Ionic Liquids and Their Binary Systems with Molecular Solvents as Catalyst and Reaction Medium for Organic Synthesis

A Dissertation Submitted to University of Dhaka for the Partial
Fulfillment of the Requirements of the Degree of
Doctor of Philosophy in Chemistry

Submitted by
GulshanAra
Registration No. 51
Session: 20013-2014

DEPARTMENT OF CHEMISTRY
PHYSICAL CHEMISTRY RESEARCH LABORATORY
University of Dhaka
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Declaration

Experiments described in this thesis were carried out by the author of this thesis in the Department of Chemistry, University of Dhaka, Dhaka-1000, Bangladesh. This work has not been presented and will not be presented for any other degree.

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Dedicated

to

My Parents, My Daughter,

My Husband,

and

My Supervisors

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(GulshanAra)

Title of the thesis:

Ionic Liquids and their Binary Systems with Molecular Solvents as Catalyst and Reaction Medium for Organic Synthesis

Submitted by:

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The general description and outline of this thesis are given below:

Chapter 1: General Introduction

Chapter 1 describes the background, necessity, and objective of the present research.

Chapter 2: Preparation and Characterization of Protic and Aprotic Ionic Liquids

Chapter 2 describesthe syntheses of both protic ionic liquids (PILs) and an aprotic ionic liquid (AIL) based on 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) and their relevant characterization. The two PILs, [DBU][OH] and [DBU][CH_3COO] were prepared by simple neutralization method of an organic base, DBU and weak acids water and acetic acid. DBU based AIL, [C_6DBU][OH] was synthesized by alkylation followed by metathesis. DBU was alkylated by 1-chlorohexane to prepare [C_6DBU][Cl]. For metathesis, the chloride anion was replaced by hydroxide anion by using solid NaOHpellet where NaCl was precipitated out from the reaction mixture. The prepared ILs were characterized by spectral and thermal analyses.For spectral analysis FTIR, ^{1}H NMR and ^{13}C NMR spectral measurements were carried out. The spectral analyses confirmed the presence of functional groups in the structure, ^{1}H NMR explained the presence of different protons and ^{13}C NMR showed the carbon skeleton of the structure of prepared ILs. TG-DTA was performed and the thermal stability of the prepared ILs was compared with the precursors used.Computational study using density functional theory was performed to describe the interaction between ions of the AIL and calculated spectra (FTIR, ^{1}H NMR, and ^{13}C NMR) were correlated with the experimental spectra of the AIL.

Chapter 3: Physicochemical Properties of Binary Systems of Protic and Aprotic Ionic Liquids with Molecular Solvents

In this chapter, preparation of binary systems of prepared ILs, [DBU][OH] with water and DBU, [DBU][CH_3COO] with acetic acid and DBU, and [C_6DBU][OH] with water at various molar ratio has been presented. The physicochemical properties of the ILs and their binary systems, investigated by the measurements of density, viscosity, and refractive index, particle size by dynamic light scattering (DLS) and conductivity with electrochemical impedance spectroscopic measurement, and the TG-DTA, FT-MIR, and FT-NIR spectral analyses, have also been discussed. The thermal stability of the binary systems, determined from TG/DTA results revealed interaction between the IL moieties and solvent molecules. The conductivity results described the mobility of ions in different binary systems of the ILs and also provided information about the rigidity of the packing of the ions of ILs. The FT-MIR and FT-NIR spectroscopic analyses suggested the presence of trapped water in the IL-rich region of the binary systems. The particle size analysis supported the presence of trapped water by describing the presence of different microstructures in water-rich and water-deficient regions. The change in the density and viscosity was used to explain the interactions between the solvent molecules and ions of ILs in terms of hydrogen bonding, ion-dipole interactions, dispersion forces etc. The refractive index measurement also gave idea about the interactions in the binary systems of ILs.

Chapter 4: Michael Addition Reaction of Acetylacetone and 2-Cyclohexene-1-oneusing the IL Systems as Catalyst and Reaction Medium

In Chapter 4, kinetic results of Michael addition reaction of acetylacetone and 2-cyclohexen-1one in prepared PILs and the AIL and their binary systems without the use of any organic solvents have been reported. The reaction was found to be catalyzed by the ILs and their binary systems with molecular solvents using no organic solvents. The mechanism of the reaction was established and the role of the ILs in the reaction was explained.The effect of the molecular solvents in the binary systems on the reaction rate was also explained from the kinetic results.The product of the Michael addition reaction was characterized by chemical and spectral analyses. The functional groups present in the structure of the product were detected by chemical analyses. FTIR, ^{1}H NMR, and ^{13}C NMR spectra were used to determine the structure of the product.

Chapter 5: Correlation of Physicochemical Properties of the IL Systems with Kinetic Results of the Michael Addition Reaction

The kinetic results of the Michael addition reaction of acetylacetone and 2-cyclohexen-1-one catalyzed by the ILs and their binary systems are correlated with different physicochemical properties of the prepared ILs and their binary systems in Chapter 5. The binary systems with high degradation temperature exhibited low conductivity which correlates well with the kinetic behavior of the Michael addition reaction.The FTMIR spectra were in good agreement with the FTNIR spectra. The particle size and thermal analyses showed sharp change due to the existence of two different microstructures in water-rich and water-deficient regions of the AIL. The change of viscosity was consistent with the conductivity behavior of the systems. The rates of the reaction were higher in binary systems having lower conductivity and viscosity. The transition of the reaction rates could be observed at the structural transition from water-rich to a water-deficientregion.

Chapter 6: Comparative study of the Kinetics of Michael Addition Reactions using the IL Systems as Catalyst and Reaction Medium

In chapter 6, kinetic results of the Michael addition reaction of acetylacetone and 2-cyclohexene-1-one catalyzed by the PILs and AIL and their binary systems without using any organic solvents were compared with each other. The kinetic results allowed the profiles of the reaction completion time vs. mole fraction of ILto be divided into two regions, IL-rich region and IL-deficient region. The rates were higher in the PIL, [DBU][OH] and its binary systems compared to the PIL, [DBU][CH_3COO] and its binary systems. The rates of the reaction in PILs and their binary systems were also compared with the rates in AIL and its binary systems. For PIL and AIL with the same anion, rate of the reaction was higher for the AIL due tolarge size of the cation. Where both cations and anions were different for the PIL and AIL, the rate of the reaction was also higher for AIL due to basic nature of the anion and larger size of the cation.

Chapter 7: General Conclusions and Outlook

Chapter 7 summarizes the results for a general conclusion and discussed the future prospect of ILs and their binary systems with molecular solvents in developing a suitable media as catalyst for organic synthesis.

Abstract

Protic and aprotic ionic liquids (ILs) derived from an organic base 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) were prepared and characterized.The structure and interactions between anions and cations of the AIL were studied computationally. Binary systems of these ILs with molecular solvents were prepared. Physicochemical properties of these ILs and their binary systems have been studied in detail. These systems have been evaluated as media and catalysts for a model reaction, Michael addition reaction through systematic kinetic studies. Efforts have been made to correlate physicochemical properties of these ILs and their binary systems withkinetic behavior.

The protic ionic liquids (PILs) were prepared by neutralization reaction between a strong base, DBU and weak acids, water and acetic acid. The aprotic ionic liquid (AIL) was synthesized by alkylation of the base DBU followed by metathesis process. Thermal analysis by thermogravimetric and differential thermal analysis (TG-DTA) and spectral analysis by Fourier transform infrared (FTIR), ^{1}H NMR, ^{13}C NMRspectrometric analyses have been performed to characterize the prepared PILs and AIL.The H-bonding between anions and cations of the AIL was explained by computational study and the spectral results (FTIR and NMR) were correlatedwith calculated spectra.The binary systems with molecular solvents like water, acetic acid, and DBU were prepared at different molar ratio. Study of physicochemical properties of these ILs and their binary systems were carried out by performing the measurement of TG-DTA, density, viscosity, refractive index, and conductivity, and analysis of spectra and particle size. The interaction between ILs and solvent molecules has been explained from variation of the degradation temperature with change in composition of the ILs in binary systems. The arrangement of ions with molecular solvents and ionic mobility of the ions of ILs in the binary systems have been discussed using the conductivity results from impedance spectroscopy. The change in density and viscosity with mole fraction of the IL provided information regarding hydrogen bonding, ion-dipole interaction, dispersion forces between the ions and molecular solvents. The FTIR (MIR and NIR) spectra indicated the presence of trapped water in IL-rich region. Particle size analysis explained different microstructures in water-rich and IL-rich region of the binary systems of the AIL with water. The ILs and their binary systems were used as catalyst and medium for the study of the kinetics of Michael addition reaction. The products of the Michael addition reaction were characterized by chemical and spectral analyses. The mechanism of the reaction has been established from the kinetic resultsand theconstituents ions of ILs and the solvent molecules were found to play important role.

Kinetic results of the Michael addition reaction have been correlated with physicochemical properties such as conductivity and degradation temperature of the binary systems of ILs. The mutual relationship between the physicochemical properties has also been discussed. The kinetic results of the Michael addition reaction using different ILs (PILs and AIL) and their binary systems have been compared and contrasted. The binary systems of ILs with molecular solvents showed enhancement in the rate compared to pure ILs and conventional organic bases.The AIL showed better catalytic performance than the PIL with the same anion due to the large size of the cation. When both the cations and anions of the PIL and AIL are varied, the better catalytic performance is exhibited by the AIL for basic nature of the anion and the bulky size of the cation. Therefore, the structural changes affect the catalytic performance of ILs on organic synthesis.Thus, ILs and their binary systems with tunable physicochemical properties can have a bright prospect in the field of organic synthetic chemistry as a better catalyst and reaction media.

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LIST OF SYMBOLS

Name	**Symbol**
Conductivity	σ
Viscosity	η
Density	ρ
Diameter of droplet	d
Refractive index	n
Molar conductivity	Λ
Average rate	v
Regression coefficient	r^2
Wavelength	[illegible]

LIST OF ABBREVIATIONS

Elaborated Form	**Abbreviated Form**
Ionic liquid	IL
Aprotic ionic liquid	AIL
Protic ionic liquid	PIL
1,8-diazabicyclo[5.4.0]-undec-7-ene	DBU
Room temperature ionic liquid	RTIL
Ethylammonium nitrate	EAN
Dimethylammonium nitrate	DMAN
Density functional theory	DFT
Molecular dynamics	MD
Dicationicionic liquid	DIL
Thin layer chromatography	TLC
1,8-diazabicyclo[5.4.0]-undec-7-ium hydroxide	[DBU][OH]
1-Butyl-3-methylimidazolium hydroxide	[BMIm][OH]
1,8-diazabicyclo[5.4.0]-undec-7-ium acetate	$[DBU][CH_3COO]$
1-hexyl-1,8-diazabicyclo[5.4.0]-undec-7-ium hydroxide	$[C_6DBU][OH]$
Thermogravimetric-differential thermal analysis	TG-DTA
Fourier transform infrared	FTIR
Reichardt'sBetaine dye	RBD
Proton-1 nuclear magnetic resonance	^{1}H NMR
Carbon-13 nuclear magnetic resonance	^{13}C NMR
Dynamic light scattering	DLS

1.1. General Introduction

Ionic liquids (ILs), a smart liquid material with unique properties, have been one of the most fascinating materials in modern science and technology. They are low melting salts (<100°C) composed exclusively of weakly coordinating ions and possess both purely ionic character and liquidity near or below room temperature. Their special properties are immeasurable vapor pressure, excellent chemical, electrochemical and thermal stability, greater ionic conductivity, wide liquidus region, outstanding dissolving capability i.e. ability to dissolve organic, inorganic, and polymeric materials, environmental compatibility, ability to be recycled, multiple functionality, task specificity and so on [1-3]. As a consequence of these properties ILs have gained popularity as environmentally friendly green solvent and havebeen widely used as suitable alternative to volatile organic solvents to be applied in electrochemical, synthetic and separation processes.

