99*, 2071.

5. Zhang, J.; Bond, A. *M. Analyst.* **2005**, *130*, 113.

6. MacFarlane, D. R.; Pringle, J. M.; Howlett, P. C.; Forsyth, M. *Phys. Chem. Chem. Phys*. **2010**, *12*, 1659.
7. Hapiot, P.; Lagrost, C. *Chem. Rev*. **2008**, *108*, 2238.
8. (a) Nambu, N.; Hiraoka, N.; Shigemura, K.; Hamanaka, S.; Ogawa, M. Bull. *Chem. Soc. Jpn.* **1976**, *49*, 3637. (b) Walden, P. *Bull. Acad. Imper. Sci.(St Petersburg)*.**1914**,1800.(c) Yoke, J. T.; Weirs, J.F.; Tollin, G. Inorg. Chem. **1963**, *2*, 1210. (d)Atwood, J. L.; Atwood, J. D. *Inorganic compounds with unusual properties, Advances in chemistry series no. 150, American chemical society, Washington D C*. **1976**, PP. 112-127.
9. Atwood, J. L. *US Pat., 4496744*, **1981**.
10. Sugden, S.; Wilkins, H. *J. Chem. Soc.* **1929**, 1291-1298.
11. Herford,I. M.; Schneider, H. *Liebiss Ann.Chem.* **1991**, 27-31.
12. (a) Hurley, F. H. *U.S. Patent 2,446,331*.**1948** (b) Hurley, F.H.; Wier, T. P. *J. Electrochem. Soc*. **1951**, *98*, 207.
13. (a) Chum, H.L.; Koch,V.R.; Mitter, L. L.; Osteryoung, R. A. *J. Am. Chem. Soc*. **1975**,*97*,3264-3265. (b) Robinson, J.; R.A. Osteryoung, R. A. *J. Am. Chem. Soc*. **1979**, *101*, 323-327. (c) Wilkes, J.S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982,** *21*,1263-1264.
14. (a) Scheffler, T. B.; Hussey, C. L.; Seddon, K. R.; Kear, C. M.; Armitage, P. D. *Inorg. Chem*. **1983**, *22*, 2099-2100. (b) Laher, T. M.; Hussey, *Inorg. Chem*. **1983**, *22*, 3247-3252. (c) Scheffler, T. B.; Hussey, C. L. *Inorg. Chem.* **1984**, *23*, 1926-1932.
15. Earle, M. J.; Seddon,K. R. *Pure and Appl Chem,* **2000,** *72*, 1391.
16. (a) Zim,D.; de Souza, R. F.; Dupont, J.; Monteiro, A. L. *Tetrahedron Lett.* **1998**, *39*, 7071-7074. (b) Welton, T. *Chem Rev.* **1999**, *99*, 2071-2083. (c) Saleh, R. Y.

W02000015594, **2000**[*Chem. Abstr*. **2000**, *132*, P222341]. (d) Adams, C.J.; Earle,M.J.; Seddon, K. R. *Green Chemistry*, **2000**, *2*, 21-23 (e) Green, L.; Hemeon, I.; Singer, R. D. *Tetrahedron Lett.* **2000**, *41*, 1343-1346.

17. (a) Chauvin, Y.; MuBman, L.; Olivier, H. *Angew. Chem.* **1995**, 107, 2941-2943.
18. Wilkes, J. S.; Zawootko, M. J. *J. Chem. Soc, Chem. Commun*. **1992**, 965-967.
19. (a) Pernak, J.; Czepukowicz, A.; Pozniak, R. *Ind. Eng. Chem. Res.* **2001**, 2379-2383.
    (b) Noda, A.; Hayamizu, K.; Watanable, M. *J. Phys. Chem. B*, **2001**, *105*, 4603-4610.
    (c) Suarez, P. A. Z; Dullius, J. E. L; Einloft, S.; de Souza, R. F.; Dupont, J. J. *Chem. Phys*. **1998**, *95*, 1626-1639.
20. Poole, C. F.; Kersten, B. R.; Ho, S. S. J.; Coddens, M. E.; Furton, K. G. *J. Chromatogr.* **1986**, 352, 407.
21. Shetty, P. H.; Youngberg, P. J.; Kersten, B. R.; Poole, C. F. *J. Chromatogr*. **1987**, *411*, 61.
22. Koch, V. R.; Nanjundiah, C.; Carlin, R. T. *World Pat*. **1997**, 9702252.
23. MacFarlane, D. R.; Meakin, P.; Sun, J.; Amini, N.; Forsyth, M. *J. Phys.Chem. B.* **1999**, *103*, 4164.
24. Davis, J. H. Jr.; Forrester, K. J.; Merrigan, T. *J. Tetrahedron Lett*. **1998**, *39*, 8955.
25. Ito, K.; Nishina, N.; Ohno, H. *Electrochim. Acta*. **2000**, *45*, 1295. 34.
26. Ohno, H., *Ed.; in Electrochemical Aspects of Ionic Liquids John Wiley and Sons: Hoboken, NJ*. **2005**.
27. (a) Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D. W. *J. Am. Chem. Soc*. **2002**, *124*, 14247. (b) Lagrost, C.; Preda, L.; Volanschi, E.; Hapiot, P. *J. Electroanal. Chem*. **2005**, *585*, 1. (c) O'Toole, S.; Pentlavalli, S.; Doherty, A. P. *J. Phys. Chem. B*. **2007**, *111*, 9281.
28. Dupont, J.; Consorti, C. S.; Saurez, P. A. Z.; de Souza, R. F. *Org. Synth*. **2002**, *79*, 236.
29. Dupont, J.; Consorti, C. S.; Saurez, P. A. Z.; de Souza, R. F. *Org. Synth.* **2004**, *10*, 184.
30. Gordon, C. M.; McLean, A. J.; Dunkin, I. R. *in Ionic Liquids as Green Solvents: Progress and Prospects;* Rogers, R. D.; Seddon, K. R. *Eds.; ACS Symposium Series 856*; *American Chemical Society: Washington, D*C, **2003**.
31. Varma, R. S.; Namboodri, V. V. *Chem. Commun*. **2001**, 643.
32. Deetlefs, M.; Sedon, K. R. *Green Chem*. **2003**, *5*, 181.
33. Leveque, J-M.; Luche, J-L.; Petrier, C.; Roux, R.; Bonrath, W. *Green Chem*. **2002**, *4*, 357.
34. Leveque, J-M.; Desset, S.; Suptil, J.; Fachinger, C.; Draye, M.; Werner, B.; Cravotto, G. *Ultrasonics Sonochem*. **2006**, *13*, 189.

35. Varma, R. S.; Namboodri, V. V. *Org. Lett*. **2002**, *4*, 3161.

36. Earle, M. J.; Gordon, C. M.; Plechkova, N. V.; Seddon, K. R.; Welton, T. *Anal. Chem*. **2007**, *79*, 758.

37. Nockemann, P.; Binnemans, K.; Driesen, K. *Chem. Phys. Lett*. **2005**, *415*,131.

38. Burrell, A. K.; Del Sesto, R. E.; Baker, S. N.; McCleskey, T. M.; Baker, G. A. *Green Chem*. **2007**, *9*, 449.

39. Page, P. M.; McCarty, T. A.; Baker, G. A.; Baker, S. N.; Bright, F. V. *Langmuir*. **2007**, *23*, 843.

40. Handy, S. T.; Okello, M.; Dickenson, G. *Org. Lett*. **2003**, *5*, 2513.

41. (a) Abbott, A. P.; Capper, G.; Davies, D. L.; Munro, H. L.; Rasheed, R. K.; Tambyrajah, V. *Chem. Commun*. **2001**, 2010. (b) Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajah, V. *Green Chem*. **2002**, *4*, 24. (c) Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajah, V. Chem. Commun. **2003**, 70. (d) Wasserscheid, P.; Boesmann, A.; Bolm, C. *Chem. Commun*. **2002**, 200.

42. Glasser, L. *Thermochem. Acta*, **2004**, *421*, 87-93.

43. Dieter, K. M.; Dymek, C. J.; Heimer, N.E.; Rovang, J.W.; and Wilkes, J.S. *J. Am. Chem. Soc*. **1988**, *110*, 2722–2726.

44. Karpinski, Z. J.; Osteryoung, R. A. *Inorg. Chem*., **1984**, *23*, 4561.

45. Suarez,P. A. Z.; Einloft, S.; Dullius, J. E. L.; de Souza, R. F.; Dupont,J. *J. Chem. Phys. Phys.-Chem. Biol.* **1998**, *95*, 1626–1639.

46. Ozawa, R.; Hayashi, S.; Saha, S.; Kobayashi, A.; and Hamaguchi, H. *Chem. Lett*. **2003**, *32*, 948-949.

47. Hayashi, S.; Ozawa, R.; Hamaguchi, H. *Chem. Lett*. **2003**, *32*, 498-499.

48. Talaty, E. R.; Raja, S.; Storhaug, V. J.; Dolle, A.; Carper, W. R. *J. Phys. Chem. B*. **2004**, *108*, 13177–13184.

49. Bradley, A. E.; Hardacre, C.; Holbrey, J. D.; Johnston, S.; McMath, S.E. J.; Nieuwenhuyzen, W. *Chem. Mater*. **2002**, *14*, 629–635.

50. Carmichael,A.J.; Hardacre,C.; Holbrey,J.D.; Nieuwenhuyzen, M.; Seddon, K. R. *Mol. Phys*. **2001**, *99*, 795–800.

51. Rovere, M.; Tosi, M.P. *Rep. Prog. Phys*. **1986**, *49*, 1001–1081.

52. Biggin, S.; Enderby, J. E. *J. Phys. C*, **1982**, *15*, L305–L309.

53. Martin, J.D. *ACS Symp. Ser*. **2002**, *818*, 413–427.

54. Cang, H.; Li, J.; Fayer, M. D. *J. Chem. Phys*. **2003**, *119*, 13017–13023.

55. Holbrey, J.D.; Reichert,W.M.; Nieuwenhuyzen, M.; Sheppard,O.; Hardacre, C.; Rogers, R.D. *Chem. Commun*. **2003**, 476–477.
56. Deetlefs, M.; Hardacre, C.; Nieuwenhuyzen,M.; Sheppard, O.; Soper, A. K. *J. Phys. Chem. B*. **2005**, *109*, 1593–1598.
57. Bronger, R. P. J.; Silva, S. M.; Kamer. P. C. J.; van Leeuwen, P. *Chem. Commun*. **2002**, 3044–3045.
58. Diego, T. De.; Lozano,P.; Gmouh, S.; M. Vaultier, M.; Iborra, J. L. *Biomacromolecules*. **2005**, *6*, 1457–1464.
59. Lozano,P.; Diego,T. De.; Carrie, D.; Vaultier, M.; Iborra,J.L. *Biotechnol. Prog*. **2003**, *19*, 380–382.
60. Swatloski, R.P.; Spear, S. K.; Holbrey, J.D.; Rogers, R. D. *J. Am. Chem. Soc*. **2002**, *124*, 4974–4975.
61. Urahata, S.M.; Ribeiro, M. C. C. *J. Chem. Phys*. **2004**, *120*, 1855–1863.
62. Urahata, S. M.; Ribeiro, M. C. C. *J. Chem. Phys*. **2005**, *122*, 024511.
63. Wang, Y. T.; Voth, G. A. *J. Am. Chem. Soc*., **2005**, *127*, 12192–12193.
64. (a) Rogers, R. D.; Seddon, K. R. (Eds). *Ionic Liquids IIIB: Fundamentals, Progress, Challenges, and Opportunities: Transformations and Processes*, ACS Symposium Series, Vol. 902, *AmericanChemical Society, Washington DC* (**2005**). (b) Rogers, R.D.; Seddon, K. R.; (Eds). *Ionic Liquids IIIA: Fundamentals, Progress, Challenges, and Opportunities: Properties and Structure*, ACS Symposium Series, Vol. 901, *American Chemical Society, Washington DC* (**2005**). (c) Scammells, J.; Scott, J. L.; Singer, R. D. *Aust. J. Chem.* **2005**, *58*, 155. (d) Anderson, J. L.; Armstrong, D. W.; Wei, G.T. *Anal. Chem.* **2006**, *78*, 2893. (e) J. Earle, J.; Seddon, K. R. *Pure Appl. Chem.* **2000**, *72*, 1391. (f) Endres, F.; El Abedin, S. Z. *Phys. Chem. Chem. Phys*. **2006**, *8*, 2101.
65. Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*, 2nd ed., Wiley-VCH, Weinheim (**2007**).
66. Harper, J. B.; Kobrak, M. N. *Mini-Rev. Org. Chem.* **2006**, *3*, 253.
67. Reichard, C. *Solvent and Solvent Effects in Organic Chemistry*, 3rd ed., Wiley VCH, Weinheim(**2003**).
68. Weingartner, H. Z. *Phys. Chem*. **2006**, *220*, 1395.
69. Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B.* **2006**, *110*, 19593.
70. Bright, F. V.; Baker, G. A. *J. Phys. Chem. B.* **2006**, *110*, 5822.
71. Lungwitz, R.; Spange, S. *New J. Chem*. **2008,** *32*, 392.

72. Lungwitz, R.; Friedrich, M.; Linert, W.; Spange, S. *New J. Chem***. 2008**, *32,* 1493.
73. Chiappe, C.; Malvaldi, M.; Pomelli, C. S. *Pure Appl. Chem*. **2009**, *81*, 769.
74. Santos, L. M. N. B. F.; Lopes, J. N. C.; Coutinho, J. A. P.; Esperanca, J. M. S. S.; Gomes, L. R.; Marrucho, I. M.; Rebelo, L. P. N. *J. Am. Chem. Soc*. **2007**, *129*, 284.
75. Red, N.; Carmichael, A. J. *J. Phys. Org. Chem*. **2000**, *13,* 591.
76. MacFarlane, D.; Pringle, J. M.; Johansson, K. M.; Forsyth, S.; Forsyth, M. *Chem. Commun*. **2006**, 1905.
77. Chowdhury, P. K.; Halder, M.; Sanders, L.; Calhoun, T.; Anderson, J. L.; Armstrong, D. W.; Song, X.; Petrich, J. W. *J. Phys. Chem. B.* **2004**, *108,* 10245.
78. Ngo, H. L.; LeCompte, K.; Hargens, L.; McEwen, A. B. *Thermochim. Acta.* **2000**, *357-358, 97.*
79. Wu, B.; Reddy, R. G.; Rogers, R. D. *Novel ionic liquid thermal strorage for solar thermal electric power systems. Proceeedings of Solar Forum 2001. Washington, DC,* **2001**.
80. Moens, L.; Blake, D. M.; Rudnicki, D. L.; Hale, M. J. *J. Sol. Energy Eng*. **2003**, *125*, 112.
81. Reddy, R. G.; Zhang, Z.; Arenas, M. F.; Blake, D. M. *Thermal stability and corrosivity evaluations of ionic liquids as thermal energy storage media. High Temp. Mater. Processes* **2003**, 22–87.
82. Van Valkenburg, M. E.; Vaughn, R. L.; Williams, M.; Wilkes, J. S. *Thermochim. Acta*. **2005**, *425,*181.
83. Holbrey, J. D.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1999**, 2133.
84. Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gra¨tzel, M. *Inorg. Chem.* **1996**, *35*, 1168.
85. Scurto, A. M.; Leitner, W. *Chem. Commun.* **2006**, 3681.
86. Scurto, A. M.; Newton, E.; Weikel, R. R.; Drauckner, L.; Hallett, J.; Liotta, C. L.; Leitner, W.; Eckert, C. A. *Ind. Eng. Chem. Res.* **2008**, *47*, 493.
87. Kazarian, S. G.; Sakellarios, N.; Gordon, C. M. *Chem. Commun.* **2002**, 1314.
88. Kanakubo, M.; Hiejima, Y.; Minami, K.; Aizawa, T.; Nnajo, H. *Chem. Commun.* **2006**, 128.
89. Trohalaki, S.; Pachter, R. *QSAR Comb. Sci.* **2005**, *24,* 485.
90. Varnek, A.; Kireeva, V.; Tetko, I. V.; Baskin, I. I.; Solovev, V. P. *J. Chem. Inf. Model.* **2007**, *47,*1111.
91. Carrera, G.; Aires-de-Sousa, J. *Green Chem.* **2005**, *7*, 20.