ILs exhibit favorable solvation behavior for a wide range of substances; organic, inorganic, organometallic compounds, polymer compounds, biomolecules, and metal ions. They usually comprise poorly coordinating ions which make them highly polar but non-coordinating solvents. ILs are immiscible with most of the organic solvents, thus they provide a non-aqueous, polar alternative for two-phase systems. Furthermore, ILs, which are not miscible with water can be used as immiscible polar phase with water. Although all other conventional solvents evaporate to the atmosphere, ILs do not evaporate and their non-volatility gives an opportunity to utilize them in high vacuum systems. The negligible volatility is the basic property which characterizes them as green solvents. Considering potential as solvents, ILs can easily replace other conventional organic solvents which are used in large quantities in chemicals processing industries to eliminate major environmental problems.

Concerning the solvent property the greatest advantage of ILs is their widely tunable properties with regard to polarity, hydrophobicity and solvent miscibility through the appropriate selection of the anion and the cation. Since each combination of cation and anion possesses set of specific chemical and physical properties the unique characteristics of modulating the constituent ions and related properties enable ILs to exert highly selective functionality which is required for the better yield in various synthetic processes.

However, typical ILs are very expensive due to high cost in production and preservation. IL-based mixed solvents have the potential to offer a novel route for tailoring properties of these designer solvents. Addition of a conventional solvent to an IL system may significantly influence physicochemical properties of ILs. Proper tuning of the properties may help exploiting the desirable chemistry of the binary systems for manifold applications. In general, high viscosity and high melting points in some cases make practical problems for wide applications of these dream materials. This necessitates the remarkable reduction of viscosity and lowering of melting temperature of ILs, which may be achievable by mixing with suitable solvents. Furthermore, ILs, due to their hygroscopic nature and ionic characteristics, need to be preserved in an inert atmosphere in glove boxes. Binary systems of ILs and molecular solvents resolve this issue since binary systems prepared from suitable combinations may be stored and used under ambient conditions. To explore the complete potential of ILs as solvent systems, a broader understanding of the physicochemical properties of ILs as well as their binary systems with molecular solvents is very crucial. Systematic analyses of viscosity, density, conductivity, surface tension, thermal stability, and other physicochemical properties may unveil interactive features in the binary systems for the application in organic synthesis.

Organic solvents used in most of the synthetic processes in chemical industries evaporate into the atmosphere with adverse effects on the environment as well as human health. ILs, on the other hand, are liquid at ambient conditions with unique array of physicochemical properties such as negligible vapor pressure and non-toxicity. ILs are proving to be increasingly promising as viable media for potentially green synthesis and separation process.

Many chemical reactions are carried out in conventional solvents. Upon the completion of reaction, chemical products must be separated from the solvent. ILs seem to be potentially good solvents for many chemical reactions in the cases where distillation is not practical, or water insoluble or thermally sensitive products are involved ina chemical reaction.

ILs offer the advantages of both homogenous and heterogeneous catalysts. Brennecke and Maginn [4] reported that the ionic nature of the IL also gives an opportunity to control reaction chemistry, either by participating in the reaction or stabilizing the highly polar or ionic transition states.

Ranu and Banerjee [5-6] reported that a basic IL, 1-butyl-3-methylimidazoliumhydroxide, [BMIm][OH], can efficiently catalyze the Michael addition reaction without requiring any other catalyst and solvent. Moreover, these [BMIm][OH]-catalyzed reactions showed many remarkable advantages such as operational simplicity, short reaction time, high yields of products, and greenness of procedure, avoiding hazardous organic solvents and toxic catalysts. This indicates that ILs can be the better and practical substitute to the traditional catalysts. ChloroferrateILs have successfully been used as efficient catalysts for Michael addition reaction[7]. To-date, only pure ILs systems have beenexploited in organic synthesis for the replacement of organic solvents although pure ILs are very expensive. Therefore, investigation ofthe interactions of molecular solvents and ILs in molecular level is very crucial to gain insight into the state of ILs and ILs-solventfor complete understanding for specific applications of ILs as an efficient catalyst as well as green solvent medium in organic synthesis.

1.1.1. Outline of the Research

In this work, protic ionic liquids (PILs) based on 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU)with different anions and aprotic ionic liquid (AIL) with long alkyl chain were prepared and characterized. Binary systems of the prepared ILs with molecular solvents at various molar ratios were prepared. The physicochemical propertiesand molecular interaction of the ILs in pure and binary systems were studied. The applicability of the studied ILs and their binary systems as catalyst and reaction medium for organic synthesis were explored and the structure of the product were determined. The effect of the ILs and their binary systems on the rate of the organic synthesis was studied and correlated with the studied physicochemical properties of the systems. The rate of the reaction using PILs with different anions and AIL were compared. Finally, the prospects of the uses of ILs, both protic and aprotic, and their binary systems with molecular solvent as catalysts and media for organic synthesis have been discussed.

1.2. Ionic Liquids

ILsare a class of materials which solely consist of cations and anions and most of them are liquid at or below 100°C(Figure 1.1). Classical solutions of electrolytes are obtained by dissolution of salts in molecular solvents. Such systems consist of solvated ions, their charged or neutral combinations and solvent molecules. On the other hand, a salt may be melted down, or in other words ‘liquefied’, by providing to the system a heat to counterbalance the lattice energyof the salt. Such a system, called molten salts or IL consists of ions and their combinations and is free of any molecular solvent. On the other hand, salts having a low melting point are liquids at room temperature, or even below, and form a new class of liquids usually called room temperature ionic liquids (RTIL). Their physicochemical properties are the same as high temperature ILs, but the practical aspects of their maintenance or handling are different enough to merit a distinction.

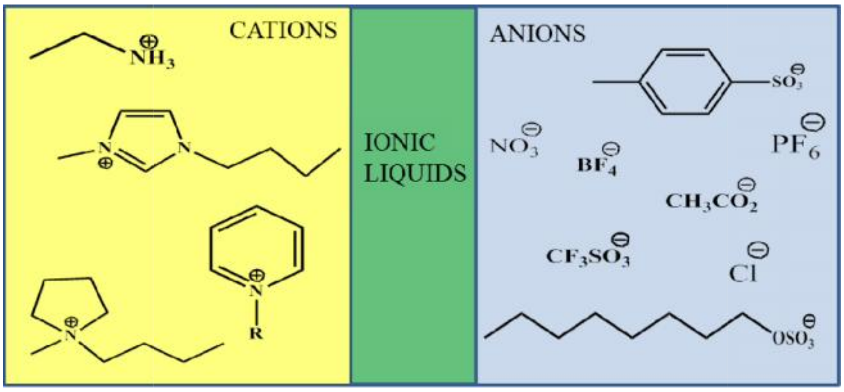


Figure 1.1. Typical ionic liquids and their constituent ions.

1.2.1. Properties of ILs

The wide variation in properties is one of the impressive features of ILs. For example, some are acidic, some basic and others neutral. Some are miscible with water and others immiscible. Some are toxic and others non-toxic. This variation in properties opens up numerous opportunities for various applications.

1.2.1.1. Vapor Pressure

ILshave negligible vapor pressures. The lack of measurable vapor pressure arises from strong Coulombic interactions between the ions in the ILs. Negligible vapor pressure is one of the most important properties of ILs. ILs generally do not evaporate in reaction vessels and cannot contribute to air pollution or cause health concerns in this context.

1.2.1.2. Liquidus Range and Thermal Stability

Liquidus range is the temperature range between melting point (or glass transition temperature) and boiling point (or thermal decomposition temperature). ILs have widerliquidus ranges compared to most of themolecular solvents.

For example, 1-alkyl-3-methylimidazolium salts typically have glass transition temperatures in the range -70 to -90 ^{o}C and thermal decomposition temperatures ranging from 250 to over 450 ^{o}C. Therefore, they have liquidus ranges of over 300 ^{o}C[8]. The liquidus range of water is 100 ^{o}C (0 to 100 ^{o}C) and that of ethanol is 192.6 ^{o}C (-114.1 to 78.5 ^{o}C).

ILs have higher thermal stability that means experiments in these solvents can be carried out at high temperatures without any notable solvent degradation.

1.2.1.3. Conductivity

ILs are composed solelyof ions, it would be expected that ILs have highconductivities. This is not the generalized case since the conductivity ofany systemdepends not only on the number of chargecarriers but also on their mobility. The large constituent ionsof ILs reduce the ion mobility which, in turn, leads tolower conductivities. Furthermore, ion pair formation and/orion aggregation lead to reduced conductivity. The conductivityof ILs is inversely linked to their viscosity. Hence,ILs of higher viscosity exhibit lower conductivity.Increasing the temperature increases conductivity and lowersviscosity.

1.2.1.4. Viscosity

Generally, ILs are more viscous than common molecularsolvents. The viscosity of ILs is determined byvan der Waals forces and hydrogen bonding. Electrostaticforces may also play an important role. Alkyl chain lengtheningin the cation leads to an increase in viscosity [9]. This is dueto stronger van der Waals forces between cations leading toincrease in the energy required for molecular motion. Also, theability of anions to form hydrogen bonding has a pronouncedeffect on viscosity. The fluorinated anions such as BF_4^- andPF_6^- form viscous ILs due to the formation ofhydrogen bonding [10]. In general, all ILs show asignificant decrease in viscosity as the temperature increases [11].

1.2.1.5. Density

ILs in general are denser than water and their densities decrease withincrease in the length of the alkyl chain in the cation [12]. ILs with shorter alkyl chains or less bulky cations have higher densities than ILs with longer alkyl chains or more bulky cations.

1.2.1.6. Melting Point

As a class, ILs have been defined to have meltingpoints below 100 ^oC and most of them are liquid at roomtemperature. Both cations and anions contribute to the lowmelting points of ILs. The increase in anion size leadsto a decrease in melting point [13]. Cations size and symmetry make animportant impact on the melting points of ILs. Largecations and increased asymmetric substitution results in amelting point reduction [14].