92. Bini, R.; Chiappe, C.; Micheli, A.; Soalro, R.; Starita Tine´, M. R. *Green Chem.* **2008,** *10*, 306.
93. Naoto, N.; Tomonori, M.; Takeo, K. **2006**, *86*, 721.
94. Huddleston, J. G.; Visser, A. E.; Reichert, W.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3,* 156.
95. Crosthwaite, J. M.; Muldoon, M. J.; Dixon, J. K.; Anderson, J. L.; Brennecke, H. F. *J. Chem. Thermodyn.* **2005**, *37*, 559.
96. Del Sesto, R. E.; Corley, C.; Robertson, A.; Wilkes, J. S. Tetraalkylphosphonium-based ionic liquids. *J. Organomet. Chem.* **2005**, *690*.
97. Kroon, M. C.; Buijs, W.; Peters, C. J.; Witkamp, G. J. *Thermochim. Acta* **2007**, *465*, 40.2536.
98. Rebelo,L. P. N.; Lopes, J. N. C.; Esperanca, J. M. S. S.; Filipe, E. *J. Phys. Chem. B*. **2005**, *109*, 6040.
99. Fraser,K.J.; Izgorodina, E. I.; Forsyth,M.; Scott,J.L.; MacFarlane,D.R. *Chem. Commun*. **2007**, 3817.
100. Holbrey, J. D. Rogers, R. D. *in Ionic Liquids in Synthesis, ed*. Wasserscheid, P.; Welton, T. *Wiley-VCH, Weinheim*, **2008**, *vol.1*, p. 57.
101. Gupta, S.; Olson, J. D. *Ind. Eng. Chem. Res.* **2003**, *42,* 6359.
102. Jacquemin, J.; Husson, P.; Padua, A. A. H.; Majer, V. *Green Chem.* **2006**, *8*, 172
103. Seddon, K. R.; Stark, A.; Torres, M. J. *Pure Appl. Chem.* **2000,** *72*, 2275.
104. Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 4th *ed.; McGraw-Hill: New York*, **1987**.
105. Gardas, R. L.; Coutinho, J. A. P. *Fluid Phase Equilib.* **2008**, *266*,195.
106. Gardas, R. L.; Coutinho, J. A. P. *AIChE J.* **2009,** *55*, 1274.
107. Coutinho, J. A. P.; Gardas, R. L. *Predictive Group Contribution Models for the Thermophysical Properties of Ionic Liquids. In Ionic Liquids: From Knowledge to Application; Plechkova, N. V., Rogers, R. D., Seddon, K. R., Eds.; ACS Symp. Ser. 1030; American Chemical Society: Washington, DC*, **2009**; p 385.
108. Bockris, J. O'M.; Reddy, A. K. N. *Modern Electrochemistry* **1970**, *Plenum Press, New York, Vol. 1. Ch. 6.*
109. Abbott, A. P. *ChemPhysChem.* **2004,** *5*, 1242.
110. Jiqin, Z.; Jian, C.; Chengyue, L.; Weiyang, F. *J. Chem. Eng. Data*. **2007**, *52,* 812.
111. Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B.* **2004**, *108*, 16593.

112. Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B.* **2005**, *109*, 6103.

113. Papaiconomou, N.; Salminen, J.; Lee, J.-M.; Prausnitz, J. M. *J. Chem. Eng. Data*. **2007**, 52, 833.

114. Okoturo, O. O.; VanderNoot, T. J. *J. Electroanal. Chem*. **2004,** *167*, 568.

115. Ohno, H., *Ed.; in Electrochemical Aspects of Ionic Liquids John Wiley and Sons: Hoboken, NJ,* **2005.**

116. Xu, W.; Cooper, E. I.; Angell, C. A. *J. Phys. Chem. B.* **2003**, *107*, 6170.2005, 109, 6103

117. Noda, A.; Hayzamizuk, K.; Watanable, M. *J. Phys. Chem. B. 105,***200**1,4603.

118. Jiqin, Z.; Jian, C.; Chengyue, L.; Weiyang, F. *J. Chem. Eng. Data* **2007**, 52, 812.

119. Every, H. A.; Bishop, A. G.; MacFarlane, D.; Oradd, G.; Forsyth, M. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1758.

120. Bonhote, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem*. **1996**, *35*, 1168.

121. Fitchett, B. D.; Knepp, T. N.; Conboy, J. C. *J. Electrochem. Soc.* **2004**, *151*, E219.

122. McEwen, A. B.; Ngo, H. L.; LeCompte, K.; Goldman, J. L. *J. Electrochem. Soc*. **1999**, *146*, 1687.

123. Dzyuba, S. V.; Bartsch, R. A. *ChemPhysChem*. **2002**, *6*, 161.

124. Law, G.; Watson,P.R. *Langmuir*, **2001**, *7*, 6138.

125. W. Martino, J. F. de la Mora, Y. Yoshida, G. Saito and J. Wilkes, *Green Chem*; **2006**, *8*, 390.

126. Freire, M. G.; Carvalho, P. J.; Fernandes, A. M.; Marrucho, I. M.; Queimada, A. J.; Coutinho, J.A. P. *J. Colloid Interface Sci.* **2007**, *314*, 621.

127. Zhang, J.; Tong, J.; Li, J.; Li, J.; Tong, J. *J. Colloid Interface Sci.* **2007**, *313*, 374.

128. Gardas, R. L.; Coutinho, J. A. P. *Fluid Phase Equilib.* **2008**, *265*, 57.

129. Gardas, R. L.; Rooney, D. W.; Hardacre, C. *Fluid Phase Equilib.* **2009,** *283*, 31.

130. Gonza´lez-Melchor, M.; Bresne, F.; Alejandre, J. *J. Chem. Phys.* **2005**, *122*, 104710.

131. Heggen, B.; Zhao, W.; Leroy, F.; Dammers, A. J.; Mu¨ller-Plathe, F. *J. Phys. Chem. B* 2010, *114*, 6954.

132. Karodia, N.; Guise, S.; Newlands, C.; Anderson, J. A. *Chem. Commun*; **1998**, 2341.

133. Anastas, P. T.; Kirchhoff, M. M. *Acc. Chem. Res*. **2002**, *35*, 686.

134. Welton, T. *Cordination chemistry Reviews*, **2004**, *248*, 2459.
135. Parvulescu, V. I. *Chem. Rev*. **2007**, *107*, 2615.
136. Wasserchied P.; Keim, W. *Angew. Chem. Int. Ed*. **2000**, *39*, 3772.

137. Sauer, J.; Sustamann, R. *Angew. Chem. Int. Ed. Engl*. **1980**, *19*, 779.

138. Griffiths, G. J.; Previdoli, F. E. J. Org. Chem. 1993, 58, 6129.
139. Blokziji, W.; Blandamer, M. J.; Engberts, B. F. N. *J. Am. Chem. Soc*. **199**1, *13*, 4241.

140. Earle, M.J.; McCormac, P. B.; Seddon, K. R. *Green Chem*. **1999**, *1*, 517.
141. Tiwari, S.; Khupse, N.; Kumar, A. *J. Org. Chem.* **2008,** *73*, 9075.
142. Tiwari, S.; Kumar, A. *Angew. Chem. Int. Ed.* **2006,** *45*, 4824.
143. Nematollahi, D.; Workentin, M. S.; Tammari, E. *Chem. Commun*. **2006**, 163.

144. Smith, M. B.; March, *J. March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, 6th ed.; John Wiley: New York,* **2007.**

145. Wheeler, C.; West, K. N.; Liotta, C. L.; Ekert, C. A. *Chem. Commun*. **2001**, 887.

146. Lancaster, N. L.; Welton, T.; Young, G. B. *J. Chem. Soc., Perkin Trans*. **2001**, *2*, 2267.

Chapter 2

Diels-Alder reaction in N-alkyl imidazolium based Ionic Liquids: A kinetic investigation using BMIM][BF_4]-Water and [BMIM][Cl] –Water Solvent systems

Introduction

Owing to their remarkable physicochemical properties (1-4) room temperature ionic liquids (RTILS) are being advocated as green solvents for chemical processes. These neoteric solvents possess insignificant vapour pressure, are non-flammable, have wide liquidus range and possess excellent potential of specifically solvating varied natured compounds. Additionally the physicochemical properties of RTILs can be tuned as per the requirement. Very recently many RTILs have been found to exhibit significant catalytic activity for a variety of industrially and synthetically important chemical reactions (5). In view of all these potentialities of RTILs, synthetic chemists have started showing great interest towards exploration of the impact of variedly constituted RTILs on the kinetics of diverse type of solvent sensitive chemical transformations.

Diels–Alder reaction is an important class of synthetically important reactions that has been found to show strong dependence on the solvent characteristics (6). The Diels-Alder reaction is one of the important C-C bond forming reactions employed for the synthesis of natural products and bio-active molecules with fine control over stereo-selectivity of the products (7). Owing to the remarkable importance of the Diels-Alder reaction in organic synthesis and chemical industry (8), activities aimed at developing newer methods to improve the yield and selectivity are always in great demand. Diels-Alder reaction is basically the [$4\pi+2\pi$] concerted cycloaddition reaction between a diene (4π) and a dienophile (2π) which is governed by Woodward-Hoffmann’s rules i.e. thermally allowed reaction (9). However Saucer and Sustmann and Houk and co-workers (10, 11) have reported that this reaction could occur by different mechanism instead of the concerted one. Initial mechanistic studies which established the formation of isopolar activated complexes during the progress of Diels-Alder reaction implied a weak solvent effect on its kinetics (10). However, the experimental reports related to rate enhancements of the Diels-Alder reaction in water have opened up new means for tuning the kinetics of such reactions through solvent variations. The much higher rate constant of Diels-Alder reaction in water ascribed to hydrophobic interactions, was first of all reported by Rideout and Breslow (12), who carried out the reaction between cyclopentadiene and methylvinyl ketone and reported 730 fold increase of rate constant in water than in 2,2,4-trimethylpentane. The report is marked as a turning point in organic chemistry because in addition to economical and environmental advantages of water the report was first to establish the surprising beneficial effects on the reaction rates of chemical transformations (12-19). Grieco and co-workers have also reported the advantageous role of water on the Diels-Alder reaction during the synthesis of quassinoids (20, 21). They have also reported the usefulness of water in rate enhancement of Diels-Alder reaction of diene carboxylates with varying dienophiles which include ammonium diene carboxylates, monosodium diene phosphonate and dienylammonium chloride (22, 23). There are numerous reports wherein addition of salts to aqueous solution of Diels-Alder reactant mixtures has been reported to strongly influence the mechanistic and kinetic aspects of the Diels-Alder reaction (12, 24-26). In these reports it has been reported that kinetics of the reaction is strongly sensitive to the nature and concentration of the additive salt. Different aqueous salt solution when used to analyse role of anions on the reaction rates by employing family of sodium salts like NaCl, NaBr, $NaBF_4$,$NaClO_4$,$NaPF_6$ and $NaAsF_6$ were found to accelerate the reaction rates and increase of rate constant dependent on size of anions. However decrease in reaction rates have been reported in case of guanidinium salts. There have been reports highlighting the impact of salt solutions on the selectivity of the Diels-Alder reaction (27, 28). Thus while salts such as LiCl, NaCl, NaBr, $CaCl_2$ were reported to enhance the selectivity i.e. N/X ratio the salts like $LiClO_4$ and $GnCl_4$ have been found to decrease the selectivity with former being more effective.

In view of their eco-green features, structured nature and salt like behaviour in aqueous solution, exploration of the impact of RTILs as solvent or as salts on the mechanistic and kinetic aspects of Diels-Alder reaction seems very attractive. Both rate and stereo-selectivity enhancements have been achieved while using ionic melts like $[EtNH_4][NO_3]$, $AlCl_3$: MCl, (MCl being N-1-butylpyridinium chloride or 1-ethyl-3-methyl-1H-imidazolium chloride) as solvent for the said reactions (29). The observed impact on the rate and stereo-selectivity of the explored reactions has been ascribed to the high cohesive energy density, hydrophobic effect, Lewis acidity of these salts/salt mixtures (30, 31). Moisture-stable ionic liquids and their solutions have also been investigated for their impact on the kinetics of the Diels-Alder reaction (32), and the results explained in light of micro-viscosity and polarity parameters like electronic transition energy E_T^N, hydrogen bond donor ability; acidity (α), hydrogen bond acceptor ability; basicity (β) and polarizability (π*) (33, 34, 35, 36, 37).

In view of the reported salt sensitive behaviour of Diels-Alder reaction in aqueous phase and interesting properties of RTIL + water mixtures absence of reports related to impact of such mixtures on the kinetics of Diels-Alder reaction seems quite surprising. In light of above mentioned facts we carried out detailed kinetic investigations on the Diels-alder reaction between cyclopentadiene and benzoquinone in differently concentrated binary mixtures of imidazolium based ionic liquids in water.

2.1. Experimental Section

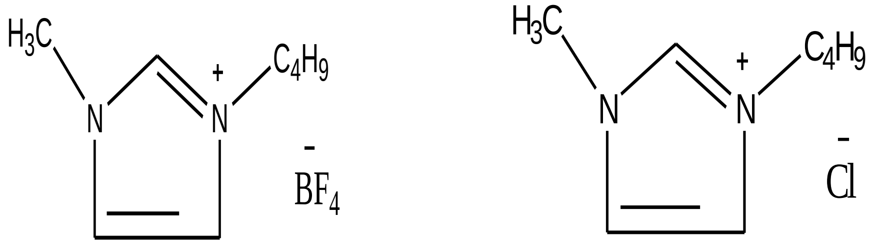
2.1.1. Materials and Methods

All the chemicals required for kinetic studies were of high purity spectroscopic grade. Acetonitrile (GR grade, 99.9%) and MeOH (GR grade, 99.9%) were purchased from Merck, India and purified following reported standard methods (38).

Synthesis of Cyclopentadiene**:** Fresh samples of cyclopentadiene were synthesized through cracking of its dimer dicyclopentadiene, following reported literature procedure (39). Briefly 200 ml of liquid paraffin were placed in a 500ml, three necked round bottom flask fitted with a large (30cm) Vigreux column, a dropping funnel and a thermometer dipping into the paraffin oil. A distillation head carrying a thermometer and a double surface condenser was attached. The liquid paraffin was heated to about 200-240^{0}C and dicyclopentadiene was added portion wise from the dropping funnel and the cyclopentadiene fraction having boiling point 40^{0}C-42^{0}C, which distils over was collected in an ice cooled receiver, protected from moisture. The dicyclopentadiene is added slowly to ensure complete breakdown of the dimer; the temperature at the top of still-head rises above 42^{0}C when addition is too rapid. The addition of dicyclopentadiene (300ml) was continued until 230g of cyclopentadiene were obtained. Since the diene dimerises readily at room temperature, it was used immediately or stored in the ice compartment of a refrigerator overnight.

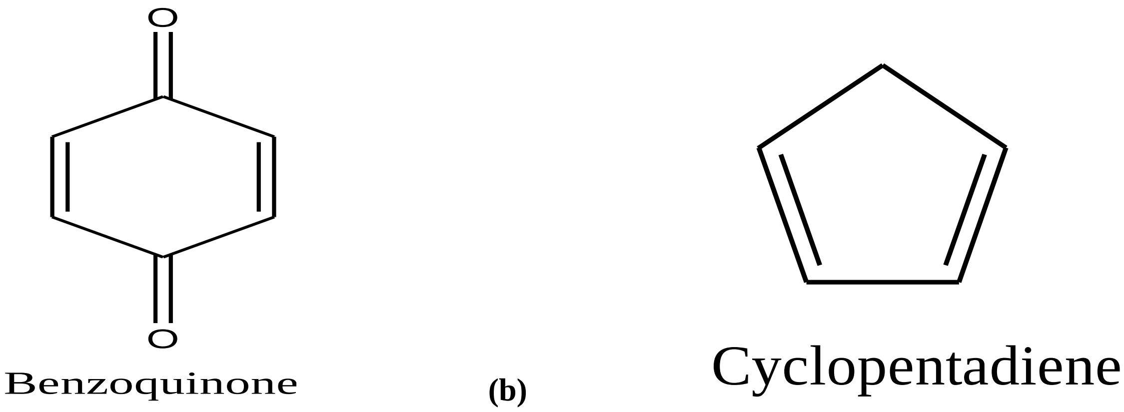
Synthesis of bezoquinone: Benzoquinone used as dienophile was synthesised following the reported procedure (39). Briefly 3.3 g of H_2Q were dissolved in 15 ml of 60% acetic acid, the mixture was cooled to about 0- 5°C in an ice bath. 4.2 g CrO_3 was separately dissolved in 7 mL of water and 3 mL of glacial acetic acid. The resulting solution was mixed to the chilled hydroquinone solution slowly with constant stirring and the temperature of bath was maintained below 5°C. Reaction mixture was stirred further for 70 minutes at the same temperature. The product was filtered, washed with 2-3 mL ice cold water several times. Bright yellow crystals of BQ were obtained (yield ca. 60%). The crystals being light sensitive were stored in dark colored sample vials.

***Synthesis of Ionic Liquids**:* Electrochemical purity grade imidazolium based room RTILs viz. [BMIM][Cl] and [BMIM][BF$_4$] were synthesized following a two step procedure (40) as reported earlier (41, 42). Briefly, in the first step 1-methylimidazole was refluxed with n-butyl chloride for 90 hrs under argon atmosphere for the synthesis of 1-butyl-3-methylimidazolium chloride as a white crystalline solid. In the next step the halide anion was exchanged with [BF$_4$]$^-$ on treatment with HBF$_4$. The ILs was vacuum dried and stored in desiccators under inert atmosphere and were characterized through ^{1}H-NMR, mass spectrometry and ^{13}C-NMR spectroscopy. The water content of dried ILs was less than 50 ppm, as analyzed by Karl Fischer titration. The chemical structure of RTILS used, diene and the dienophile in present study are presented in scheme 2.1.



1-butyl-3-methyl imidazolium tetrafluoroborate 1-butyl-3-methyl imidazolium chloride

(a)



Scheme 2.1. Structure of ionic liquids (a) and reactants (b) used for the Diels alder reaction.

2.1.2. Kinetic measurements:

For the kinetic measurements, to the RTIL-Water binary solvent systems (with RTIL concentration varying from 0.0-2.0 M), taken in quartz cuvette of path length 1cm, under a continuous stirring appropriate amount of benzoquinone and cyclopentadiene stock solutions were added so that their resulting concentrations in well mixed mixture were 0.1 and 10 mM respectively. The progress of the reaction was monitored by following the decay of the absorbance peak of the dienophile i.e benzoquinone at λ=245.5 nm using a Schimadzu 1650 PC Spectrophotometer. The temperature of cell was controlled and maintained at 25^0C by using circulating water bath with an accuracy of $\pm 0.1^0$C.

Surface tension measurements of various RTILS-Water solvent systems corresponding to different concentration (molarity) were made by the platinum ring detachment method with a Krüss-9 (Germany) tensiometer equipped with a thermo-stated vessel holder. Measurements were made after temperature equilibration at 25^0C (±0.1%) by circulating water from a HAAKE GH thermostat through the vessel holder. The results were accurate within ±0.1% mNm^{-1} and three concordant readings were taken to ensure reproducibility.

Density measurements of various RTIL-Water solvent mixtures were made at 25^0C by using the Anton Paar DMA 4500M density meter.

Finally coefficients of viscosity of different solutions of RTIL-Water solvent systems were carried out using Anton Paar MCR102 rheometer. The viscosity measurements were made at 25^0C using measuring system with specification (CP50-1, Angle = 1.006^o & diameter = 49.985mm).

2.1.3. Computational analysis

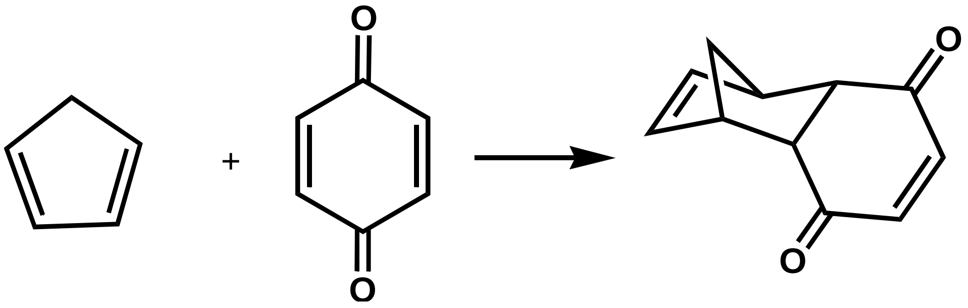
Structural optimizations were performed using the Gaussian 03 quantum chemistry package (43). The initial geometries were optimized by DFT level of theory using Becke's three parameter hybrid functional (B3LYP) (44, 45) and the 6-31G (d, p) basis set. Frequency analysis was performed on the optimized structure at the same level of theory and no imaginary frequencies were found.

2.2. Results and Discussion

The kinetic plots depicting variation of absorbance at λ=245.5 (λ_{max} of benzoquinone) versus time (sec) for the Diels-Alder reaction between cyclopentadiene (10 mM) and benzoquinone (0.1 mM) (scheme 2.2) as recorded in variedly concentrated ionic liquid – water solvent media viz. [BMIM][BF_4] + Water and [BMIM][Cl] + Water solvent systems are presented as Figure 2.1. Since the concentration of the diene (cyclopentadiene) was kept about hundred times higher than the dienophile (benzoquinone), the recorded UV data were analysed in light of integral rate law corresponding to pseudo first order reactions;

$$k = \frac{1}{t}\left(ln\frac{A_o}{A_t}\right) \tag{2.1}$$

where, '*k*' is the pseudo Ist order rate constant, '*t*' is time in seconds,' 'A_o' is absorbance at zero time and 'A_t' is the absorbance at time, *t*. The rate constants reported in the presented work as enlisted in Table 1, and plotted in Figure 2.2.a. are an average of results from three kinetic runs recorded under similar conditions. The results from different runs were observe to be reproducible within ±5%.



(1) (2) (3)

Scheme 2.2. Diels –alder reaction between diene (1) and dienophile (2) to form product (3).

The presented data (Table 2.1.; Figure 2.2.a.) clearly indicate that addition of the used RTILs decreases the magnitude of the rate constant for the investigated reaction with an extent depending upon the nature and the concentration of the RTIL. It is evident that the addition of [BMIM][BF_4] is more effective in decreasing the rate constant than its [BMIM][Cl] counterpart. Previously published reports suggest that a variety of factors like internal pressure, Lewis-acid catalysis, hydrogen bonding, hydrophobic hydration, aggregation etc. (12, 46-50) can be responsible for the observed impact of salt-water reaction media on the kinetics of Diels-Alder reactions. To know the exact cause responsible for the observed rate deceleration due to addition of RTILs in present case, extensive examination of variations in bulk (density, viscosity) and surface properties of the investigated solvent systems was undertaken.

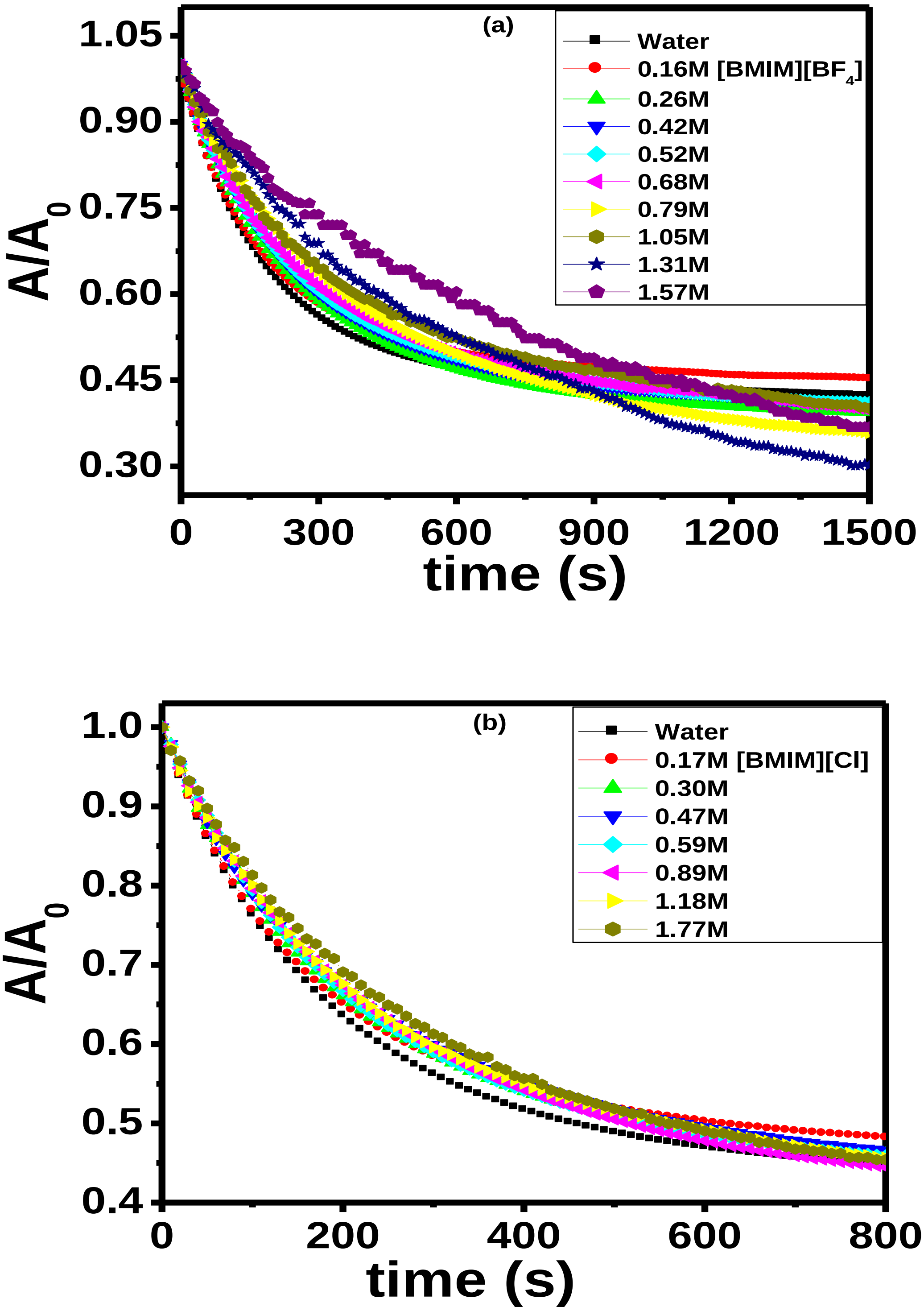


Figure 2.1. Variation of absorbance with time by changing concentration of ionic liquids in RTILS-Water solvent media (a) [BMIM][BF$_4$](b) [BMIM][Cl].

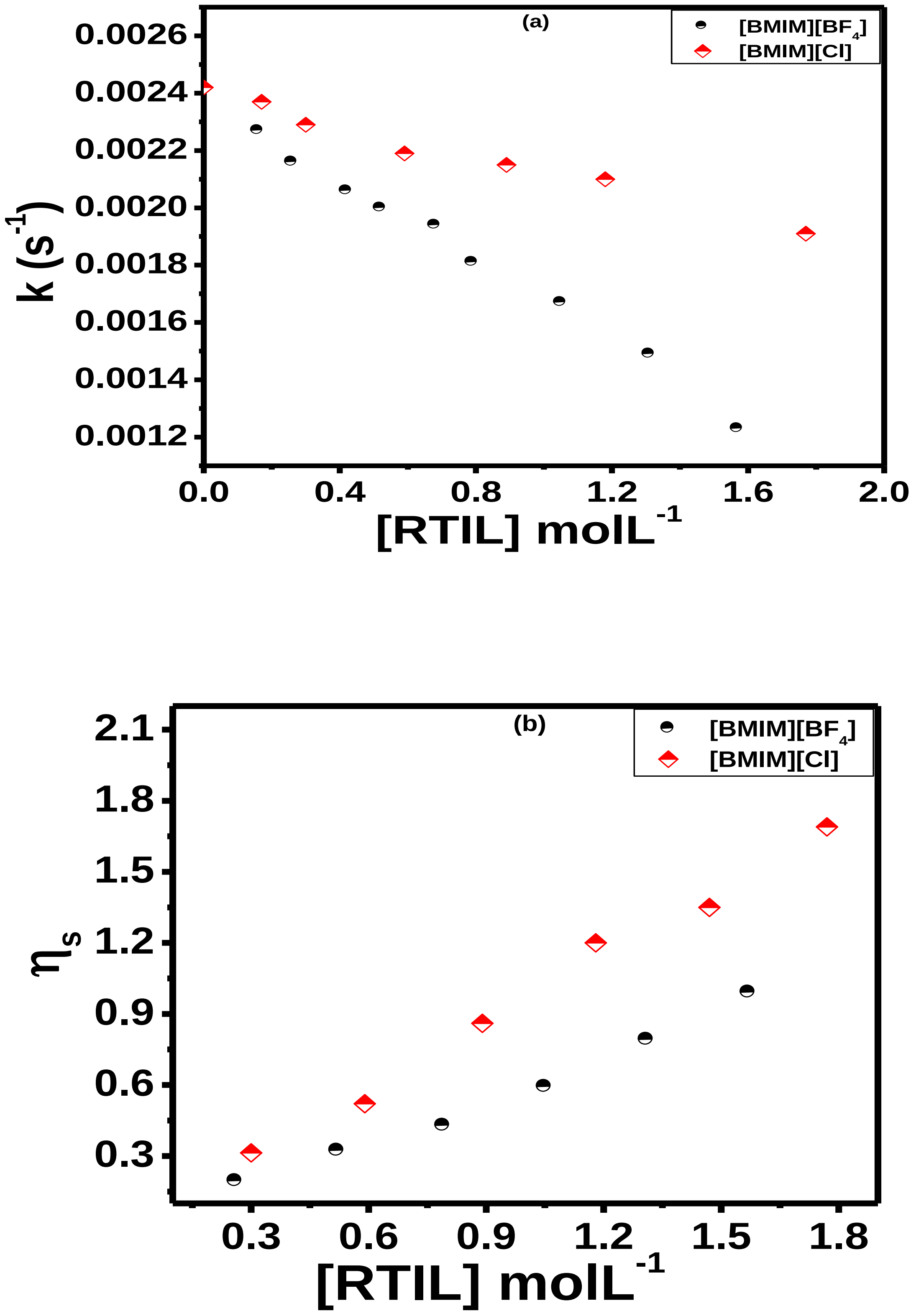


Figure 2.2. Variation of (a) rate constant and (b) specific viscosity with changing concentration of ionic liquids in RTIL-Water solvent mixtures

Figure 2.2 (b) depicts the variation in specific viscosity as a function of concentration of RTIL in the water. As clear from these plots addition of both RTILs increases the viscosity of water in a concentration dependent manner. Previous reports (51) have established that increase in the viscosity does retard the rate of intermolecular Diels-Alder reaction. On prima facie it can be suggested that the observed impact of RTILs on the kinetics of the investigated Diels–alder reaction is on account of the increase in the viscosity that reduces the translational diffusion motion and hence the rate of the reaction. Interestingly the slope of the linear fit equations for the data presented in figure 2.2 (b) suggest that specific capacity of [BMIM][Cl] to increase the relative viscosity of water is more than that of [BMIM][BF_4], which implies that the former should be more effective in reducing the rate than the later which is not in agreement with our observations (See Figure 2.2.a.) in the present investigation.

In addition to impact of transport characteristics, change in the structural organization of the solvent on addition of salt has been reported (52-54) to markedly influence the kinetics of Diels-alder reactions in Salt + water reaction media. To explore the same, we carried out density measurements of the RTIL+ water mixtures used as solvents in the present study. Figure 2.3 (a) depicts the variation in density as a function of RTIL concentration of the used solvent systems. The data was processed for estimation of excess volume in the investigated systems and the same are depicted in Figure 2.3 (b). As evident from the figure, while excess volume for water + [BMIM][BF_4] systems is positive for water + [BMIM][Cl] the excess volume is negative. The sign of the excess volume indicates that both RTILs mix non-ideally with water; while negative deviation (stronger interactions) is exhibited by water + [BMIM][Cl] system, positive deviations (weaker interactions) are displayed by water + [BMIM][BF_4] system. In light of the published reported related to mechanistic aspects of Diels-alder reactions in salt + water systems our density plus viscosity data implies that addition of [BMIM][BF_4] even if decreases the kinetics its deceleration effect on the kinetics should be lesser than that of [BMIM][Cl], this is totally opposite to what we observed in our kinetic investigations.