1.2.2. Structure of ILs

Of the three forms of matter (solids, liquids, and gases), the physical structure of liquids is the least well-understood. It is challenging to the explanation of molecular association in liquids because they are an intermediate phase, with features common to both solids and gases [15]. There are also still gaps in our knowledge of the forces that control structure on tiny dimensions[16-18].Until recently; liquids were thought to be structurally homogeneous systems [19]. Liquid structure,though much more disordered,was believed to be similar to the parent solid, sincemolecules diffuse rapidly and randomly through the liquid. This would mean that structure exists only over negligible distances and time scales. However, advances in theoretical, computational, and experimental techniques have provided extraordinary resolution pictures of the physical structure of liquids[20-24]. Liquids possess reasonably well defined structure in the bulk phase and at interfaces, and that this structure supports solvent behavior.

Walden discovered a pure salt, ethylammonium nitrate (EAN) that was liquid at ambient temperatures[25].It was earlier believed that ions never form a liquid at room temperature unless diluted in a molecular solvent asestablished theories of liquids dealt with uncharged molecules (water, benzene, ethanol) or atomic fluids (mercury, argon, bromine), and ions in solution[26]. EAN isstrikingly similar to water in many respects as it was clear, colorless, and odorless, with solid-like density (1.21 g cm^{-3}) and reasonably high viscosity. However, Walden's key finding was its electrical conductivity; a property inherent to all liquids that contain mobile ions[27]. The conductivity of EAN was consistent with a composition of purely anions and cations. So, EAN is the first ILdiscovered by Walden.

ILs can dissolve both polar and apolar compounds. This is incompatible with standard models of liquids of uniform polarity; solvents can be either polar or nonpolar and thus prefer to dissolve similar materials according to the statement "like dissolves like".

ILs exist as liquids at ambient temperatures because of their chemical structure. The anion and cation are chosen precisely to destabilize the solid-phase crystal. Thus, while there are no set rules to making an IL, in general this can be achieved within a relatively large window of ion structures by balancing ion-ion interactions and symmetry. For instance, the cation alkyl chain must be long enough to reduce Coulombic forces and disrupt lattice packing, but not be too long (n< 12) as this will increase melting pointof the salt despite the enhanced asymmetry; cohesive interactions increase with length of nonpolar groups as per linear alkanes. However, Davis et al. recently produced low melting salts from very long chain (>C16) cations by introducing a *cis* double bond on the alkyl group [28]. This highlights the complex array of packing and chemical factors that controls IL melting point [29].

1.2.2.1. Classification by Structure

ILs, like solvents generally, are usually classified on the basis of chemical structure. However, ILs possess structural features suggestive of molten salts, ionic surfactants, ionic crystals, [30] and molecular liquids, and the number of potential neat ILs is massive [31]. This makes classifying ILs challenging, as multiple labels are often appropriate for a given IL, depending whether the anion, cation, or a functional group is considered most important. Protic [32] and aprotic [33] ILs are the two most common IL types, based on the well-established division between proton-donating (protic) and nonproton-donating (aprotic) molecular solvents.However, this definition is not so rigid as it would seem; Davis et al. characterized dicationic ILs with one protic and one aprotic charge center, enabling both functionalities to be expressed[34].There are also two more types of ILs based on the structure, inorganic and solvate (chelate) ILs. Most of the ILs consist of organic cations and organic or inorganic anions. But inorganic ILs consist both inorganic cations and inorganic anions. Inorganic ILs are obtained in both PILs and AILs. There are protic example like hydrazinium nitrate (melting point 80 ^{o}C) and aprotic example like lithium chlorate (115 ^{o}C) [35]. The solvate ILs include multivalent cation salts and the first member of this class molten salt hydrate, like $Ca(NO_3)_2.4H_2O$. Figure 1.2 shows chemical structures of representative popular anions and cations[36].

ILsare solvents that can participate in a variety of attractive interactions ranging from the weak, nonspecific, and isotropic forces (e.g., van der Waals, solvophobic, dispersion forces) [37-39] to strong (Coulombic), specific, and anisotropic forces (e.g., hydrogen bonding, halogen bonding, dipole-dipole, magnetic dipole, electron pair donor/acceptor interactions) [40-41]. The variety and strength of intermolecular forces in ILs fine-tune local arrangements in the bulk and near interfaces. However, some interactions have an entropic contribution, paving the way for complex, higher order self-assembled structures. The amphiphilic nature of many ions provides a basis for ordering similar to ionic surfactant systems.

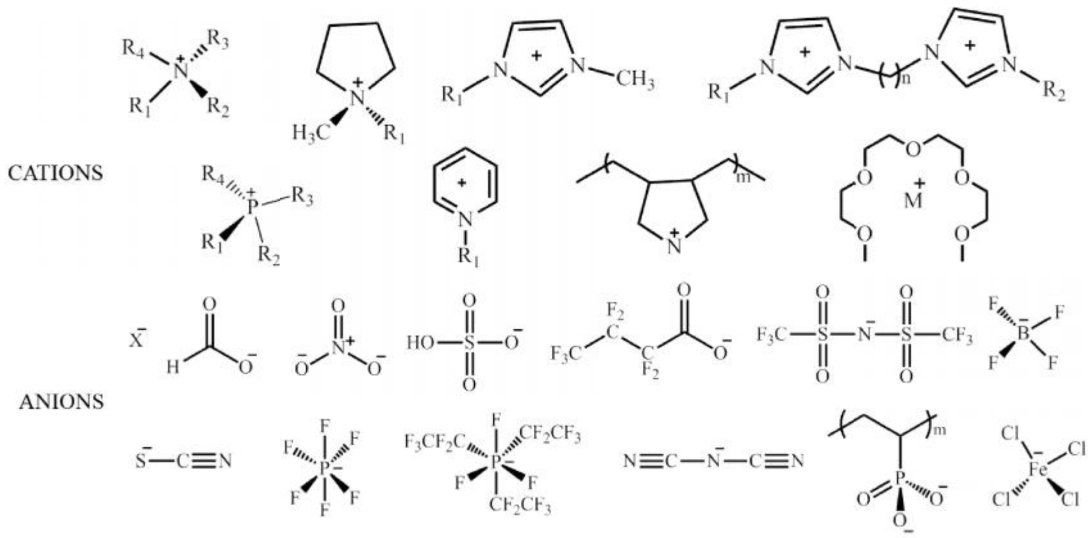


Figure 1.2. Chemical structures of cations and anions used in ILs. From left to right, the cations (top row): ammonium, pyrrolidinium, 1-methyl-3-alkylimidazolium, 1,3-bis[3-methylimidazolium-1-yl]alkane; (second row):phosphonium, pyridinium, poly(diallyldimethylammonium), metal (M^+) tetraglyme. The anions (third row): halides, formate, nitrate, hydrogen sulfate, heptafluorobutyrate,bis(perfluoromethylsulfonyl)imide,tetrafluoroborate, (bottom row):thiocyanate, hexafluorophosphate,tris(pentafluoroethyl)trifluorophosphate,dicyanamide, poly(phosphonic acid), and tetrachloroferrate.

1.2.2.2. The Bulk Structure of ILs

Historically, ILs were thought to fall within the traditional picture of molecular liquids as homogeneous, coherent, and essentially irregular systems [42]. Most researchers regarded the bulk structureof ILs as similar to a highly concentrated salt solution or a molten salt. Recently, it is suggested that ILs are structured solvents, from supramolecular (ion pairs, ion clusters) to mesoscopic (H-bond networks, micelle-like, and bicontinuous morphologies) length scales [43-46]. Understanding these structures iskey to sorting out their complex physical, chemical, and dynamic behavior.

1.2.2.3. Crystal Lattice Structure

The structure of molecular liquids can be inferred from its parent solid crystal, IL crystal structures are expected to provide clues to ion arrangements in the liquid phase. In fact, IL bulk structure was initially inferred from the structure of crystal analogues; the arrangements of ions were assumed to be isotropic, with some local resemblance to the solid or liquid crystal state. Thus, melting was thought to induce a behavior similar to that of molecular liquids, where a high structured crystal phase decays into a disorganized liquid. ILs are unlikely to have great differences in their structures and interionic interactions (compared to molten salts) [47], and ILs possess analogous structural patterns in both the solid and liquid phase although significant randomness in organization is necessary to describe the structure of a liquid [48]. This has been extended recently with quasi- or pseudo- lattice models, which view the bulk ion organization as a collapsed solid crystal[49-51].

Evidence of polar/nonpolar segregation, analogous to amphiphilic self-assembly structures in a liquid and widespread in the crystal structure of conventional amphiphiles is seen in IL crystal structure [52]. 1-Alkyl-3-methylimidazolium halide [C_nMIm][X] (where n = 12-18) have been shown to arrange into well-defined, bilayer crystal lattices. The overall structure of these ILs liquid crystal phases is best described as sheets of imidazolium rings and anions, separated by a domain of interdigitated alkyl chains (layer-layer separations of 2.4-3.3 nm). A H-bond network forms within this lattice [53]. The interlayer distance was inversely proportional to theabilityof the anion to form a 3-D H-bond network, with smallest cation-cation spacing for Cl^-anions and largest for NTf_2anions[54]. NMR experiments showed that the nature of the H-bond network in the lattice is highly anion dependent for the same imidazolium cation of ILs [55-56].

1.2.2.4. Supramolecular Solvent Structure

Ion Pairs or Free Ions

Ion pairs are the simplest repeating units in ILs (Figure 1.3). Thus, it is tempting to represent local arrangements in terms of the ion pair structure with the concentration of free ions. Many ILs are also known to evaporate as ion pairs, which suggest that they may be present in the bulk phase [57-59]. It has also been shown that a pair of oppositely charged ions dispersed in water behaves as one unit. Because ILs represent an infinitely concentrated or solventless ionic solution, tight ions pairs would be expected in this model, and have been studied in a variety of ways for ILs.

The observation of critical behavior in mixtures of EAN and octanol was used to suggest ion pairs in EAN [60]. Weingärtner et al. derived ion pair association constants from conductivity measurements that were 1-2 orders of magnitude larger than predicted for ion pairs in aqueous solution. This suggested that liquid EAN exists in a chemical equilibrium between ion pairs and “free” ions:

$$EA^{+}[NO_3^{-}] \rightleftharpoons EA^{+} + NO_3^{-}$$

The key conclusion, however, was that ion pairs are much more favored in the pure IL bulk than in corresponding solutions of aqueous electrolytes sinceH-bonds arethought to stabilize the ion pair by shielding the long-range Coulombic forces in solution. Early dielectric spectroscopy measurements revealed EAN could be described as a system of ion pairs plus free ions [61].

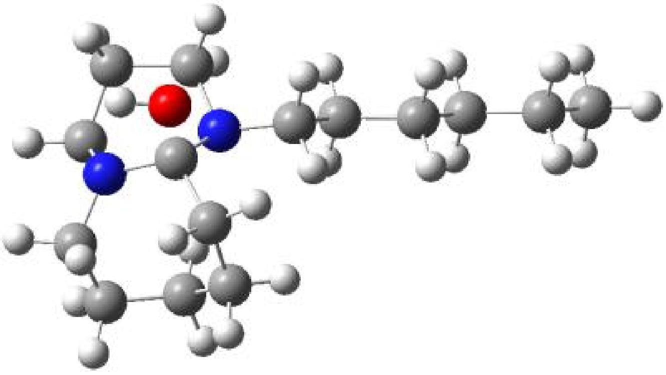


Figure1.3. Ion pairs.

H-Bond Networks

The phase transfer of rare gases and hydrocarbons from cyclohexane to EAN was accompanied by negative enthalpy and entropy values i.e. the proton donor and acceptor sites on the ions may form a 3-D H-bonded network resembling water (Figure 1.4) [62]. This hypothesis explained detection of cationic and nonionic surfactant micelles in EAN as solvent [63-64]. H-bonding was thought to be essential for inducing the solvophobic interactions that drive amphiphilic self-assembly [65].

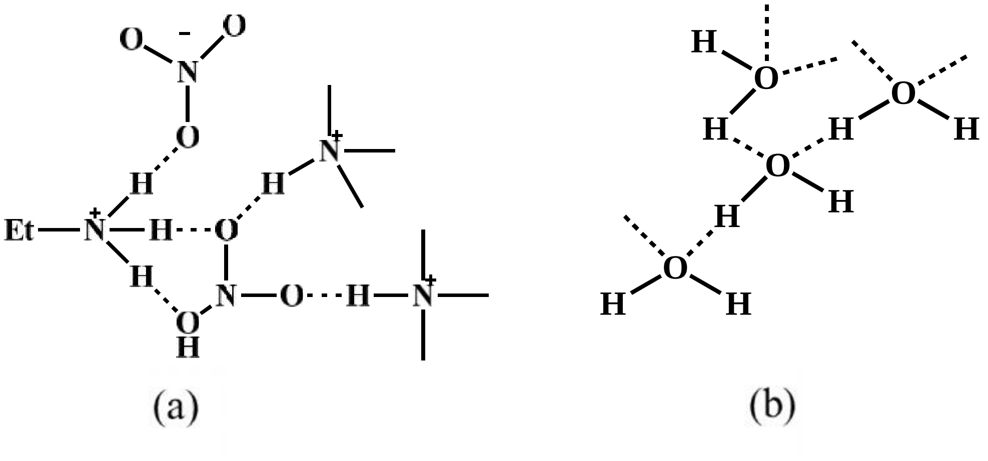


Figure1.4. Model of (a) EAN and (b) H-bond(dashed line) network structureof water.

The measurement of FTFIR spectra of EAN, PAN, and dimethylammonium nitrate (DMAN) in the region (30-600 cm^{-1}) demonstrated H-bonding that excites H-bond bending, stretching, and vibrational modes in molecular liquids [66]. Complementary density functional theory (DFT) calculations enabled the spectra to be deconvoluted and specific H-bond interactions assigned. In every PIL, the frequency difference between the asymmetric and symmetric stretches was approximately 65 cm^{-1}, suggesting comparable H-bonding strengths. The measured peak positions and frequency differences were consistent with the far-IR spectra of pure water. This led to conclude that the H-bond networks in PIL are structurally indicative of water.

Ion Clusters

The liquid state has often been modeled as time-dependent molecular clusters of finite size and number. In water, for example, the solvent structure has been described as flickering clusters, linear molecular chains, or larger, unspecified units based on suggestions that it is a mixture of high- and low-density forms [67-69]. The clustering of molecules in a liquid phase is associated with familiar properties of the system (heat capacity, expansivity, and compressibility) as well as critical phenomena and super cooled or first-order transitions [70].

Recently, there have been many similar attempts to describe IL bulk structure as a population of (net neutral or net charged) ionic clusters or aggregates. ILs form a clustered supramolecular structure to maintain a 3D H-bond network [71].

Electrospray ionization mass spectrometry (EI-MS) has been the principal technique employed to corroborate the ion cluster model, in which the bulk structure is depicted as a sea of polydispersed aggregates. EI-MS experiments of AILs have been performed by many groups, with the presence of clusters inferred from high mass/charge ratio fragments [72-77]. In most cases, large aggregates were detected of the form $[C]_a[A]_b$ (C = cation, A = anion) for *a* and *b* values between 2 and 5.

1.2.2.5. Self-Assembled Solvent Structure

Micelle-like Nanostructure

From molecular dynamics (MD) simulations, a reverse micelle-like structure in AILs $[C_nMIm][PF_6]$ (n = 6, 8, 10, 12) was proposed [78]. The spherical anion attracted five or so cations such that the imidazolium heads solvate the negative charge and alkyl chains are expelled outward, producing dynamic, near-spherical aggregates with a polar interior and apolar exterior. This study also indicated the presence of long-lived, nanometer-sized voids in the bulk. The presence of voids or cavities between molecules has often been associated with hetereogeneity in disordered phases and pure liquids [79-81].

XRD measurements were used to confirm a micellar-like solvent morphology for $[C_nMIm][PF_6]$ ILs [82]. A micelle-like model for self-assembly in PILs was developed from small- and wide-angle X-ray scattering patterns of a wide range alkylammonium, dialkylammonium, trialkylammonium, and cyclic ammonium cations combined with organic or inorganic anions. The cations were thought to form discrete hydrophobic cores surrounded by charged regions. This suggests nanostructure is more pronounced with increasing cation amphiphilicity. The choice of anion also influenced the degree of nanostructure, although the structural reason for this order could not be determined.

It is concluded that binary IL−water mixtures may not be regarded as homogeneous solvents, but have to be considered as nanostructured with polar and nonpolar regions [83]. Later fluorescence spectroscopic data [84] and systematic measurements of physical properties as a function of alkyl chain length [85] were consistent with thisobservation. The cation headgroups and anions are distributed relatively homogeneously in the bulk, but crucially the alkyl tails aggregated together into spatially heterogeneous domains. This effect was more pronounced for longer alkyl chains, suggesting ion amphiphilicity is an important factor in IL structure. For n = 1-3, tail aggregation was only weakly apparent [86-87].

1.2.3. Ionicity of ILs

ILsare liquids comprised entirely ofions. However, not all of the ions present appear to be available to participate in conduction processes, to a degree that is dependent on the nature of the IL and its structure. Among the interactions taking place in ILs, Coulombic interactions are predominant. They increase the cohesive energy, consistent with the extremely low vapor pressure of ILs. Although ideal ILs consist of non-associated ions, in reality they form aggregates or clusters to some extent. There is experimental evidence of ionic association in ILs [88-91].

Therefore it is also important to evaluate the “ionicity” of ILs and correlate this property with conventional solvent parameters, which apply to molecular liquids. A qualitative description of ionicity can be a useful indicator for characterizing the properties of ILs. Figure 1.5 shows the variation of typical ions arranged in order of Lewis acidity for cations and Lewis basicity for anions.

The ionic structure controls Lewis acidity and basicity which follow the order presented in Figure 1.5 [92]. Conceptually, a salt can be classified into one of four different groups: a strongly Lewis-acidic cation with a strongly Lewis-basic anion (type I), a weakly Lewis-acidic cation with a strongly Lewis-basic anion (type II), a strongly Lewis-acidic cation with a weakly Lewis-basic anion (type III), and a weakly Lewis-acidic cation with a weakly Lewis-basic anion (type IV). Type I salts result in a strong cation-anion interaction to form typical ionic crystals. These salts need solvents to dissociate into ions which are generally not the case with typical ILs. Type IV can be ILs which indicates ionic dissociation without solvent molecules. In other words, these ions behave like “solvated ions”. For type II and III salts, solvents allow the high degree of dissociation of the salts. Although type II and III salts are liquids at ambient temperatures, the ionicity of such ILs may be lower than that of typical ILs (type IV). In this respect, the ionicity of these classes of salts (II and III) is an important parameter for task-specific ILs. For example, halide-based ILs are effective solvents for the dissolution of cellulose and carbohydrates [93-94].While lithium ILs are non-flammable electrolytes in rechargeable lithium batteries[95]. Thus the ionicity of ILs becomes of quite general significance.

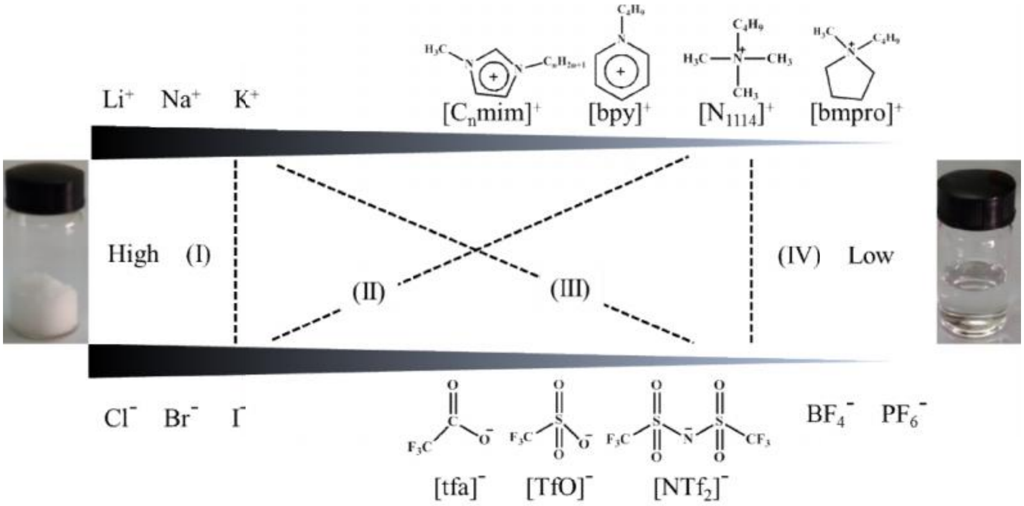


Figure1.5. Various combinations of salts, arranged in order of Lewis acidity for cations and Lewis basicity for anions. [C_nMIm]: 1-alkyl-3-methylimidazolium, [BPy]: N-butylpyridinium, [BMPyr]: *N*-butyl-*N*-methylpyrrolidinium, [N_{1114}]: trimethyl-butylammonium, [Tfa]: trifluoroacetate, [TfO]: trifluoromethanesulfonate, [NTf_2]: bis(trifluoromethanesulfonyl)amide.