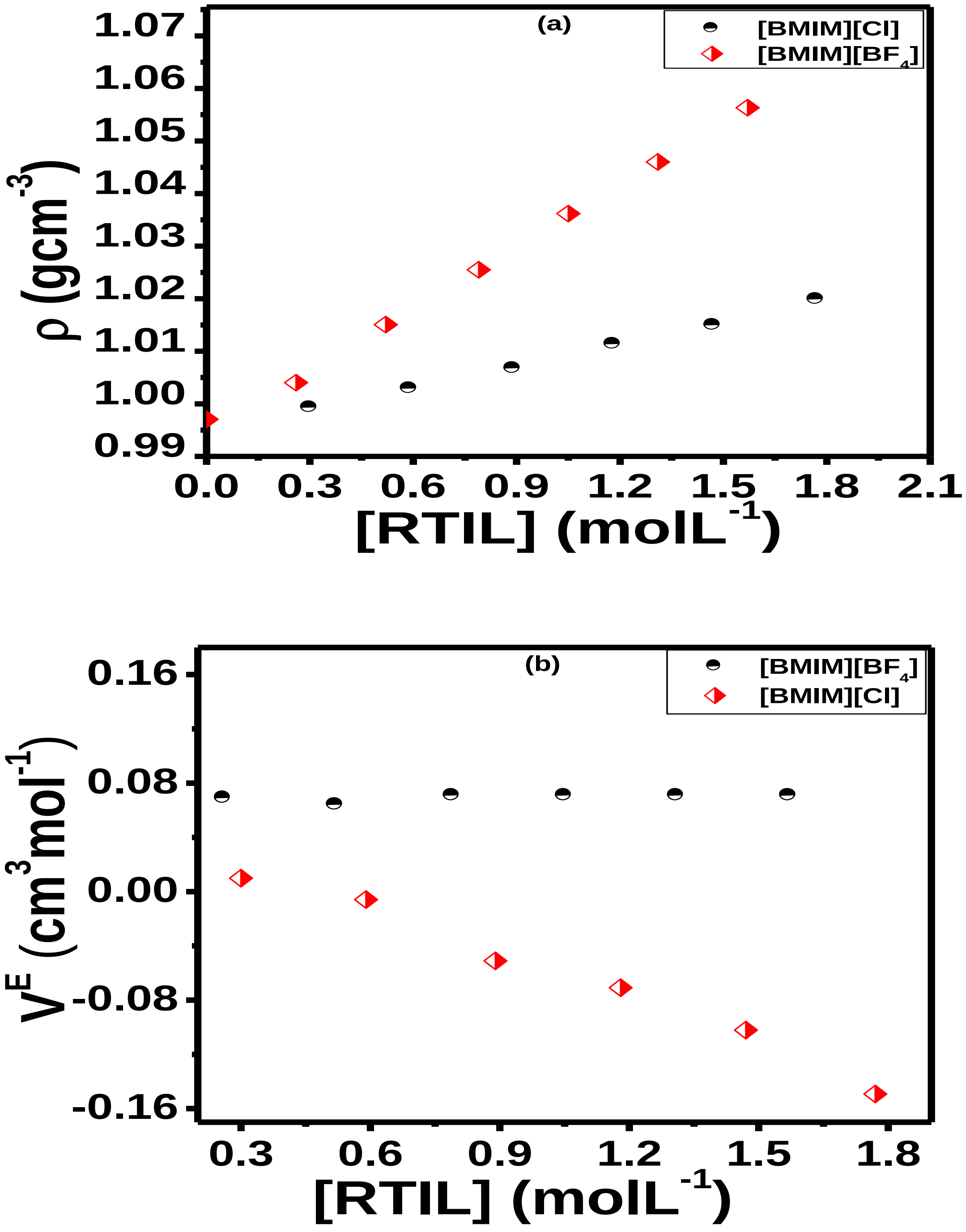


Figure 2.3. Variation of density (a) and excess volume (b) with concentration of ionic liquid in RTIL-Water solvent media

Variation in hydrophobic interactions on salt addition is another factor that has been reported (52-55) to be responsible for alteration in kinetic profile of Diels-Alder reactions. In these investigations it has been reported that variations in the extent of stabilisation of reactants/transition state on account of variations in hydrophobic surface area of the transition state and/or change in the extent of the hydrophobicity of the solvent system in aqueous solution do markedly influence the kinetics of the Diels-Alder reaction. The resultant variations are quantified in terms of thermodynamic relation;

$$\boldsymbol{\delta}(\Delta G^0)_{solution} = \delta(\Delta G^0)_{cavitation} + \delta(\Delta G^0)_{solute\ solvation} \qquad (2.2)$$

where,

$\delta(\Delta G^0)_{solution}$ represents the variation in free energy of solubilisation of the reactants, which is a measure of change in solubility of the reactants on addition of salt.

$\delta(\Delta G^0)_{cavitation}$= Change in Gibb’s energy of cavitation on addition of salt and

$\delta(\Delta G^0)_{solute\ solvation}$= Change in Gibb’s energy of solvation of the reactants on addition of salt.

To explore the actual reasons that are responsible for our observations related to dependence of kinetics on the composition of solvent system, we carried out surface tension measurements for the RTIL+ water systems used in our kinetic investigations. Figure 2.4 depicts the variation in surface tension of water with the addition of RTILs. As clear from the figure both the RTILs decrease the surface tension of water in a concentration dependent manner with [BMIM][BF$_4$] being more effective than the [BMIM][Cl]. This is in agreement with the report published by Russo et al. (56). The data presented in Figure 2.4 when analysed in light of Gibb’s Adsorption Isotherm as shown in equation 3. (57) indicate that for both the used RTILs viz. [BMIM][BF_4] and [BMIM][Cl] surface excess is positive and more for the former than the later.

$$\Gamma = -\frac{1}{RT}\left(\frac{d\gamma}{dlnc}\right) \tag{2.3}$$

Where,' Γ ' is the surface excess , 'R' is the gas constant, 'T' is the temperature, 'γ ' is the surface tension and 'c' is the concentration in mol/l.

Conventional ions are usually negatively adsorbed in water, and thereby exhibit negative surface excess in their aqueous solutions. The hydrophobic character of imidazolium based ionic liquids has been ascribed to the hydrocarbon chain and the imidazolium group of the cation. The higher hydrophobicity of [BMIM][BF_4] in comparison to [BMIM][Cl] in the present case can be attributed to the larger anion size and diffuse nature of the negative charge of BF_4^- that reduces its ability to hydrogen bonding and hence solubility in water (58). The observed decrease in surface tension of water with addition of RTIL which is similar to what has been reported earlier for Bu_4NCl, implies that addition of RTILs to water will lead to decrease in the energy required to produce a solvent cavity into which hydrophobic solutes (reactants of the investigated Diels-Alder reaction) can go into and thereby increases their solubility. In view of the reported behaviour of Bu_4NCl, it can be expected that both the RTILs will show a negative value for $\delta(\Delta G^0)_{solute\ solvation}$. To establish the same quantum chemistry calculations were performed to obtain gas phase optimized geometries, electronic energies of RTIL constituents, reactants of the investigated Diels-Alder reaction and interaction energies among the RTIL cation with cyclopentadiene and benzoquinone. For this GAUSSIAN 03 set of codes (43) at the density functional theory level with details given elsewhere (44,45). Frequency analysis of the resultant geometries was performed at the same level of theory and basis set to check whether the obtained structures are the stable minimum energy structures and no imaginary frequencies were found. The optimised geometries of most stable conformations of imidazolium ion plus reactants are presented as Figure 2.5.1 and 2.5.4. While in case of bezoquinone the most stable conformation was one where the benzoquinone is localized near C-2 position of the imidazolium cation in case of cyclopentadiene, in the most stable conformation the cyclopentadine ring lies parallel to the imidazolium ring. This can be ascribed to the strong electrostatic (hydrogen bonding) interactions between acidic C_2-H (of imidazolium cation) and O (of benzoquinone) and π-π interactions among cyclopentadiene and imidazolium cation. While the interaction energy for the most stable conformation for bezoquinone plus imidazolium cation was found to be -1.073 $kJmol^{-1}$, in case of cyclopentadiene plus imidazlium cation the said value of said quantity was -1.221 $kJmol^{-1}$ for the most stable conformation as tabulated in Table 2.2. These calculations clearly establish that the imidazolium cation shows a positive interaction with both the reactants which implies that $\delta(\Delta G^0)_{solute\,solvation}$ for the present case will be definitely negative. In light of the reported ion association constants for [BMIM][BF_4] and [BMIM][Cl] in water (59); the magnitude of $\delta(\Delta G^0)_{solute\,solvation}$ for [BMIM][BF_4] is expected to be higher than that for [BMIM][Cl], nevertheless this magnitude will be small in comparison to $\delta(\Delta G^0)_{cavitation}$ in both the RTILs. The negative values for both $\delta(\Delta G^0)_{cavitation}$ and $\delta(\Delta G^0)_{solute\,solvation}$ imply an increase in solubility of reactants (1 and 2) with addition of RTILs, with the effect being more for [BMIM][BF_4] than [BMIM][Cl]. The increase in the solubility on account of this salting in character of RTILs can therefore be responsible for the observed decrease in rate of the investigated Diels-Alder reaction. Above discussion implies that had the salting in behaviour of the used RTILs been the sole reason for the observed variation in kinetics then addition of [BMIM][BF_4] should be more effective for deceleration than [BMIM][Cl] analogue which is in agreement with the observed trend.

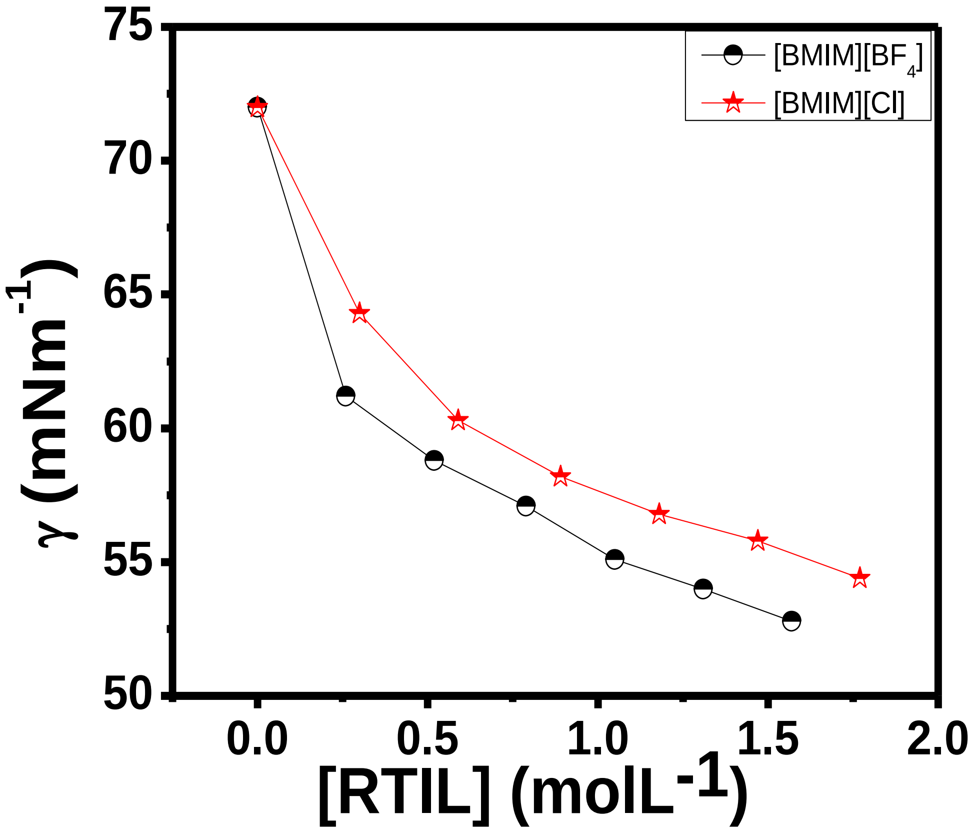
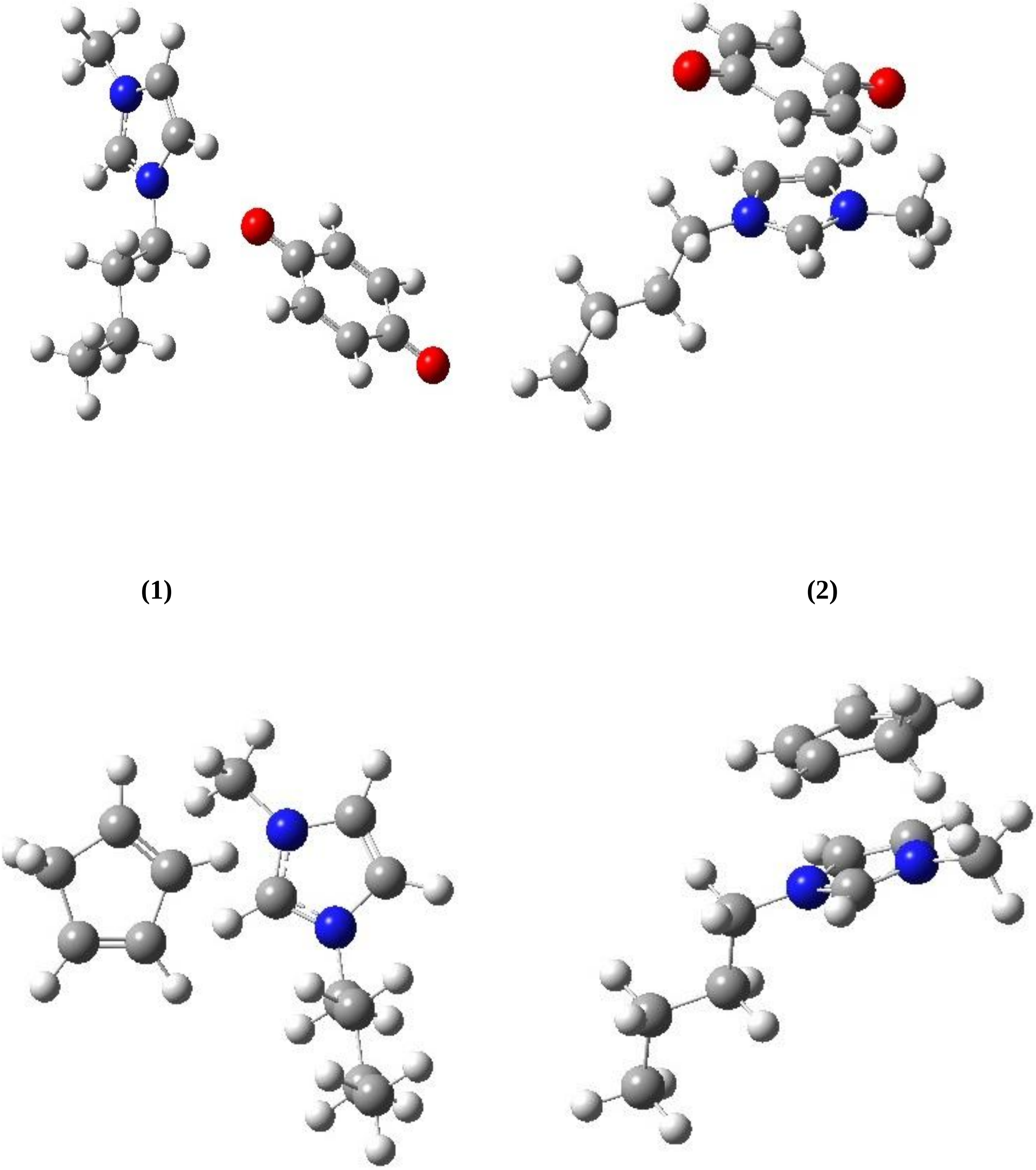


Figure 2.4. Variation of surface tension as a function of concentration of ionic liquids in RTIL-Water solvent media.



(1) (2)

(3) (4)

Figure 2.5. Optimised geometries of stable conformations of imidazolium ion plus reactants at relatively different orientations (1, 2) Imidazolium ion+Benzoquinone (3, 4) Imidazolium ion + Cyclopentadiene

Table 2.1. Surface tension (γ), density (ρ) and coefficient of viscosity (η) of [BMIM][BF$_4$]-Water and [BMIM][Cl]-Water solvent mixtures and the estimated value of rate constant (*k*) for Diels-Alder reaction between benzoquinone and cyclopentadiene in these mixtures, at 273.15 K.

Conc. of RTIL-Water solution (molL^{-1})	Rate constant k (s^{-1})*10^{-3}	Surface Tension γ (mNm^{-1})	Density ρ (gcm^{-3})	Coefficient of viscosity η (Pa.s)
[BMIM][BF$_4$]				
0.00	2.42	71.99	0.99705	0.00100
0.26	2.16	61.19	1.00403	0.00102
0.52	2.00	58.79	1.01507	0.00113
0.79	1.81	57.09	1.02551	0.00122
1.05	1.67	55.09	1.0362	0.00136
1.31	1.49	53.99	1.04603	0.00153
1.57	1.23	52.79	1.05633	0.00170
[BMIM][Cl]				
0.00	2.42	71.99	0.99705	0.00100
0.30	2.29	64.29	0.99931	0.00101
0.59	2.19	60.29	1.00292	0.00117
0.89	2.15	58.19	1.00679	0.00143
1.18	2.10	56.79	1.01138	0.00155
1.47	1.99	55.79	1.01498	0.00181
1.77	1.91	54.39	1.01991	0.00207

TABLE 2.2. Interaction energies of various conformations of imidazolium ion with benzoquinone and cyclopentadiene at side on and stacked orientation modes.

System	Relative Orientation	Interaction energy *(kJmol^{-1})*
Qu-Im(1)	Side on	1.073
Qu-Im(2)	Stacked	0.620
Cp-Im(3)	Side on	0.595
Cp-Im(4)	Stacked	1.221

Conclusion

We conclude that the investigated RTILs viz. [BMIM][BF_4] and [BMIM][Cl] act as solubility modifiers which through the disordering they cause in the solvent (water), and positive interactions with the reactants decrease the hydrophobic effect of reactants (1 and 2), that leads to an increase in their water solubility (salting in) and decrease of their reactivity for the concerted Diels-Alder type reaction. The present investigation establishes that both [BMIM][BF_4] and [BMIM][Cl] are potential chaotropic agents which can have remarkable impact on the structuring properties of proteins and nucleic acids.

References

1. (a) Welton, T. *Chem. Rev*. **1999**, *99*, 2071. (b) Rogers, R. D.; Seddon, K. R. *Ionic Liquids: Industrial Applications to Green Chemistry; ACS Symposium Series 818; American Chemical Society: Washington, DC*, **2002**. (c) Poole, C. F. *J. Chromatogr*. A. **2004**, 1037, 49.(d) Earle, M. J.; Seddon, K. R. *Pure Appl. Chem*. **2000,** *72*, 1391. (e) Chiappe, C.; Pieracinni, D. J. *J. Phys. Org. Chem*. **2005**, *18*, 275. (f) Weingartner, H. *Angew. Chem., Int. Ed*. **2008**, *47*, 654. (e) Hallett, J. P.; Welton, T. *Chem. Rev*. **2011**, *111*, 3508.
2. (a) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed*. **2000**, *39,* 3772 (b) Wasserscheid,P.; Welton, T. *Ionic Liquids in Synthesis; Wiley-VCH: Weinheim, Germany*, **2003**.
3. (a) Lane, G. H.; Bayley, P. M.; Clare, B. R.; Best, A. S.;MacFarlane, D. R.; Forsyth, M.; Hollenkamp, A. F. *J. Phys. Chem. C* **2010**, *114*, 21775. (b) Forsyth, S. A.; Pringle, J. M.; MacFarlane, D. R. *Aust. J. Chem*. **2004**, *57*, 113. (c) Torriero, A. A. J.; Siriwardana, A. I.; Bond, A. M.; Burgar, I. M.; Dunlop, N. F.; Deacon, G. B.; MacFarlane, D. R. *J. Phys. Chem. B* **2009**, *113*, 11222.
4. Sheldon, R. *J. Chem. Soc., Chem. Commun*. **2001,** *23*, 2399.
5. Wasserscheid, P; Keim, W. *Angew. Chem. Int. Ed*. **2000,** *39*, 3772-3789.
6. (a) Paulaitis, M. E; Alexander, G. C. *Pure & Appl. Chem*. **1987,** *59*, 61-68.
   (b) Kiselev, V. D; Kashaeva, E. A.; Shihab, M. S; Medvedeva, M.D; Konovalov, A. I. *Russian Chemical Bulletin*, **2000**, *49*, 6. (c) Trost, B. M; O'Krongly, D; Belletire, J. L. *J. Am. Chem. Soc.* 1980, *102,* 7595-7596.
7. (a) Lubineau, A.; Auge, J.; Queneau, Y. *Synthesis* **1994**, 741.(b)Lubineau, A.; Queneau, Y. *Tetrahedron* **1989**, *45*, 6691. (c) Lubineau, A.; Queneau, Y. *Tetrahedron Lett*. **1985**, *26*, 2653. (d) Lubineau, A.; Malleron, A. *Tetrahedron Lett*. **1985**, *26*, 1713. (e) Lubineau, A.;

Queneau, Y. *J. Org. Chem*. **1987**, *52*, 1001. (f) Lubineau, A.; Bienayme, H.; Queneau, Y.; Scherrmann, M. C. *New J. Chem.* **1994,** *18,* 279.

8. (a) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon: Oxford, **1990**.(b) Desimoni, G.; Tacconi, G.; Barco, A.; Polloni, G. P. *National Product Synthesis through Pericyclic Reactions*; ACS Monograph 180; American Chemical Society: Washington, D.C., **1983**. Fringuelli, F.; Tatichi, A. *Dienes in the Diels-Alder Reactions*; Wiley: New York, **1990**.(c) Lubineau, A.; Auge, J.; Queneau, Y. *Synthesis* **1994**, 741(d) Pindur, U.; Lutz, G.; Otto, C. *Chem. Rev.* **1993**, *93*, 741.(e) Cativiela, C.; Garcia, J. I.; Mayoral, J. A.; Salvatella, L. *Chem. Soc. Rev.* **1996**, 209.(f) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497.
9. Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinhein, 1970. Also see: *Angew Chem., Int. Ed. Engl.* **1969**, *8,* 781.
10. Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.
11. Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem., Intl. Ed. Engl.* **1992**, *31*, 682.
12. Rideout, D. C.; Breslow, R. *J. Am. Chem. Soc*. **1980**, *102*, 7816.
13. Breslow, R. *Acc. Chem. Res*. **1991**, *24*, 159.
14. Blokzijl, W.; Engberts, J. B. F. N.; Blandamer, M. J. *J. Am. Chem. Soc*. **1990**, *112,* 1197.
15. Blokzijl, W.; Engberts, J. B. F. N. *J. Am. Chem. Soc*. **1991**, *113,* 5440.
16. Blokzijl, W.; Engberts, J. B. F. N. *Angew. Chem., Int. Ed*. **1993,** *32,* 1610.
17. Pirrung, M. C. Chem.—*Eur. J.* **2006**, *12*, 1312.
18. Grieco, P. A. *Organic Synthesis in Water; Blackie: London,* **1998**.
19. Li, C.-J; Chan, T. H. *Organic Reactions in Aqueous Media; Wiley: Chichester*, **1997**.
20. Grieco, P. A.; Ferrino, S.; Vidari, G. *J. Am. Chem. Soc*. **1980**, *102*, 7586.
21. Vidari, G.; Ferrino, S.; Grieco, P. A. *J. Am. Chem. Soc.* **1984**, *106*, 3539.

22. Grieco, P. A.; Garner, P.; He, Z. *Tetrahedron Lett.* **1983**, *24*, 1897.

23. (a) Grieco, P. A.; Yoshida, K.; Garner, P. *J. Org. Chem.* **1983**, *48*, 3137. (b) Grieco, P. A.; Larsen, S.; Fobare, W. F. *Tetrahedron*, **1986**, *27*, 1975.

24. Breslow, R.; Rizzo, C. J. *J. Am. Chem. Soc.* **1991**, *113*, 4340.

25. Breslow, R. *Acc. Chem. Res.* **1991**, *24*, 159.

26. Breslow, R.; Maitra, U.; Rideout, D. C. *Tetrahedron Lett*. **1983**, *24*, 1901.

27. Rizzo, C. J. *J. Org. Chem.* **1992**, *57*, 6382.

28. (a) Holfmeister, F. *Ach. Exptl. Pathol. Pharmakol.* **1888**, *24*, 247.
(b) For details, see: Collins, K. D.; Washabaugh, M. W. *Quart. Rev. Biophys.* **1985**, *18,* 323.

29. Samii, A. A.; de Savignac, A.; Rico, I.; Lattes, A. *Tetrahedron*, **1985**, *41*, 3683.

30. (a) Evans, D. F.; Yamauchi, A.; Roman, R.; Casassa, E. Z. *J. Colloid Interface Sci.* **1982**, *88*, 89. (b) Evans, D. F.; Yamauchi, A.; Wei, G. J.; Bloomfield, V. A. *J. Phys. Chem*. **1983**, 87, 3537.

31. Lee, C. W. *Tetrahedron Lett*. **1999**, *40*, 2461.

32. Earle, M. J; Seddon, K. R. *Pure & Appl. Chem*., **2000,** *72*, 1391–1398

33. Tiwari, S.; Kumar., A. *Angew. Chem., Int. Ed*. **2006**, *45*, 4824.

34. Tiwari, S.; Khupse, N.; Kumar, A. *J. Org. Chem.* **2008,** *73*, 9075.

35. Khupse, N. D.; Kumar, A. *J. Solution Chem*. **2009**, *38*, 589.

36. Khupse, N. D.; Kumar, A. *J. Phys. Chem. B* **2010**, *114,* 376.

37. Khupse, N. D.; Kumar, A. *J. Phys. Chem. B* **2011**, *115*, 711.

38. Perrin, D. D.; Armarego, W.L.F.; Purification of Laboratory Chemical, Pregamon Press, Great Britian, 3rd Edition, **1998.**

39. Vogel, A. I; Tatchell, A. R.; Furnis, B. S.; Hannaford, A. J.; Smith, P. W. G. *Vogel's Textbook of Practical Organic Chemistry(5th edition)* Pearson Education Limited, UK.

1989

40. (a) Dupont, J.; Consorti, C.S.; Saurez, P.A.Z.; deSouza, R.F.; *Org. Syn.* **2002,** *79,* 236.
    (b) Dupont, J.; Consorti, C.s.; Saureez, P.A.Z.; deSouza, R.F.; *Org. Syn.* **2004,** *10,* 184.
41. Bhat, M. A.; Chaudhari, V. R.; Ingole, P. P.; Haram, S. K. *J. Phys. Chem. B* **2009**, *113*, 2848.
42. Bhat, M. A.; Ingole, P. P.; Electrochemica Acta. **2012**.03.115.
43. Frisch, M. J. et al. GAUSSIAN03, Revsion B 03, Gaussian, Inc, Wallingford CT, **2004**.
44. Becke, A. D. *J. Chem. Phys.* **1993**, *98***,** 5648.
45. Lee, C; Yang, W; Parr, G. R. *Phys. Rev. B.* **1988**, *37***,** 785.
46. Li, C.-J.; Chan, T.-H. *Organic Reactions in Aqueous Media*; Wiley: New York, **1997**.
47. Engberts, J. B. F. N. *Angew. Chem., Int. Ed. Engl*. **1993**, *32*, 1545.
48. Blokzijl, W.; Blandamer, M. J.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1991**, *113*, 4241.
49. (a) Otto, S.; Blokzijl, W.; Engberts, J. B. F. N. *J. Org. Chem.* **1994**, *59*, 5372. (b)Blokzijl, W.; Engberts, J. B. F. N. *ACS Symp. Ser.* **1994**, *568*, 303. (c) Engberts, J. B. F. N. Pu*re Appl. Chem.* **1995**, *67*, 823. (d) Wijnen, J. W.; Engberts, J. B. F. N. *J. Org. Chem.* **1997**, *62*, 2039. (e) Mersbergen, D.; van Wijnen, J. W.; Engberts, J. B. F. N. *J. Org. Chem.* **1998**, *63*, 8801. (f) Meijer, A.; Otto, S.; Engberts, J. B. F. N. *J. Org. Chem.* **1998**, *63*, 8989.
50. Furlani, T. R.; Gao, J. *J. Org. Chem.* **1996**, *61*, 5492.
51. Tiwari, S; Kumar, A. *J. Phys. Chem. A.* ***2012****, 116,* 1191-1198.
52. (a) Long, F. A.; McDevitt, W. F. *Chem. Rev.* **1952**, *52*, 119. (b) McDevitt, W. F.; Long, F. A. *J. Am. Chem. Soc.* **1952**, *74*, 1773. (c) Gordon, J. E. *The Organic Chemistry of Electrolyte Solutions*; Wiley: New York, 1975.

53. (a) Pawar, S. S.; Phalgune, U.; Kumar, A. *J. Org. Chem.* **1999**, *64*, 7055 (b) Reiss, H.; Frisch, H. L.; Lebowitz, J. L. *J. Chem. Phys.* **1959**, *31*, 369. (c) Masterton, W. L.; Lee, T. P. *J. Phys. Chem.* **1970**, *74*, 1776. (d) Pierotti, R. A. *Chem. Rev.* **1976**, *76*, 717 and references therein. (e) Kumar, A. *J. Am. Chem. Soc.* **1993**, *115*, 9243.

54. (a) Liu, W.; Cheng, L.; Zhang, Y.; Wang, H.; Yu, M. *J. Mol. Liq*. **2008**, *140,* 68. (b) Sanchez, L. G.; Espel, J. R.; Onink, F.; Meindersma, G. W.; de Haan, A. B. *J. Chem. Eng. Data* **2009**, *54*, 2803.

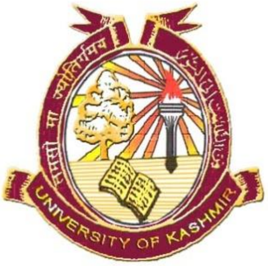
55. Fujit, A. T; Watanabe, H; Tanaka, S. *Chem. Phys. Letters*. **2007,** *434*, 42-48.

56. Russo, J. W; Hoffmann, M. M. *J. Chem. Eng. Data*. **2011**, *56*, 3703–3710.

57. Dong, B; Zhao, X; Zheng, L; Zhang, J; Li, N; Inoue, T. *Colloids and interface A.* **2008**, 317, 666-672.

58. Deetlefs, M; Hardacre, C; Nieuwenhuyzen, M; Padua, A. A. H; Sheppard, O; Soper, A. K. *J. Phys. Chem. B.* **2006,** *110,* 12055-12061.

59. (a) Zhu, G; Wu, G; Xu, X; Ji, X. *Spectrochim Acta A Mol Biomol Spectrosc*. **2011**, 74-8. (b) Bester-Rogac, M; Stoppa, A; Hunger, J; Hefter, G; Buchner R. *Physical Chemistry Chemical Physics:PCCP*. **2011**, 17588-98.



Chapter 3

Nucleophilic Substitution reaction in RTIL-Methanol solvent systems [BMIM][CH_3COO], [BMIM][Cl] and [BMIM][PF_6]: A kinetic investigation

Introduction

Solvent is ubiquitous feature of chemistry that plays an important role in governing rates and selectivity of chemical reactions. On account of the solubility requirements for homogeneous reactions, organic compounds are the preferred solvents for majority of the industrially and synthetically important reactions. This has led to the usage of volatile organic compounds (VOCS) as solvents for chemical transformations. The undesirable impact of VOCS on the living organisms and the climate we live in (1) has initiated a tremendous research activity aimed at design of new synthetic methodologies and discovering more eco-friendly solvent systems that can ensure the replacement or minimization of potentially toxic VOCS (2, 3, 4). In search of eco-friendly solvents, ionic liquids (ILs) on account of their unusual and interesting physico-chemical properties (5) have emerged among front runners. It is due to their negligible vapour pressure, excellent solvating potential that makes them to solubilise a wide range of inorganic and organic materials and their high thermal stability and wide liquidus range that allows their usage over a wide range of temperatures, and other physico-chemical properties which can be tailored as per requirement, that despite concerns over their unknown toxicities ILs are widely proposed as green solvents. It is in these contexts that since last few decades' researchers have been paying enormous attention towards exploration of the potentialities of ILs as solvents/catalysts/cosolvents for a variety of industrially and synthetically important reactions.

Most of the chemical reactions in synthesis involve incorporation of new functional groups or functional group exchanges. Among numerous reactions discovered so far in this context, the nucleophilic substitution reactions are considered a powerful method for inserting functional group into the carbon sekelton (6, 7). The nucleophilic substitution reactions are of considerable practical use for transformations in medicinal and agriculture chemistry (8). Hughes and Ingold broadly classified aliphatic nucleophilic substitution into two categories which proceed by two different mechanisms namely (a) SN^1 -follow Ist order kinetics and involves racemisation if the substrate is optically active and (b) SN^2 -follow 2nd order kinetics and proceeds with inversion of configuration (9). Besides being a useful synthetic strategy for many types of synthetically and industrially important intermediates/products, nucleophilic substitution reaction provides a familiar avenue for the examination of solvent effects on the chemical transformations (10, 11). In the past the effects of molecular solvents on the nucleophilic substitution reactions have been easily understood and explained in light of Hughes-Ingold model, according to which high polarity solvents accelerate the reaction in which the charge density is created, decelerate the reaction in which charge density is destroyed, and a negligible effect on the reaction that involve little or no charge density on going from reactants to the transition state (12, 13, 14, 15, 16). Application of the Hughes-Ingold approach to a variety of chemical reactions with ionic liquids as solvents have achieved limited success (10,17,18,19,20,21). It has been reported that nucleophilic substitution reactions of neutral electrophile p-nitrobenzenesulfonate with a range of neutral (mono, di and tributylamine) and anionic (halides and other ions) nucleophiles in different ionic liquids can be explained in terms of Kamlet-Taft LSER approach (22, 23). Welton et al. in their investigations, the role of charged electrophile on SN^2 reaction in ionic liquids, have found that the results can be better explained in light of the Kamlet-Taft description (24). Similarly the kinetic trends of esterfication reaction between methoxyacetic acid with benzyl alcohol in a range of ionic liquids and molecular solvents have also been explained by using the linear solvation energy relationship based on Kamlet-Taft scale (α, β and π*) and it has been reported that hydrogen bond basicity of the solvent is the dominant parameter in determining the rate of nucleophilic substitution reaction and best rates are achieved in the low basicity solvents (25). Welton et al. based on their investigations over the nucleophilic substitution reaction with charged nucleophile and neutral substrate in different ionic liquids and molecular solvents, have concluded that there is no simple correlation of dielectric constant and rate constant, thus invalidating the Hughes-Ingold rule (26). In these studies the complex results have been analysed using the LSER approach, wherein the decrease in rate constants has been attributed to negative α values. The negative α values of solvent implies its hydrogen bonding to the nucleophile, that stabilizes it more than that of activated complex which is a less hydrogen bond acceptor than the nucleophile itself. The nucleofugality of the leaving group is also an important contributor to rates of SN^2 reaction that can be subjected to solvent effects. Nucleophilic substitution reaction of NaN_3 with a range of primary, secondary and tertiary halides and tosylates have been found to occur with a rate that increases in the order $[C_4C_1im][NTf_2]$< $[C_6Pyr][NTf2]$< $[C_4C_1im][PF_6]$. The observed trend in the rate constants in the above mentioned ILs has been attributed to the ability of these ILs to form hydrogen bonds with the leaving groups (27). Nucleophilic conversion of alcohols to alkyl halides has also been attempted in 1:1 mixture of p-toloune sulphonic acid and $[C_nC_1im][X]$ where n= 4 or 8; X= Br or I as halogenating mixture, and good conversion yields have been reported (28). In these attempts it has been found that more hydrophilic ionic liquids lead to a tremendous increase in rate constants of nucleophilic substitution reactions (29). Also use of RTILS as environmentally benign media for the cyanide displacements on the benzyl chloride, thus replacing phase transfer catalysed biphasic systems has been investigated (30). The ability of ILs to accelerate the nucleophilicity of potassium salts of aromatic acids towards α-aryloxy synthesis was recently explored by Chen and co-workers (31). In addition to the above cited reports numerous other nucleophilic substitution reactions are reported in literature wherein ILs have been reported to result in increase in rate constants and yields over conventional solvents that is attributed to the unique properties of these neoteric solvents (27,32). Recently Welton et al. reported a comprehensive investigation related to anion effects of imidazolium based ionic liquids on the the rate kinetics of nucleophilic substitution reactions (33). The nucleophilic substitution reactions between methyl-p-nitrobenzenesulfonate with halides in these studies have been found to react differently in different ILs because of change in the nucleophilicities of halide ions. It has been found that reactivity varies as $Cl^- > Br^- > I^-$ in case of $[BMIM][BF_4]$ and $Cl^- < Br^- < I^-$ in $[BMIM][NTf_2]$. Motivated by the above cited reports about nucleophillic substitutions reactions in ILs we decided to investigate the impact of imidazolium based ILs on the kinetics of aliphatic nucleophilic substitution reaction at sulfonyl sulphur with neutral substrate and charged nucleophile. For the same we carried out detailed kinetic investigations on the nucleophilic substitution reaction of p-tolunesulfonyl chloride with sodium azide (NaN_3) in RTIL plus methanol binary solvent systems. Kamlet-Taft model was used to analyse the increased rate in RTILS-Methanol solvent systems over methanol.