Angell and co-workers [33, 96-97]described a qualitative approach to this question based on the Walden rule-

$$\Lambda\eta = k \qquad (1.1)$$

whereΛ is the molar conductivity and η is the viscosity; k is a temperature dependent constant. The Walden rule was originally based on observations of the properties of dilute aqueous solutions, but has been found to be applicable in non-aqueous electrolyte solutions [98] and molten salts[99].On a plot of log (molar conductivity, Λ) versus log (reciprocal viscosity, η^{-1}) this rule predicts a straight line that passes through the origin; this has become known as “Walden plot”. Data for 0.01 M KCl solution (where the ions are known to be fully dissociated and to have equal mobility) provide a useful calibration point that effectively allows estimation of the constant k and hence allows the placement of a reference line on the Walden plot. From the deviations from the reference line in the Walden plot, Angel et al. have classified specific ILs as either “good” ILs, “poor” ILs or non-ionic (molecular) liquids (Figure1.6).

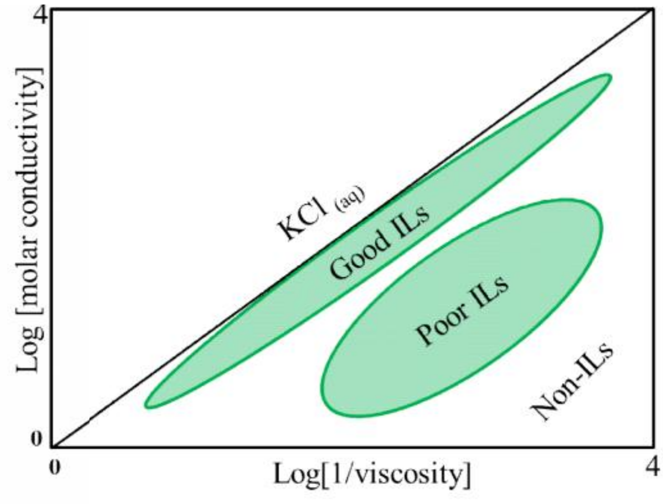


Figure1.6. Walden plot to classify ILs proposed by Angell et al.[100].

The data for the aprotic ILs lie slightly below the reference line, indicating that their molar conductivity is lower than that expected from the fluidity (η^{-1}) on the basis of the ideal Walden line, probably as a result of ion aggregation. The magnitude of the deviation below the ideal line, depending on the anionic structure, is consistent with the order of the Lewis basicity, suggesting that Coulombic interactions between ions can strongly influence ionicity. A strong cation-anion attraction causes poor IL ionicity. This trend is more visible when comparing type II, III and IV salts. While most typical aprotic ILs (type IV) are intermediate between the “good” and “poor”, the lithium ILs (salt III) show larger deviations from the KCl line and can therefore be classified as poor ILs. Similarly, halide based ILs (type II) show poorer ionicity than ILs with weakly basic anions in the Walden plot [101]. Furthermore many of the protic ILs formed by proton transfer reactions from Brønsted acids to Brønsted bases deviate from ideal behavior and are located in “poor” IL region [33, 98, 102].This suggests an incomplete proton transfer as well as ionic association. Thus, the Walden plot illustrates qualitative features of ionicity over a wide range of ILs.

The Walden plot represents a relatively qualitative approach to understand ionicity. In a variety of contexts a number of workers [103-104] used the Nernst-Einstein equation, which for a 1:1 salt can be written as-

$$\Lambda = \frac{N_A e^2}{kT}(D^+ + D^-) \tag{1.2}$$

as a way of assessing the impact of ion correlation on conductivity in a more quantitative fashion. Here N_A is Avogadro number, e is the electronic charge, k is Boltzmann constant and D^+ and D^- are the diffusion coefficients of the cation and anion respectively. The molar conductivity can be calculated if the individual diffusion coefficients are known. Comparison of the calculated and measured molar conductivities, $\Lambda_{NE}$and Λ_M, respectively, is then often interpreted in terms of a deviation, Δ-

$$\Lambda_M = (1-\Delta)\Lambda_{NE} \tag{1.3}$$

Such comparisons were carried out for a range of molten salts [105-106] and were found to produce quite small values of Δ (of the order of ±0.1). In other words the deviation from the Nernst-Einstein equation in these molten salts can be as small as 10%. This indicates that the Nernst-Einstein equation can work moderately well in highly Coulombic systems such as molten salts. These represent a very useful point of reference for the more complex organic salts that make up the family of ILs. Watanabe and co-workers [107-110] carried out similar investigations in a range of ILs and the ratio Λ_M/Λ_{NE} (=1-Δ) was calculated and discussed in terms of the degree of “ionicity” of the salt involved. The main cause of deviations from the Nernst-Einstein equation was ion aggregation and therefore Λ_M/Λ_{NE} was a measure of ionicity. They found that in the ILs (studied) ionicity was around 0.5-0.8 (corresponding to Δ = 0.5-0.2). Understanding the molecular and structural effects that control “ionicity” is therefore very important.

1.2.4. Generations of ILs

Historically there are three generations of ILs.

The first generation ILs arehaloaluminateILs. The earliest examples in this category are the eutectic mixtures of aluminium chloride and ethyl pyridinium halides [111]. This category includes the dialkylimidazoliumchloroaluminates room temperature ILs[112]. They are formed by mixing aluminum chloride and a dialkylimidazoliumchloride. These ILs have been studied extensively as solvents and catalysts. They react with water and therefore have to be handled in a dry-box**.**

The second generationILs are the non-haloaluminateILs. They have been used extensively as solvents in organic chemistry. The first examples were described by Wilkes and Zaworotko[113]. They include dialkylimidazoliumILs with weakly coordinating anions such as hexafluorophosphate $[PF_6]^-$ and tetrafluoroborate $[BF_4]^-$ these ILs were thought to be stable in water and air but it was subsequently shown that they undergo hydrolysis under certain conditions resulting in the formation of toxic and corrosive hydrogen fluoride [114]. Hydrophobic dialkylimidazoliumILs with $[NTf_2]^-$ anions are also included this category.

The third generation is the task-specific ILs and chiral ILs.

Task-specific ILs are functionalized ILs and designed with functionalized cations or anions that impart specific properties to the IL.

ILs with chiral cations or chiral anions are chiral ILs which are potentially useful as solvents or catalysts for asymmetric organic synthesis. One example of chiral IL is di(1-phenylethyl)Imidazolium nitrate (Figure 1.7).

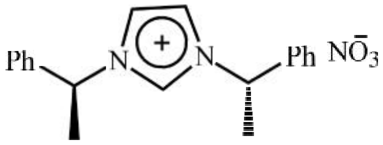


Figure 1.7. Structure of di(1-phenylethyl)imidazolium nitrate (Chiral IL).

The generations generally refer to pyridinium and particularly imidazoliumILs as these are the families of ILs that have been studied most extensively in recent years. Other types of ILs do not fall conveniently into these categories. For example, ethylammonium nitrate is not considered to be a first-generation IL even though it was first reported in 1914, before the appearance of first-generation ILs.There are some other different ILs, they are-

Aprotic and Protic ILs

ILs can be subdivided into two classes, namely, protic – those that contain an acidic proton on the cationic species and aprotic – those containing no acidic proton. Aprotic ILsare salts consisting entirely of cations, which are not protonated, and anions. Examples are the resonance stabilized alkyl pyridinium and dialkylimidazolium cations, likeethylmethylimidazoliumtetrafluoroborate,$[C_2MIm][BF_4]$ andbutylmethylimidazoliumbis(trifluoromethylsulphonyl)imide, $[C_4MIm][NTf_2]$.

Protic ILs are formed by proton transfer from an acid that can donate a proton (Brønsted acid, HA) to a base that can accept a proton (Brønsted base, B):

$$HA + B \rightarrow [BH]^+ + A^-$$

Generally the base is organic in character, but there are also inorganic examples. The classic example of a protic IL is ethylammonium nitrate, $[C_2H_5NH_3][NO_3]$, which is formed by the protonation of ethylamine:

$$C_2H_5NH_2 + HNO_3 \rightarrow [C_2H_5NH_3]^+ + [NO_3]^-$$

Another example is 1-methylimidazolium tetrafluoroborate [HMIm][BF_4], which is prepared by the reaction of 1-methylimidazole and tetrafluoroboric acid[115]. The salt hydrazinium nitrate has a melting point of only 70 ^{o}C and hydraziniumformate and hydrazinium acetate are both molten below 100 ^{o}C[116]. The electrical conductance of hydraziniumformate at room temperature is higher than that of any aprotic IL. Many eutectic mixtures of ammonium salts are liquid below 100 ^{o}C and have been used as fuel cell electrolytes [117]. These include: the hydronium compounds such as hydronium triflate which has melting point 35 ^{o}C and has a very high electrical conductivity. The organic bases are not necessarilythe primary, secondary or tertiary amines, but also with nitrogen atoms in heterocyclic rings (which may or may not be resonance stabilized) [118**].**

An important aspect of protic ILs is that the properties of the ILs formed on proton transfer depend very strongly on the relative strengths of the acid and base between which the proton is transferred [98]. While the concentration of protonated species is always very high (5-10 M in most cases), theproperties may vary from strongly acidic to strongly basic in character, as is readily seen by simple tests with proton sensitive probes, such as the common indicator ions. For example, a wide pH range litmus paper registers bright pink in contact with triethylammoniumtriflate but dark blue in contact with triethylammonium acetate. The systematic and quantitative measurement of basicity in these solvent free liquids is a recent achievement.

Protic ILsdo not necessarily consist entirely of ions. Such liquids may contain a small percentage of molecular species if the proton transfer is incomplete. Protic ILsare volatile by their nature because the acidic proton can be abstracted by the basic anion at ambient temperature. The acid-base equilibrium for the abstraction reaction allows the formation of neutral molecular species that readily evaporate. AILs can be distilled without significant decomposition. For these ILs there is no feasible mechanism to transfer a proton from the cation to the anion. In other words, the only possible mechanism for volatilization of these ILs is as intact ions, either alone or aggregated. This is represented schematically in Figure 1.8.

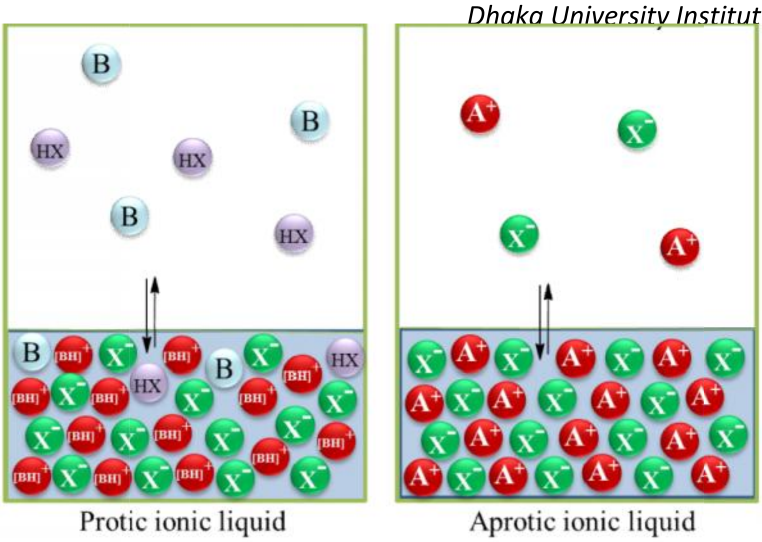


Figure1.8. Schematic representation of the differences between protic and aprotic ILs. For the protic ILs, a dynamic equilibrium exists between the ionic and dissociated forms: $[BH]^{+}X^{-}(l) \leftrightarrow B(l) + HX(l) \leftrightarrow B(g) + HX(g)$. Green circles represent anions, red circles represent cations, and other colored circles represent neutral molecules; l, liquid phase; g, gaseous phase. For the gaseous phase over the aprotic IL, the representation is purely schematic and has no implication for the actual degree of aggregation[119].