3. 1. Experimental Section

3. 1. 1. Materials

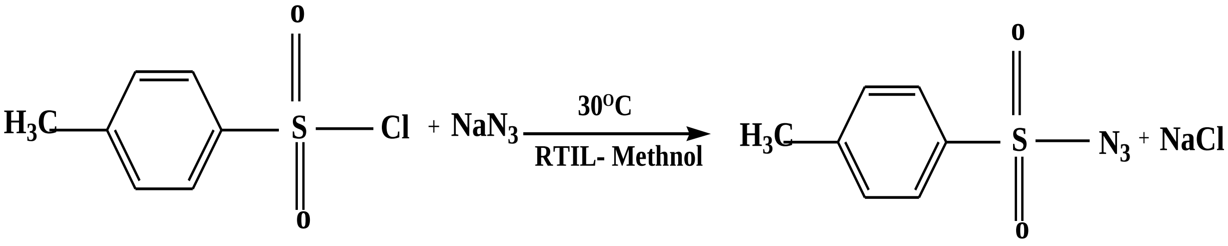
The reactants for the chosen nucleophillic substitution reaction viz. sodium azide and p-toluenesulfonyl chloride were obtained from Merck-Germany. Methanol was procured from Merck India, while spectroscopic grade room temperature ionic liquids viz. [BMIM][Cl], $[BMIM][CH_3COO]$ and $[BMIM][PF_6]$ as used for the planned kinetic investigations were synthesised following reported methods. The materials required for synthesis viz. acetonitrile (GR grade, 99.9%), methanol (GR grade, 99.9%), ethylacetate, dichloromethane were purchased from Merck-India and were purified following the standard methods. While precursors 1-methyimidazole, 1-chlorobutane used for the synthesis were obtained from Spectrochem, India. Briefly in the first step 1-methylimidazole was refluxed with n-butyl chloride for 90 hours under inert gas atmosphere like argon for the synthesis of precursor compound 1-butyl-3-methylimidazolium chloride as a white crystalline solid. In the next step halide ion i.e Cl^- was exchanged with PF_6^- or CH_3COO^- ion on treatment with HPF_6 or CH_3COONa to get [BMIM][PF_6] or [BMIM][CH_3COO]. The synthesised RTILS were dried and stored in dessicators under inert atmosphere and were characterised through ^{1}H-NMR, mass spectrometry and ^{13}C-NMR spectroscopy. The water content of these ionic liquids was restricted to 50ppm, as analysed by Karl Fischer titration.

3. 1. 2. Kinetic procedure

The selected aliphatic nucleophilic substitution reaction between p-tolounesulfonyl chloride and sodium azide was carried out under pseudo first order conditions using an excess of sodium azide (NaN_3) by a factor of 10-100. All the experimental runs were monitored within 1cm quartz cuvette using a UV-Visible spectrophotometer following the decrease of absorbance of p-tolunesulfonyl chloride at appropriate wavelength of 243-245nm. In a typical kinetic experimen, a stock solution of 0.1M of p-tolunesulfonyl chloride in methanol was prepared by adding exactly weighed 0.0381g to make a total solution of 2ml. Then 10 μl from stock solution was taken by using micro pipette to prepare 0.33 mM solution of p-tolounesulfonyl chloride in methanol. Also an exactly weighed 0.0195g of NaN_3, were added to methanol as solvent to prepare its stock solution of 0.15M. Then 50 μl from this stock were added to methanol taken in a cuvette to prepare 3ml solution of sodium azide of molarity 2.5mM. Thus out of 3ml solution taken in cuvette, the concentration of p-tolounesulfonyl chloride (0.33mM) and sodium azide (2.5mM) were fixed in a typical experimental run. Similar experimental runs were carried out in different RTIL-Methanol binary mixtures using various RTILS viz. [BMIM][Cl], [BMIM][CH_3COO] and [BMIM][PF_6].

The kinetic investigations were carried out by using Schimadzu 1650 PC UV-Visible Spectrophotometer equipped with thermostat for controlling the temperature with an accuracy of 0.1^{0}C. All the experiments were carried out at a fixed temperature of 30^{0}C.

3. 2. Results and discussion



(1) (2) (3) (4)

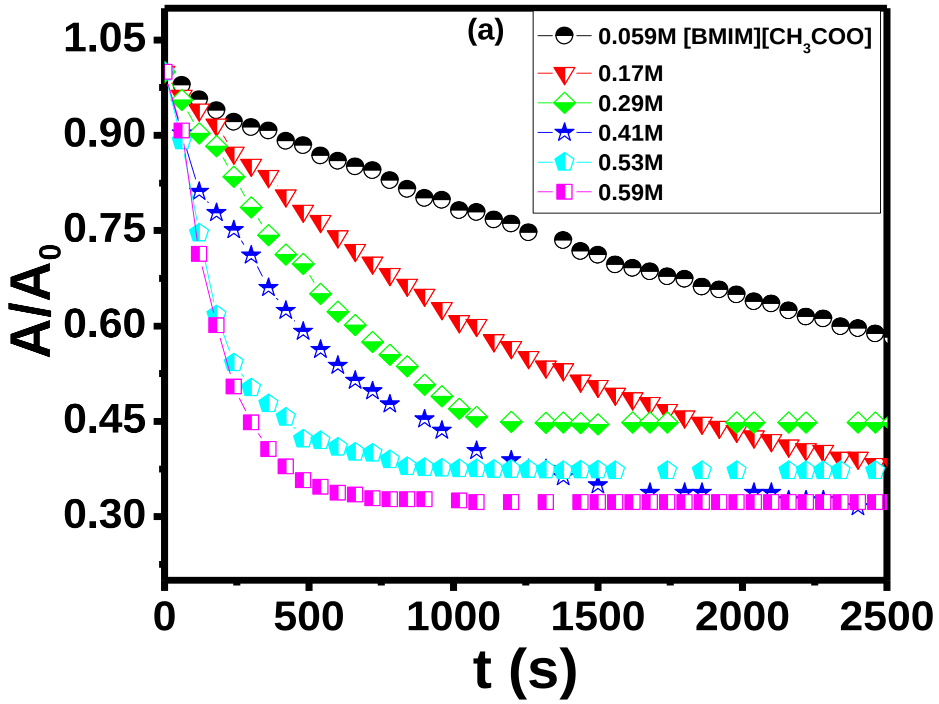
Scheme 3.1. Nucleophilic Substitution reaction between p-tolounesulfonylchloride (1) and sodium azide (2) to form p-tolounesulfonyl azide (3) and sodium chloride (4)

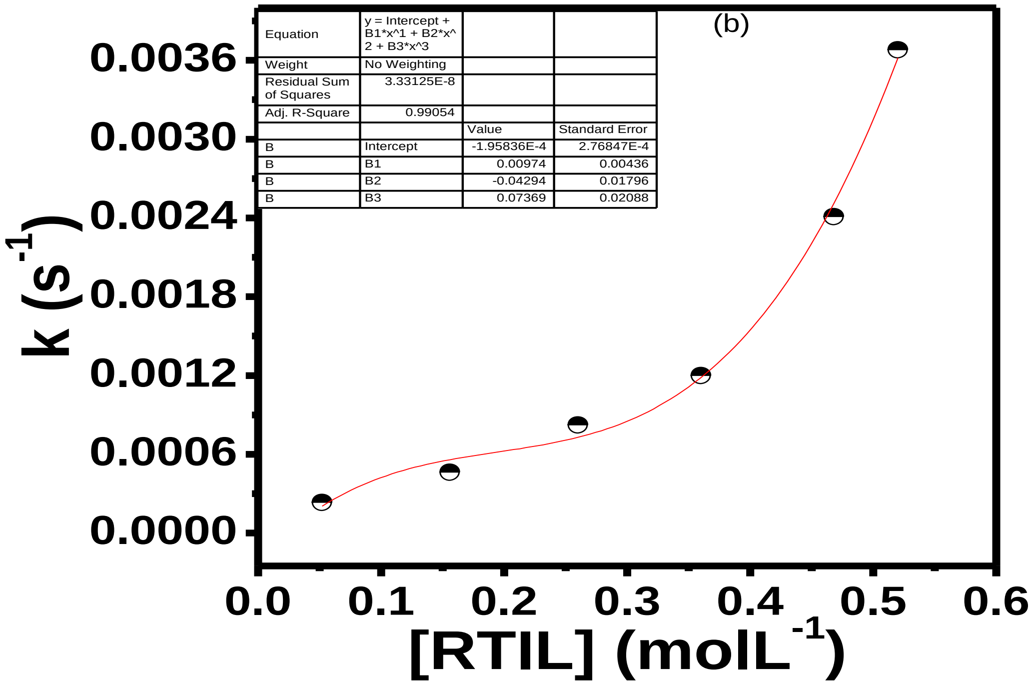
The kinetics of selected aliphatic nucleophilic substitution; the reaction between p-tolunesulfonyl chloride (1) and sodium azide (2) as presented in scheme 3.1., was investigated in methanol and RTIL plus methanol binary solvent systems in order to explore and understand the solvent dependence of its kinetics at microscopic level. The reaction is reported to follow first order kinetics with respect to each reactant and overall 2nd order kinetics. For the presented kinetic investigations the experiments were performed at 30 ^{0}C and in presence of excess of the sodium azide (nucleophile). Under these experimental conditions where in the effect of p-tolunesulfonyl chloride was isolated by taking the sodium azide in excess, the reaction is expected to follow pseudo-first order kinetics. Kinetic data recorded for the reaction in three types of RTIL-methanol solvent mixtures viz. [BMIM][CH_3COO]-methanol, [BMIM][Cl]-methanol and [BMIM][PF_6]-methanol which were variedly concentrated with respect to RTIL is presented in Figures 3.1.a,3.2.a & 3.3.a respectively. The kinetic data (absorbance vs. time) were fit to equation 3.1.

$$\boldsymbol{k = \frac{1}{t}\, ln\, (A_o/A_t)} \tag{3.1}$$

Where, k is pseudo ist order rate constant A_o is absorbance at zero time’t=0’, A_t is the absorbance at time’t’. The estimated values of k for the investigated nucleophillic substitution reaction in RTIL plus methanol as solvent system differently concentrated with

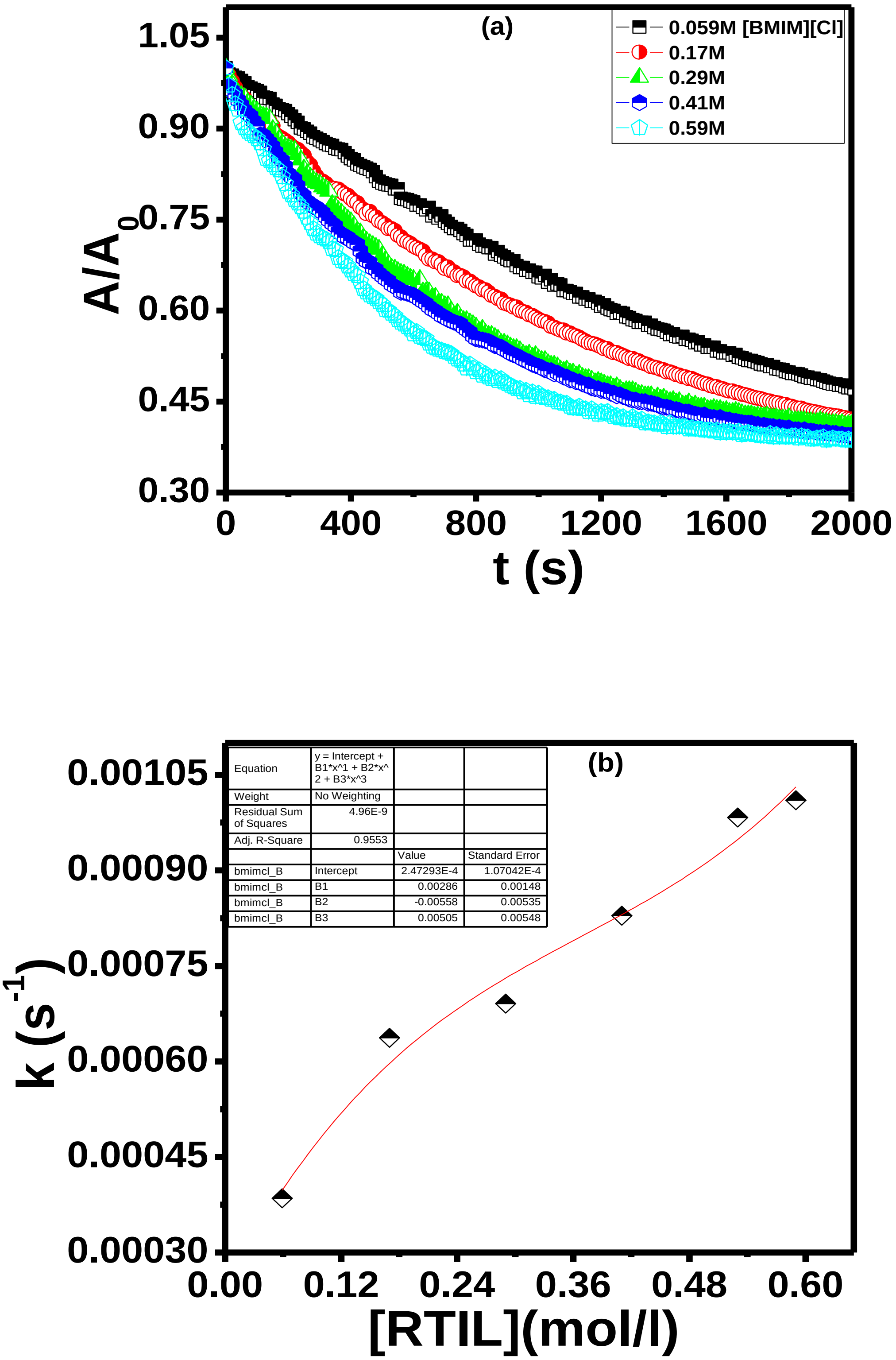
RTILs viz. [BMIM][CH_3COO], BMIM][Cl] and [BMIM][PF_6] are tabulated as Table.3.1. and to visualize the trend the same are depicted in Figure 3.1.b, 3.2.b & 3.3.b respectively. The estimated values of rate constants from the above analysis as enlisted in Table 3.1., and plotted in Fig. 3.4 are an average of results from three kinetic runs recorded under similar conditions. The results from different runs were observed to be reproducible within ± 5%. As clear from these values the addition of imidazolium based RTILs to methanol increases the rate constant for the investigated nucleophilic substitution reaction with an extent that depends on the nature and concentration of the added RTIL.