For 1-alkyl-3-methylimidazolium salts, distillation occurs without decomposition. Here a possibility of transferring the 2-H proton from the cation to the anion, creating a carbine and a free acid. The decomposition of $[C_2MIm][NTf_2]$ found no evidence for the formation of $HNTf_2$ at 300 ^{o}C [120]. Further, if the 2-H proton on the cation is replaced with a methyl group, the new IL $[C_4dMIm][NTf_2]$ (where $[C_4dMIm] \equiv$ 1-butyl-2,3-dimethylimidazolium) is volatile and less decomposed than $[C_4MIm][NTf_2]$ [119]. If a proton transfer mechanism were dominant, the 2-methylated IL would have had its volatility suppressed with a much greater level of decomposition. So, for AILs the proton transfer mechanism appeared highly improbable.

Organic and Inorganic ILs

These are obtained in both aprotic and protic forms. Most of the ILs, reported, consist of organic cations and organic or inorganic anions. For example, $[C_4MIm][NTf_2]$ consists of organic cations and organic anions and $[C_2py][BF_4]$ of organic cations and inorganic anions. Inorganic ILsare also known. The examples of inorganic ILs are hydrazinium bromide, $[N_2H_5][Br]$, and hydrazinium nitrate, $[N_2H_5][NO_3]$ with melting point of 86.5 and 70 ^{o}C, respectively. The protic molten salt $[NH_4][HF_2]$ has a melting point of 125 ^{o}C. Another example is ammonium hydrogen sulphate, $[NH_4][HSO_4]$, which has a melting point of 116 ^{o}C.

DicationicILs

Generally ILs are composed of one type of cation and one type of anion. DicationicILs (DILs) also attracted great concern as theyrepresent an interesting variation of the cationic companion. Imidazolium-based and pyrrolidinium-based DILs have been synthesized and studied properties [121]. The head groups were linked with an alkyl chain (from 3 to 12 carbons long) and reacted with four different traditional anions (Br, NTf_2, BF_4 and PF_6). The thermal stability of these ILs in the range of -4 to >400 ^{o}C, are found to be greater than those of most traditional monocationic ILs. Besides that, a decrease in melting point was observed when longer alkyl chains were used as spacer, which might be due to an increase in the number of closely related configurational states and possibly crystalline polymorphs for these ILs. In contrast, the density of the ILs decreased with increasing alkyl chain. However, the length of the alkyl chain did not give a significant effect on surface tension of the ILs. Instead, the increase of length of the substituted alkyl group on the imidazolium rings resulted to a decrease of the surface tension of the ILs. While the solubility of these DILs in water and heptane tend to be similar to those of the monocationic ILs, except for one case in which the dication was very hydrophobic.

DILs can be classified as homoanionic and heteroanionic. These DILs can further be categorized as symmetrical and asymmetrical DILs for both homoanionic and heteroanionic DILs.

HomoanionicDicationicILs

HomoanionicdicationicILs are typical types of DILs which consist of a dication and two identical anions. Symmetrical (geminal) DILs (Figure 1.9)consist two same cation candidates such as imidazolium or pyrrolidinium, which may contain cyclic or aliphatic chain, via either a rigid or flexible spacer. Common spacer is an alkyl chain. Some examples of symmetrical dicationic ILs are:

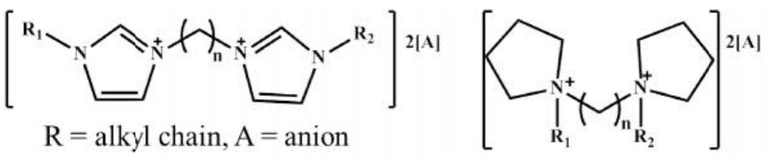


Figure1.9. Examples of symmetrical dicationic ILs.

They represent several advantages over the traditional monocationic ILs in terms of thermal stability and volatility, as well as tenability of physical and chemical properties [122]. Therefore, they have good potential to be used as lubricants, solvents for high temperature uses, gas chromatography stationary phases, separation media and catalyst for esterification and trans-esterification reactions [123-124].

Symmetrical or germinal ILs in general contain short or intermediate length of substituted alkyl group on the head group in the range of 0 to 8 carbons long. Ding and co-workers synthesized an imidazolium-based dicationic IL containing alkyl group of 14 carbons long [125]. The properties of the dicationic IL was then compared with that of monocationic ILs with similar length of substituted alkyl group. It was found that the dicationic IL possessed higher thermal stability and lower critical micelle concentration (CMC) values than that of monocationic ILs. The solubility of both monocationic and dicationic ILs in nine different solvents were also investigated. It was found that both compounds were immiscible with low polarity solvents (toluene, cyclohexane, ethyl acetate and petroleum ether) but miscible in high polarity solvents (methanol, acetonitrile and chloroform). However, dicationic IL has lower solubility in acetone and water compared to that of monocationic IL. This might be due to more hydrophobic nature of dicationic IL.

Asymmetrical DicationicILs

Asymmetrical dicationic ILs consist of different head groups of cation which are also attached via a spacer such as alkyl chain. These ILs can be said to have dual functionality as they have two different head groups. Two imidazolium-based and aliphatic ammonium-based asymmetrical dicationic ILs have been synthesized[126].The structure of the asymmetrical dicationic ILs are shown in the Figure 1.10, with *n*=2,5.

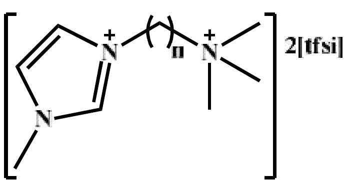


Figure1.10. Structure of asymmetrical imidazolium and ammonium-based dicationic ILs.

The thermal properties were studied and in a form of yellow solid at ambient temperature. The ILs were found to be soluble in polar solvents such as water and methanol. The dication affected the melting point of these ILs by following the order of triphenylphosphinium>pyridinium>imidazoliumdications and symmetrical > asymmetrical dicationic ILs. Symmetrical ILs have higher melting points due to easier packing while dicationic ILs with ring-type head group would have higher melting points attributed to the added π- π stacking. Besides that, the anion exists in either a linear or a bent form, depending on the dications [127].

HeteroanionicDicationicILs

Heteroanionicdicationic ILs have one dication and two different anions. They are also symmetrical and asymmetrical dicationic ILs. A series of heteroanionicasymmetrical dicationic ILs with aromatic or aliphatic compounds via alkyl chain of 3 carbons long have been synthesized [127]. The dianions were either PF_6^-/Br^- or NTf_2^- / Br^-. These dicationic ILs were found to be miscible with water, methanol and ethanol but immiscible with acetone, ethylacetate, tetrahydrofuran, diethyl ether, chloroform and hexane. Besides that, these ILs are miscible with methanol/diethyl ether and methanol/ethyl acetate co-solvents. The thermal stability of these ILs affected by different second head groups follows the order of the following; ammonium <piperidinium<imidazolium<pyrrolidinium. While for the anion effect, the dicationicILs containing PF_6^-/Br^- has higher thermal stability than NTf_2^-/Br^-, which is in contrast with previous homoanionicdicationic ILs finding. This might be due to higher nucleophilicity of bromide anion to attack electrophilic S=O double bond in NTf_2^- anion in initial weight loss step at elevated temperature [127-129].

1.2.5. Why areILsLiquid?

The first low melting salt, ethylammonium nitrate (m.p. 12 ^oC), was synthesized by Walden [24] in 1914. Hurley and Wier [130] in 1951 developed low melting salts with chloroaluminate ions for low-temperature electroplating of aluminum. In the mid-1980s, low melting point ILs were proposed as solvent for organic synthesis by Fry and Pienta [131] and Boon et al. [132]. The low melting salts having melting point below 100 ^oC created a new unique media for chemical reactions.

The melting point of any salt is dictated by the electrostatic potential which exists between its cations and anions and for salts such as NaCl this potential is very high. In turn, the melting points of salts are reflections of this electrostatic potential, specifically expressed as their lattice energy, E, (equation 1.4)

$$E = k\frac{Q_1Q_2}{d} \tag{1.4}$$

Here k is the Madelung constant, Q_1 and Q_2 are the charges on the ions and d is the interionic separation. With large ions, d is effectively larger, resulting in a smaller lattice energy and lower melting point. And mismatches in the sizes and shapes of the ions tend to inhibit efficient ion packing, also contributing to an effective increase in d. consequently, salts of ions in which there is a significant ion size and/or shape mismatch are expected to exhibit significantly diminished lattice energies, with lower melting points as a result. However, the electrostatic potential still prevails, with every cation and anion in the sample attracted to the other. These phenomena appear to account for the low melting points and non-measurable vapor pressures of ILs.

When a solid melts to form a liquid (the thermodynamic process known as fusion), the enthalpy (H), and entropy (S) of the substance change. These changes, combined with a temperature term (T), give the well-known equation for the Gibbs free energy change for a process:

$$\Delta G = \Delta H - T\Delta S \tag{1.5}$$

At the melting temperature ΔG is zero. At other temperatures, ΔG is positivefor solid and negative for liquid state. This means that a salt should be liquid at temperature T if the ΔG is negative at that temperature. Thus, room-temperature ILs should have negative values of $\Delta G°$ at 298.15 K and 10^5 Pa. By using Born-Fajans-Haber cycle, the calculation of ΔG for ILs has shown the value negative [133] at 298.15 K and 10^5

Pa which indicate that the liquid state of ILs is more thermodynamically favorable. The large size and weakly coordinating nature of ions are responsible for small lattice enthalpy. The large size and conformational flexibility of the ions (particularly the cations) increase the difference in entropy. The combination of these two parameters gives small ΔG values. For common salts such as NaCl, the value of ΔH (800 kJ mol^{-1}) is large and ΔS is small (0.158 kJ mol^{-1} K^{-1}). So the resultant ΔG is too large and the solid state is thermodynamically favorable [133].

1.2.6. Synthesis of ILs

The synthesis of ILs can be described in two steps (Figure 1.11)

Step-1. Preparation of the desired cation

The desired cation can be prepared either by the protonation of the amine by an acid or through quaternization reactions of amine with alkyl halides.

Step-2. Anion metathesis or anion exchange

Anion metathesis can be carried out by treatment of halide salts with metal salts or anion exchange with Lewis acids to form Lewis acid-based ILs. Anion metathesis is the methodology of choice for the preparation of water and air stable ILs based upon 1,3-dialkylimidazolium cations. This method involves the treatment of the halide salt with the silver/sodium/potassium salts of NO_2^-, NO_3^-, BF_4^-, SO_4^- and CH_3COO^- or with the free acid of appropriate anion.