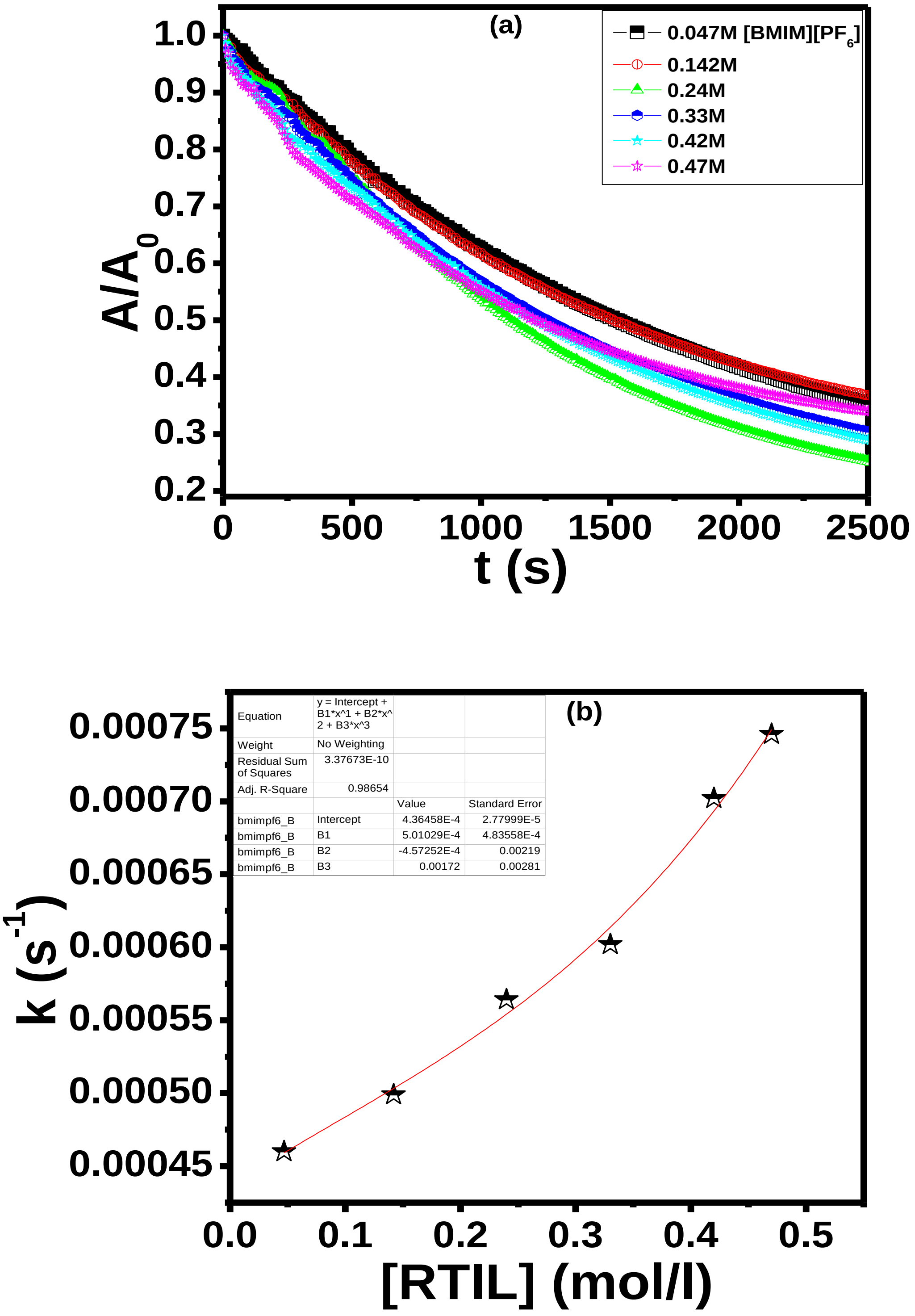
Equation	y = Intercept + B1*x^1 + B2*x^2 + B3*x^3		
Weight	No Weighting		
Residual Sum of Squares	3.33125E-8		
Adj. R-Square	0.99054		
		Value	Standard Error
B	Intercept	-1.95836E-4	2.76847E-4
B	B1	0.00974	0.00436
B	B2	-0.04294	0.01796
B	B3	0.07369	0.02088

Figure 3.1. Variation of absorbance versus time(s) (a) and rate constant(s^{-1}) versus conc. of [BMIM][CH_3COO] (b) in [BMIM][CH_3COO]-Methanol solvent system.



Equation	y = Intercept + B1*x^1 + B2*x^2 + B3*x^3		
Weight	No Weighting		
Residual Sum of Squares	4.96E-9		
Adj. R-Square	0.9553		
		Value	Standard Error
bmimcl_B	Intercept	2.47293E-4	1.07042E-4
bmimcl_B	B1	0.00286	0.00148
bmimcl_B	B2	-0.00558	0.00535
bmimcl_B	B3	0.00505	0.00548

Figure 3.2. Variation of absorbance versus time(s) (a) and rate constant (s^{-1}) versus conc. of [BMIM][Cl] (b) in [BMIM][Cl]-Methanol solvent system.



Equation	y = Intercept + B1*x^1 + B2*x^2 + B3*x^3		
Weight	No Weighting		
Residual Sum of Squares	3.37673E-10		
Adj. R-Square	0.98654		
		Value	Standard Error
bmimpf6_B	Intercept	4.36458E-4	2.77999E-5
bmimpf6_B	B1	5.01029E-4	4.83558E-4
bmimpf6_B	B2	-4.57252E-4	0.00219
bmimpf6_B	B3	0.00172	0.00281

Figure 3.3. Variation of absorbance versus time(s) (a) and rate constant (s^{-1}) versus conc. of [BMIM][PF_6] (b) in [BMIM][PF_6]-Methanol solvent system.

Table 3.1. Rate constant k/s^{-1} for the reaction between sodium azide (NaN_3) and p-tolounesulfonyl chloride in RTIL-Methanol solvent media at 30^0C

Concentration ($molL^{-1}$)	Rate constant 'k * 10^{-4} '(s^{-1}) at 30^0C
[BMIM][CH_3COO]	
0.000	2.19
0.052	2.34
0.156	4.62
0.261	8.24
0.362	12.00
0.468	24.10
0.520	36.80
[BMIM][Cl]	
0.000	2.19
0.059	3.85
0.170	6.37
0.291	6.91
0.410	8.29
0.532	9.83
0.590	10.10
[BMIM][PF_6]	
0.000	2.19
0.047	4.60
0.142	4.99
0.240	5.64
0.330	6.02
0.420	7.02
0.470	7.46

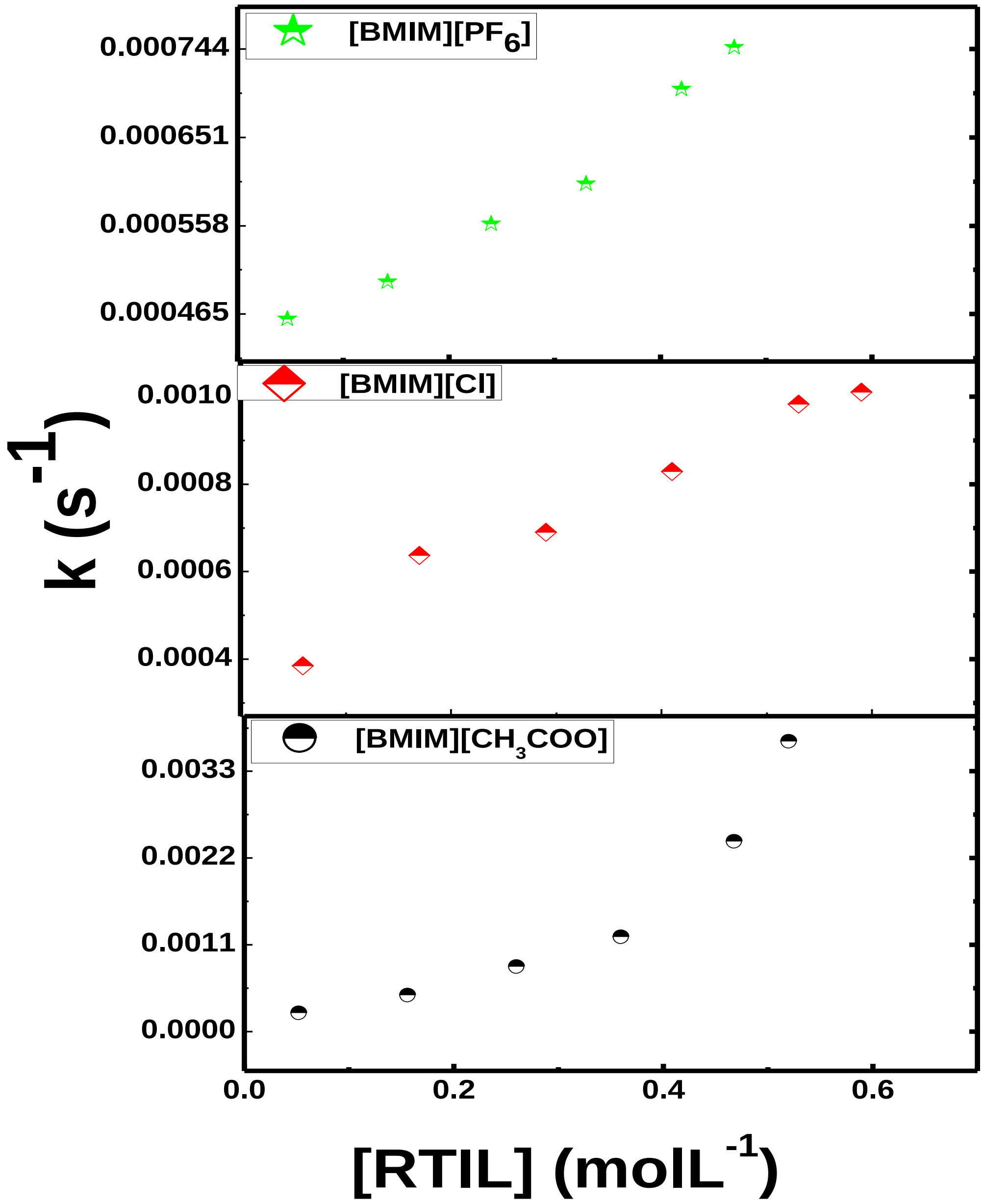
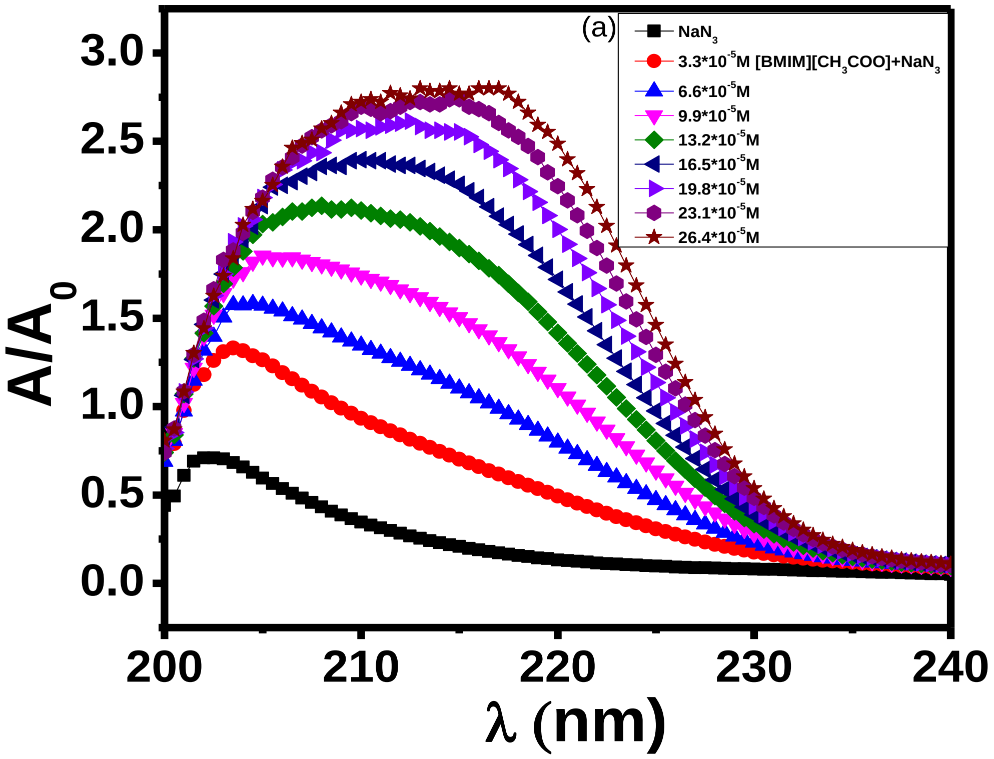
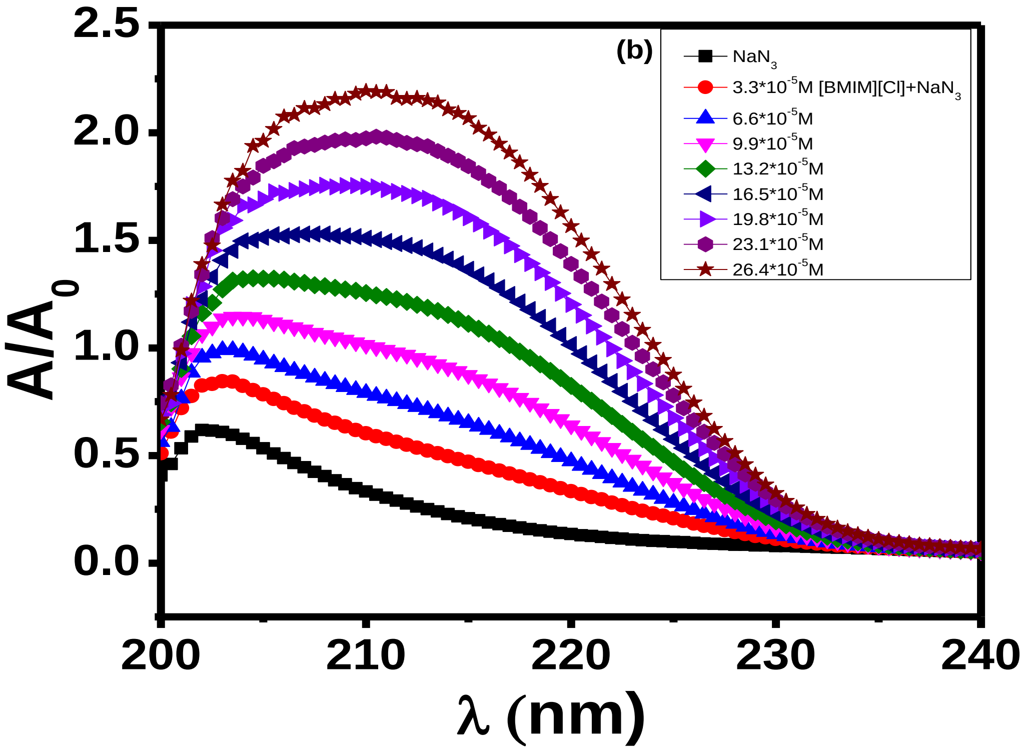


Figure 3. 4. Variation of rate constant as a function of conc. (molL^{-1}) of ionic liquids in RTIL-Methanol solvent media.

Table 3.2. Kamlet-Taft Parameters for the solvents used in this kinetic investigation

Solvent	α	β	π^*	Ref
Methanol	0.76	0.61	0.73	(12,41)
[BMIM][PF_6]	0.68	0.21	1.02	(42)
[BMIM][Cl]	0.48	0.94	1.02	(42)
[BMIM][CH_3COO]	0.57	1.18	0.89	(43)


(a)
NaN3
3.3*10-5M [BMIM][CH3COO]+NaN3
6.6*10-5M
9.9*10-5M
13.2*10-5M
16.5*10-5M
19.8*10-5M
23.1*10-5M
26.4*10-5M
A/A0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
200
210
220
230
240
λ (nm)


(b)
NaN3
3.3*10-5M [BMIM][Cl]+NaN3
6.6*10-5M
9.9*10-5M
13.2*10-5M
16.5*10-5M
19.8*10-5M
23.1*10-5M
26.4*10-5M
A/A0
0.0
0.5
1.0
1.5
2.0
2.5
200
210
220
230
240
λ (nm)

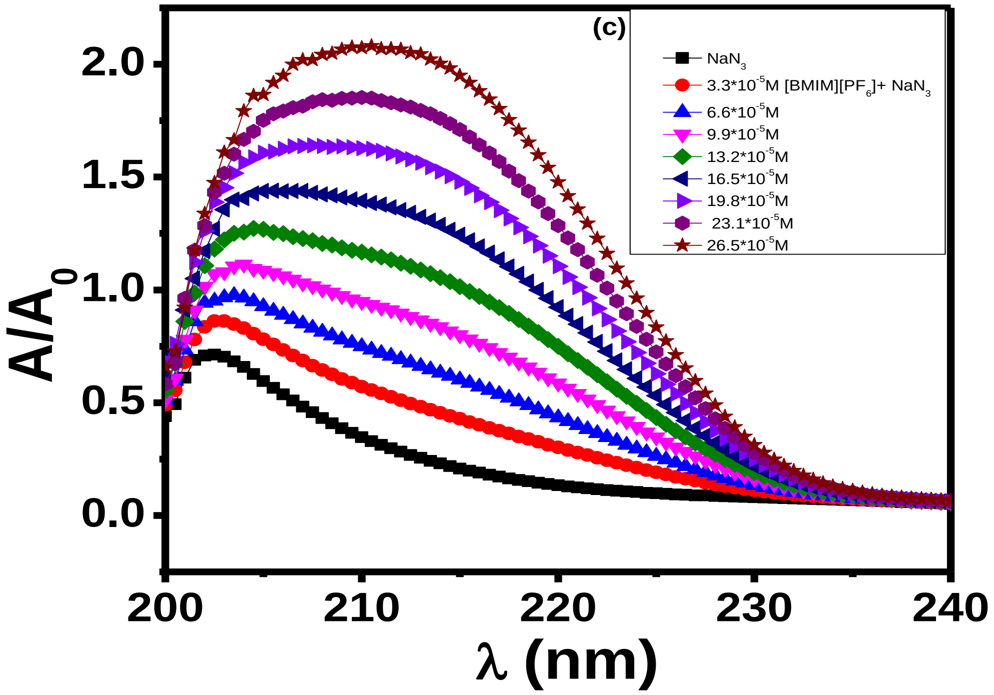


Figure 3.5. UV-Spectra of NaN_3 with changing concentration of ionic liquids in RTIL-Methanol solvent mixtures (a) [BMIM][CH_3COO] (b) [BMIM][Cl] (c) [BMIM][PF_6]

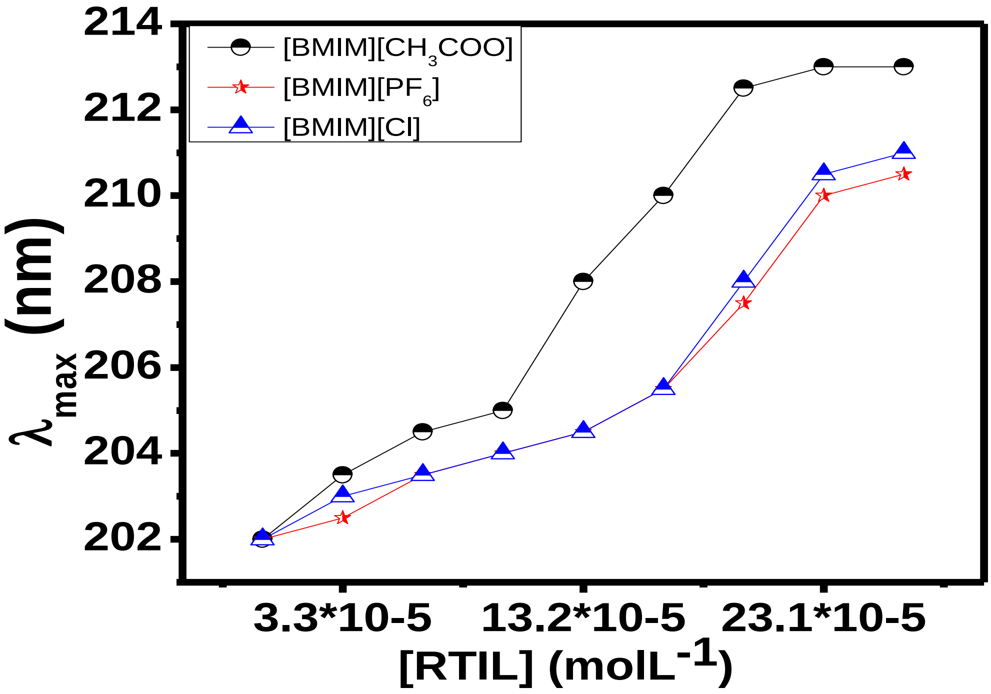


Figure 3.6. Variation of λ_{max} with changing concentration of ionic liquids in RTIL-Methanol solvent systems.

Mechanistically the aliphatic nucleophilc substitution reaction between p-tolunesulfonyl chloride and sodium azide is an SN^2 reaction of type 1. i.e. a charged nucleophile (azide) reacting with neutral substrate(p-tolunesulfonyl chloride) (12). SN reaction at sulphur is facilitated by the presence of vacant d-orbitals which interact with the nucleophile to give rise to a reasonably stable transition state. In present case this implies that the activated complex Y^{δ}-..R…$X^{\delta-}$ formed during the course of reaction has charge density scattered and thus lower than that of reactants. Hence formation of activated complex results in decrease in overall charge separation and hence the reaction is expected to be promoted by relatively less polar media. Therefore according to Hughes-Ingold rules, the rate of such reactions should decrease with increase in polarity of solvent. Assuming imidazolium based RTILs to behave as salts, this implies that with the increase in concentration ($molL^{-1}$) of RTILs in RTIL-methanol solvent media polarity of the solvent media would increase and hence the rate constant of the explored SN reaction is expected to show a decrease which is quite opposite to our observations. Present investigations hence is one of the examples wherein the observed results can`t be explained in light of Hughes-Ingold model, according to which the solvent-solute interactions are solely electrostatic in nature. In past such observations which could not be explained in terms of single polarity parameter of solvent systems have been explained and analysed by using LSER model set by Kamlet-Taft which takes into account all specific interactions else than polarity that can contribute to solvent effects on kinetics of reactions. According to Kamlet-Taft approach the solvent systems can not only change the absolute reaction rate but also the relative nucleophilicities of nucleophiles and the resultant impact on the reaction kinetics can be quantified through equation developed by Kamlet-Taft (34,35,36,37) as presented in Eq.3.2

$$\ln \boldsymbol{k_2} = \boldsymbol{XYZ_o} + \boldsymbol{a\alpha} + \boldsymbol{b\beta} + \boldsymbol{s\pi}^* \qquad \textbf{(3.2)}$$

Where, XYZ_o, a, b and s are solvent independent coefficients characteristic of the process and indicator of its sensitivity to the accompanying solvent property; α, β and π^*. While α is a quantitative scale of hydrogen bond-acidity of a solvent or its ability to donate a hydrogen bond; β is a scale of hydrogen bond basicity of the solvent or its ability to accept a hydrogen; and π^* is the solvent dipolarity/ polarizability, which is a scale of the ability of solvent to stabilise a charge or dipole. The values of these parameters as reported in literature for methanol and the imidazolium based ionic liquids used in the present study are presented in Table 3.2. (12, 38-43)

Solvatochromic studies on binary solvent mixtures of ionic liquids (44) in molecular solvents have established that addition of former to the later change the microscopic parameters viz. α, β and π^* in a concentration dependent manner with values moving in the direction of pure ionic liquids. In view of these reports it can be assumed that for the mixed solvent systems as used in present case the value of π^* and β should increase with increase in RTIL concentration with an extent dependent on the nature of RTIL. Since the Kamlet-Taft parameter α which gives the hydrogen bond acidity of the solvent is largely characteristic of cation of ionic liquid, the value of α is expected to decrease with increase in concentration of RTIL by an extent independent of the nature of RTIL. In view of the values for α, β and π^* as enlisted in table 3.2, it seems that while β values will change by greater extent in case of [BMIM][CH_3COO] plus methanol the variations in π^* values with increase in concentration of RTIL will be more for BMIM][Cl] and [BMIM][PF_6] plus methanol systems. While increase in π^* is expected to decrease the *k* values, the observed increase in the said values with increase in concentration of explored RTILs and similar nature of the moiety (imidazolium cation) responsible for the expected variation in α implies that in present case variations in the β with change in composition is the dominating factor that affects the overall kinetics. Increase in the β is expected to increase the basicity of the medium that in turn will increase the nucleophilicity of the negatively charged azide anion. To establish the same UV-visible spectra for azide in methanol in presence of changing concentrations of [BMIM][CH_3COO], [BMIM][Cl], [BMIM][PF_6] were recorded and the same are presented in Figure 3. 5. UV-spectrum of azide in methanol shows a sharp peak at around 200 nm in pure methanol, this has been attributed to the charge (electron) transfer to the polarized solvent (45). The solvent dependence of the position of this band is a measure of the solvent impact on the nucleophilicity of the azide ion. As clear from the spectra depicted in Figure 3.5 with increase in concentration of RTILs, the band becomes more intense and is shifted towards higher wavelengths. The variation of λ_{max} with the increasing addition of RTILs as observed in the UV-visible spectra for azide in methanol in presence of changing concentrations of [BMIM][CH_3COO], [BMIM][Cl], [BMIM][PF_6] is depicted in Figure 3.6. As clear from these figures increase in concentration of the RTIL shifts the λ_{max} of the charge transfer band of azide ion to higher wavelengths with the shift being more for [BMIM][CH_3COO]. This observed shift in the λ_{max} of azide anion with addttion of RTIL is a clear evidence for increase in the nucleophilicity of the azide anion (45)**.** In light of the above cited factors, observations and expected variations in α, β and π^* with increase in concentration of RTIL the *k* values for the investigated nucleophillic substitution reaction are expected to increase in the order [BMIM][CH_3COO]>> [BMIM][Cl]> [BMIM][PF_6] a trend that matches our observations. Thus highest rate achieved in [BMIM][CH_3COO]-Methanol solvent systems is because of the large β value which reflects the highly basic medium.

Conclusion

The impact of imidazloium based room temperature ionic liquids on the reaction kinetics of nucleophilic substitution reaction between the p-tolunesulfonyl chloride and sodium azide in methanol was investigated. It was observed that addition of RTILs increase the rate kinetics in order [BMIM][CH_3COO]>> [BMIM][Cl]> [BMIM][PF_6] . The experimental results demonstrated that a simple Hughes-Ingold polarity rule is inadequate to describe the system, and can be explained only in light of multi parameter Kamlet-Taft equation. For the investigated nucleophillic substitution reaction it was found that β value that represents the hydrogen bond basicity of the solvent is the dominant factor that determines the overall impact on the kinetics of the selected nucleophilic substitution reaction.

References

1. (a) Yost, M. G.; Rose, M. A.; Morgan, M. S. *Appl. Occup. Environ. Hyg*. **2003**, *18*, 160-169. (b) Welles, W. L.; Wilburn, R. E.; Ehrlich, J. K.; Floridia, C. M. *J. Hazard Mater*. **2004**, *115*, 39-49. (c) Tsai, J.-H.; Hsu, Y.-C.; Yang, J.-Y. *Sci. Total Environ*. **2004**, *328*, 131-142. (d) Agostini, E.; Chini, M.; Ciucci, I.; Corezzi, M.; Mazzini, M. *Adv. Air Pollut*. **2004**, *14*, 647-656.

2. Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, UK, **1998**.

3. Tanaka, K.; Toda, F. *Chem. Re*v. **2000**, *100*, 1025–1074.

4. Clark, J. H.; Tavener, S. J. *Org. Process Res. De*v. **2007**, *11*, 149–155.

5. Welton, T. *Chem. Re*v. **1999**, *99*, 2071–2083.

6. Scammells, P. J.; Scott, J. L.; Singer, R. D. *Aust. J. Chem.* **2005**, *58*, 155–169.

7. (a) Hartshorn. S. R. *Aliphatic Nucleophilic Substitution*; Cambridge University Press: Cambridge, 1973. (b) Kartritzky, A. R.; Brycki, B. E. *Chem. Soc. Rev*. **1990**, *19*, 83-105.

8. Weissermel, K.; Arpe, H. J. *Industrial Organic Chemistry*, 3rd ed.; VCH: New York, **1997**.

9. Smith, M. B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, 6th ed*.; John Wiley: New York, **2007**.

10. (a) Cowdrey, W. A.; Hughes, E. D.; Ingold, C. K.; Masterman, S.; Scott, A. D. *J. Chem. Soc*. **1937**, 1252-1271. (b) Lewis, G. N. *Valence and the structure of atoms and molecules*; Chemical Catalog Company: NY, **1993**; p 113. (c) Oslen, A. R. *J. Chem. Phys*. **1933**, *1*, 418-423.

11. Chiappe, C.; Pieraccini, D. *J. Phys. Org. Chem.* **2005**, *18,* 275.
12. Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley-VCH: Weinheim, Germany, **2003**.
13. Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Bell: London, **1969.**
14. Hughes, E. D.; Ingold, C. K. Mechanism of Substitution at a Saturated Carbon Atom. Part IV. A Discussion of Constitutional and Solvent Effects on the Mechanism, Kinetics, Velocity and Orientation of Substitution. *J. Chem. Soc.* **1935**, 244.
15. Hughes, E. D. *Trans. Faraday Soc.* **1941**, *37,* 603.
16. Hughes, E. D.; Ingold, C. K. *Trans. Faraday Soc.* **1941**, *37,* 657.
17. Cooper, K. A.; Dhar, M. L.; Hughes, E. D.; Ingold, C. K.; MacNulty, B. J.; Woolf, L. I. Mechanism of Elimination Reactions. Part VII. Solvent Effects on Rates and Product Proportions in Uni and Bi-molecular Substitution and Elimination Reactions of Alkyl Halides and Sulphonium Salts in Hydoxylic Solvents. *J. Chem. Soc.* **1948**, 2043.
18. Skrzypczak, A.; Neta, P. *Int. J. Chem. Kinet.* **2004**,*36,* 253.
19. Swiderski, K.; McLean, A.; Gordon, C. M.; Vaughan, D. H. *Chem. Commun.* **2004**, 590.
20. McLean, A. J.; Muldoon, M. J.; Gordon, C. M.; Dunkin, I. R. *Chem. Commun.* **2002**, 1880.
21. Grodkowski, J.; Neta, P.; Wishart, J. F. *J. Phys. Chem. A* **2003**, *107,* 9794.
22. Skrzypczak, A.; Neta, P. *J. Phys. Chem. A.* **2003**, *107,* 7800.
23. Crowhurst, L.; Falcone, R.; Lancaster, N. L.; Llopsis-Mestre, V.; Welton, T. *J. Org. Chem.* **2006**, *71,* 8847.
24. Ranieri, G.; Hallet, J. P.; Welton, T. *Ind. Eng. Chem. Res***. 2008**, *47*, 638-644.
25. Well, T. P.; Hallet, J. P.; Williams, C. K.; Welton, T. *J. Org. Chem.* **2008,***73*, 5585-5588.

26. (a) Lancaster,N. L.;Welton,T.; Young,G. B. *J. Chem. Soc., Perkin Trans*. 2 **2001**, 2267. (b) Lancaster, N. L.; Welton, T. *J. Org. Chem*. **2004**, *69*, 5986. (c) Crowhurst, L.; Falcone, R.; Lancaster, N. L.; Llopis-Mestre, V.; Welton, T. *J. Org. Chem*. **2006**, *71*, 8847.

27. Chiappe, C.; Pieraccini, D.; Saullo, P. *J. Org. Chem***.** **2003**, *68*, 6710-6715.

28. Nguyen, H.-P.; Kirilov, P.; Matondo, H.; Baboulene, M. *J. Mol. Catal. A* **2004**, *218*, 41.

29. Boonanahalli, S. K.; Kim, D. W.; Chi, D. Y. *J. Org. Chem*. **2004**, *69*, 3340.

30. Wheeler, C.; West, K. N.; Liotta, C. L.; Eckert, C. A. *Chem. Commun*. **2001**, 887-888.

31. Liu, Z.; Chen, Z.-C.; Zheng, Q.-G. *Synthesis* **2004**, 33-36.

32. Judeh, Z. M.A.; Shen, H.-Y.; Chi, B. C.; Feng, L.-C.; Selvasothi, S. *Tetrahedron Lett*. **2002**, *43*, 9381-9384.

33. Lancaster, N. L.; Salter, P. A.; Welton, T.; Ypung, G. B. *J. Org. Chem*. **2002**, *67*, 8855-8861.

34. Kamlet,M. J; Abboud, J. L; Taft, R. W. *J. Am. Chem. Soc.*, **1977**, *99,* 6027.

35. Kamlet, M. J; Taft, R. W. *J. Am. Chem. Soc.*, **1976**, *98,* 377.

36. Taft, R. W; Kamlet, M. J. *J. Am. Chem. Soc.*, 1**976**, *98,* 2886.

37. Yokoyama,T; Taft, R. W; Kamlet, M. J. *J. Am. Chem. Soc.*, 1976, **98**, 3233.

38. Kamlet, M. J.; Addoud, J.L.; Abraham, M.H.; and Taft, R.W. *J. Org. Chem*. **1983**, *48,* 2877.

39. Gonc¸alves, R. M. C.; Simo˜ es, A. M. N.; Albuquerque,L. M. P. C.; Rose´s, M.; Ra`fols, C.; Bosch, *E. J. Chem. Res*. (S), **1993**, 214.

40. Nicolet, P.; Laurence, C. *J. Chem. Soc. Perkin Trans. 2*, **1986**, 1071.

41. (a) Reichardt,C. Solvents and Solvent Effects in Organic Chemistry, VCH, Weinheim, 2nd edn., **1990**; (b) Reichardt,C. *Chem. Rev*., **1994**, *94,* 2319.

42. Jelicˇ ic´ , A; Garcia,N; Lo¨ hmannsro¨ ben, H. G ; Beuermann,S. *Macromolecules,* **2009**, *42*, 8801.

43. Doherty, T. V; Mora-Pale,M; Foley,S. E; Linhardt ,R. J; Dordick,J. S. *Green Chem*., **2010**, *12*, 1967.

44. MANCINI, P. M; G.G. FORTUNATO, G. G; VOTTERO, L. R. *Physics and Chemistry of Liquids.* **2004**, *42*, 625–632.

46. Burak. I; Treinin, A. J. Chemical Physics, **1963,** 39, 189.