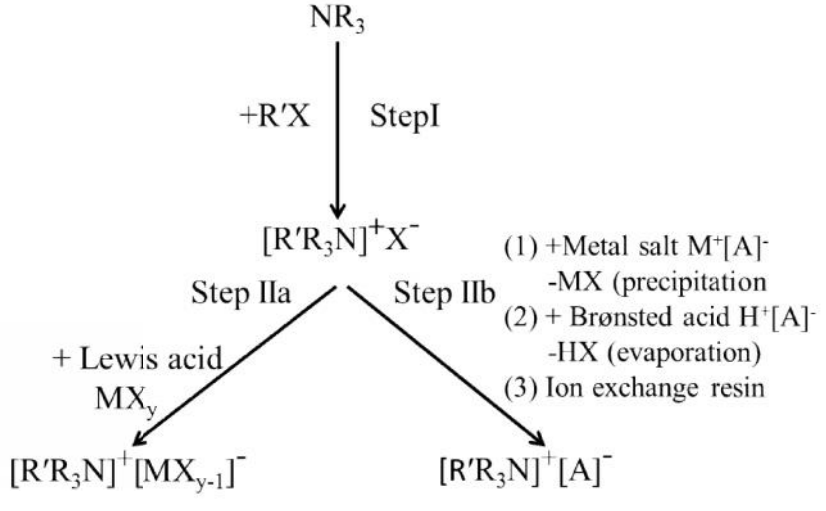


Figure 1.11. Synthesis path for the preparation of ILs [134].

Several new and improved methodologies using nonconventional techniques, such as irradiation with microwaves (MW) and power ultrasound (US), whether used alone or in combination, have considerably improved the synthesis of ILs [135-137]. The efficient, solventless, one-pot synthetic protocols have made ILs cheaper and thus encourage a wider use of these neoteric solvents [138-140].

1.2.7. Applications of ILs

Compared to conventional organic solvents, the use of ILs (ILs) for synthesis and extraction has a number of advantages determined by the unique combination of their properties. These liquids have negligible vapor pressure, a liquid range of up to more than 400K and density being greater than that of water. ILsare miscible with substances having very wide range of polarities and can simultaneously dissolve organic and inorganic substances. These features of ILs offer numerous opportunities for modification of existing and for the development of new extraction processes. In some cases, such processes would be impossible with conventional solvents because of their limited liquid range or miscibility. Even greater potential is the use of ILs for chemical synthesis because the charged nature of these solvents can influence the synthesis itself.

The unique properties of ILs are determined by the structure and interaction of ions in the liquid. They are usually composed of large asymmetric organic cations and inorganic or organic anions. Most commonly considered for extraction and synthesis are those with cations based on the imidazolium or pyridinium ring with one or more alkyl groups attached to the nitrogen or carbon atoms, however quaternary ammonium salts have also been widely used for electrochemical synthesis. Anions include halide ions, tetrafluorobarate (BF_4^-), tetrachloroaluminate ($AlCl_4^-$), hexafluorophosphate (PF_6^-) and bis(trifluoromethyl-sulfonyl) imide $(CF_3SO_2)_2N^-$. Many new cations have recently been proposed. In addition to the interactions existing in conventional organic solvents (hydrogen bonding, dipole-dipole and van der Waals interactions) ILs have ionic interactions (mutual electrostatic attraction or repulsion of charged particles), which makes them very miscible with polar substances. At the same time the presence of the alkyl chain on the cation determines their solubility in less polar fluids. Hydrogen bonding in ILs is thought to exist between an oxygen or halide atom on the anion and the hydrogen atoms on the imidazolium or pyridinium ring of the cation [141].

To date, most chemical reactions have been carried out in molecular solvents. For two millennia, most of our understanding of chemistry has been based upon the behavior of molecules in the solution phase in molecular solvents. Recently a new class of solvents has emerged-ILs. These solvents are often fluid at room temperature and consist entirely of ionic species. They have many fascinating properties which make them of fundamental interest to all chemists since both the thermodynamics and kinetics of reactions carried out in ILs are different to those in conventional molecular solvents then the chemistry is different and unpredictable at the current state of knowledge. However, in addition to the scope for exciting new discoveries with which they tease us, ILs have no measurable vapor pressure and can emit no volatile organic compounds (VOCs). They have attracted enormous attention as media for green synthesis.

1.2.7.1. As Solvents

ILs are attractive as potential solvents for a number of reasons. They

-show negligible vapor pressure and thus are effectively non-volatile
-have relatively high thermal stability
-can solubilize inorganic, organic and polymeric materials
-are highly polar but non-coordinating solvents, and
-provide a non-aqueous polar alternative for two-phase systems to effectively carry out catalyst–product separation.

ILshave been applied as solvent for organic reactions with number of advantages such as: control of product distribution, increased rate, ease of product recovery, catalyst immobilization, and recycling. These help replacingsolvents of volatile organic compounds in organic and biochemical reactions.

ILs as “Green Solvents”

Solvents are used in large quantities in the chemical industry. Therefore, solvents define a major part of the environmental performance of a process and also impact on cost, safety and health issues. The idea of ‘‘green’’ solvents expresses the goal to minimize the environmental impact resulting from the use of solvents in chemical production. Recently, four directions towards green solvents have been developed:

- substitution of hazardous solvents[142-144];
- use of ‘‘bio-solvents’’,[145]
- substitution of organic solvents [146-149] and,
- use of ILs that show low vapor pressure, and thus less emission to air [150-151]

An important feature of ILs is their immeasurably low vapor pressure. For this reason, they are called ‘green’ solvents, in contrast to traditional VOCs. To improve the safety and environmental friendliness of the conventional separation technique, ILs can be used as ideal substitutes because of their stability, non-volatility and adjustable miscibility and polarity. They have attracted enormous attention as media for green synthesis. Replacement of conventional solvents by ILs would prevent the emission of VOCs, a major source of environmental pollution. ILsare not intrinsically “green”-some are extremely toxicbut they can be designed to be environmentally benign, with large potential benefits for sustainable chemistry [152].

ILs as “Designer Solvents”

ILsare made solely of cations and anions, and the properties of ILs can be altered with the variation in ionic component. This means their properties can be adjusted according to the requirement of a particular process. Hence, ILsare stated as *Designer solvents.* As they are made up of at least two components which can be varied (the anion and cation), the solvents can be designed to possess a particular set of properties. Hence, the term “designer solvents” has come into common use [153]. This means that melting point, viscosity, density, and hydrophobicity can be varied by simple changes to the structure of the ions. For example, the melting points of 1-alkyl-3-methylimidazolium tetrafluoroborates [154] and hexafluorophosphates [155] are a function of the length of the 1-alkyl group, and form liquid crystalline phases for alkyl chain lengths over 12 carbon atoms. Another important property that changes with structure is the miscibility of water in these ILs. For example, 1-alkyl-3-methylimidazolium tetrafluoroborate salts are miscible with water at 25 °C where the alkyl chain length is less than 6, but at or above 6 carbon atoms, they become immiscible with water. Hence, a change in the structure of a cation can have a significant impact on the solubility characteristic of ILs.

1.2.7.2. Electrochemical Applications of ILs

ILs are widely used as electrolytes in electrochemistry because of their unique properties like wide potential window, high solubility of metal salts, avoidance of water and high conductivity compared to non-aqueous solvents.

ILs in Batteries

The life of modern electronics is batteries. Cellular phones, laptop computers, digital cameras and other portable electrical devices have demands upon the batteries which power them. Current commercial batteries are based on lithium-ion technology in which the anode consists of graphite or a similar material and the electrolyte is a liquid or polymer gel containing molecular solvents/plasticizers [156]. Usually metallic Lithium is not compatible with the liquid solvents used in Li-ion battery electrolytes. The presence of liquids requires a special battery pack sealing to prevent leakage since volatiles can lead to explosions. As ILs have negligible vapor pressures, ILs have been suggested for electrolyte applications [157]. This gives the batteries much safer characteristics. Furthermore, many applications require Li^+ cation conductivity to be more than 10^{-3} S cm^{-1} and portable electronic devices need to be operated at or close to the ambient temperature of about 25^oC. Room temperature ILshave conductivities of 10^{-2} S cm^{-1} or higher at that temperature [158]. So ILs have become an attractive alternatives as electrolyte in batteries. Application of ILs in batteries achieved some advantages like conductivity of polymer electrolytes, metal cycling efficiency, Li^+ cation transport in electrolyte and optimization of conductivity.

ILs in Fuel Cells

Fuel cells are important because they are used in various transports, stationary and portable applications [159]. The performance of the fuel cell is greatly affected by the poisoning of the platinum catalyst by carbon monoxide present in hydrogen. To counter this, extra pure hydrogen is required which in turn increases the operating costs. This can be avoided if the fuel cell is operated at temperatures above 140 ^oC. But the conductivity decreases strongly above 80 ^oC due to a decrease in humidity and cannot be used at higher temperatures. The use of ILs owing to their unique properties such as high conductivity, low vapor pressure, and wide liquid temperature range would solve these problems.

ILs have been commercially applied to alkaline fuel cells. [BMIm][BF_4] and [BMIm][PF_6] are outstanding electrolytes for fuel cells to achieve an overall cell efficiency of 67%, and the system can operate with water and hydrogen at 1 atm pressure without an efficiency loss [160]. It was also observed that fuel cells with the application of ILs show good performances of thermal and chemical stability, even with operation at high temperatures. In addition, the use of IL in commercial polymeric electrolyte membrane fuel cells can achieve efficiency enhancements by improving the ion transport in the polymer.

ILs in Solar Cells

There is a crucial need to develop alternative renewable energy sources because the rapid depletion of fossil fuels as well as the terrible environmental problems of their combustion. On the other hand the demands for energy are rising fast. Solar energy has large potentials for fulfilling a crucial part of the sustainable energy demands for future generation. Dye-sensitized solar cells (DSSCs) have been attracting much scientific and technological attention as a low cost alternative to the traditional photovoltaic devices. The DSSCs can reach efficiencies of 10% for converting solar energy to electric power and have a low cost of production. However, despite the high conversion efficiencies achieved for DSSCs, there are a number of problems associated with the use of by liquid electrolytes, such as leakage and volatilization of the liquid, possible desorption and photo-degradation of the attached dyes and corrosion of counter electrodes. ILs have been extensively employed to mitigate the problems of liquid electrolytes. IL polymer gel electrolytes show the same benefits as ILs but have a superior advantage to be an all-solid-state device. Moreover, the smart mixtures of room temperature ILs were also used to improve photo-voltage and the overall transport properties of the device for dye-sensitized solar cells.

1.2.7.3. ILs in Organic Synthesis and Catalysis

ILs exhibit many properties which make them potentially attractive media for homogeneous catalysis. The notable ones are listed below.

1. They do not evaporate and are easy to contain.
2. They generally have reasonable thermal stability.
3. They are able to dissolve a wide range of organic, inorganic, polymeric and organometallic compounds.
4. They can solubilize gases (*e.g.* H_2, CO and O_2) which makes them attractive solvents for catalytic hydrogenations, carbonylations, hydroformylations, and aerobic oxidations.
5. They can be used in two-phase systems as some of them are immiscible with organic solvents and some with aqueous systems.
6. Their properties can be designed by changing the structure of cations and anions.
7. They are often composed of weakly coordinating anions. For this, they have a strong rate-enhancing effect on reactions involving cationic intermediates.

ILs have been used to develop various novel and greener methodologies. They have played multiple roles like catalyst, solvent and catalyst supports. In some cases it was observed that ILs enable efficient catalytic reactions in comparison with conventional molecular solvents.There are three major applications in organic synthesis depending on the nature of the ILs [161]. The first one involves the use of organoaluminate ILs in reactions promoted by Lewis acids. The second application is related to the use of ILs as ‘‘neutral’’ solvents or liquid support for the transition metal catalysts. The third application takes the advantage of task-specific IL as a ligand, catalyst, or extracting solvent.

ILs in Synthesis

One of the principles of green chemistry is that the use of auxiliary substances such as solvents and separation agents should be made unnecessary and if used should be innocuous [162]. The toxic and hazardous properties of many solvents particularly chlorinated hydrocarbons posture crucial environmental concerns such as atmospheric emissions and contamination of water effluents. It is recognized that employing the use of nonconventional solvents as alternatives for environmentally unfriendly traditional solvents can reduce waste solvent productionand hence reduce the negative impacton environment to a great extent [163]. The most prevalent of these new solvent systems includes water, supercritical fluids (like supercritical CO_2), ILs and solventless processes [164].

As solvents, ILs have found applications in a number of reactions. Dupont et al. reviewed the application of ILs as catalytic phase in various organometallic reactions [165]. Catalytic applications of metal nanoparticles have been explored in IL media by Migowski and Dupont [166-167].

Task Specific ILs

The task specific ILs are designed with functionalized cations and/or anions that impart specific properties or reactivity to the IL [168]. Task specific ILs are also known as functionalized ILs. Davis Jr. and Forrester introduced the term “task specific IL” for such ILs in which functional group is incorporated as a part of the cation and/or anion structure [169-170]. The covalent attachment of some functional group to cation/anion or both of an ordinary IL imparts it the capacity to behave not only as solvent but also as reagent and/or catalyst in the chemical reactions (Figure 1.12) [171].

Few examples are:

(i) Brønsted acidic ILs containing sulphonic acid groups were used as solvent and/or catalyst for esterification and other acid catalyzed reactions [172].

(ii) ILs bearing appended amines can separate carbon dioxide from gas streams [173].

(iii) ILs with large aromatic head groups show enhanced activity for extraction of aromatics in aqueous biphasic systems [174].

(iv) ILs with a tethered hydroxyl group (-OH) have been used as phase transfer catalyst in the synthesis of ethoxybenzene [175].

(v) ILs containing metal ligating group find use in the extraction of metal ions from aqueous solution [176].

(vi) ILs with appended carboxylate groups have been used as supports for “IL-phase” synthesis which is a versatile extension of the solid phase synthesis concept [177].

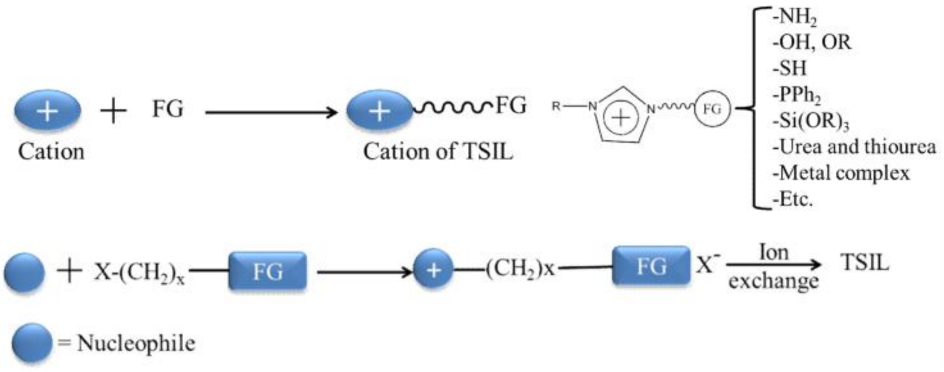


Figure1.12. Synthesis of TSIL.

A task specific IL can be any of the following two types:

(i) A room temperature IL, having covalently attached functional group, behaves not just as reaction media but also as reagent/catalyst.

(ii) A binary system of some functionalized salt, which may be solid at room temperature, dissolved in conventional IL.

ILs as Catalyst

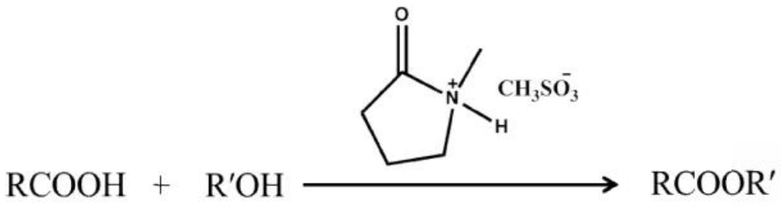
Although ILs are introduced as alternative green reaction media because of their unique physical and chemical properties, they are also showing their significant role in controlling the reaction as catalysts [178-183].

Depending upon the functional group attached to the cation and/or anion, the IL may behave as an acidic, basic, or organocatalyst.

As Acid Catalysts

In view of green chemistry, the substitution of harmful liquid acids by reusable ILs is one of the most promising catalytic systems in chemistry. The acidic nature of Brønsted acidic ILs as catalysts has been exploited for many organic transformations like Pechmann reaction, Koch carbonylation, asymmetric Aldol condensation, Aza-Michael reaction, Beckmann rearrangement, synthesis of chalcones, oxidation reactions and Prin’s reaction, synthesis of furfural, biodiesel, Hantzsch reaction, and Mannich reaction [184-195].

Esterification of alcohols by carboxylic acids has been carried out in a halogen free Brønsted acidic IL (N-methyl-2-pyrrolidinium methyl sulphonate) under mild conditions, and without additional solvent (Scheme 1.1) [196].

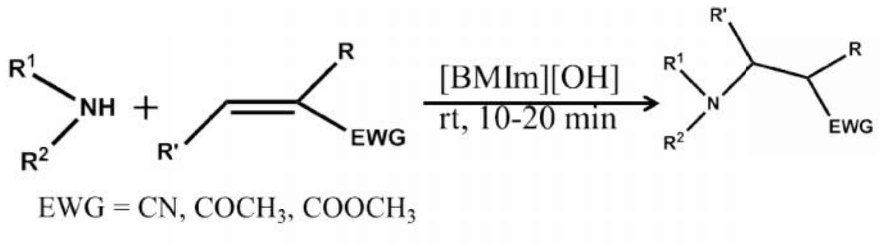


Scheme 1.1. Esterification of alcohols catalyzed by an IL.

Basic functionalized ILs have produced unique interest because they showed more advantages such as convenient recycling and higher catalytic efficiency than the mixture of inorganic base and IL for some base-catalyzed processes [197].

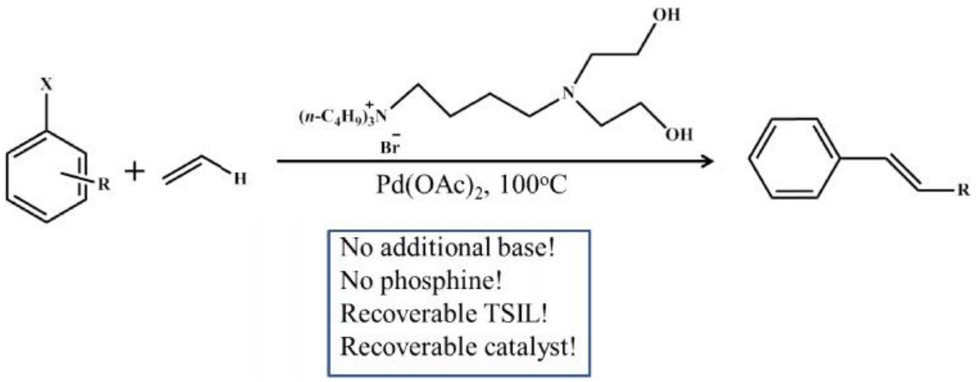
Basic ILs have been used to catalyze a number of reactions like aza-Michael addition reaction, Michael addition of active methylene compounds, condensation reaction of aldehydes and ketones with hydroxylamine, synthesis of quinolones and pyrroles[198-202].

Xu et al. developed a green procedure for the Michael addition of *N*-heterocycles to α,β-unsaturated compounds at room temperature using a basic IL [BMIm][OH] as a catalyst and reaction medium [203](Scheme 1.2).



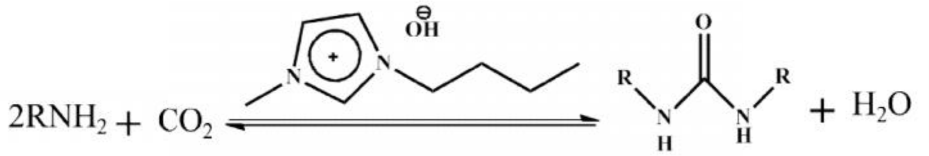
Scheme 1.2. Michael addition reaction catalyzed by an IL.

Wang and coworkers described synthesis and application of ethanolamine functionalized IL for the palladium catalyzed Heck reaction (Scheme 1.3) [204].



Scheme1.3. Heck reaction catalyzed by task specific IL (General).

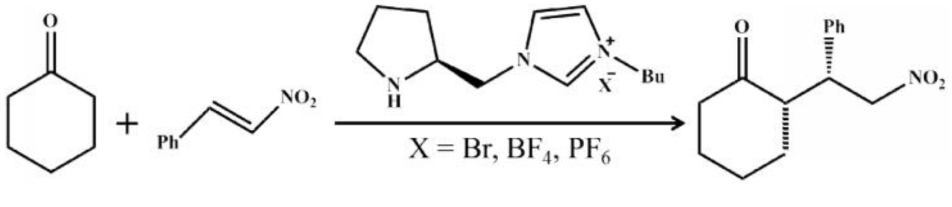
IL performs a multifunctional role of base, ligand and reaction media with added advantage of recyclability of the system. The catalyst system is very effective for a wide range of substrates giving excellent yields. Basic IL [BMIm][OH] has been successfully used as an efficient catalyst for the synthesis of substituted urea starting from carbon dioxide and amines [205]. The main advantages of this methodology are solvent-free reaction conditions, no need of dehydrating agents to remove the water formed as a by-product, recyclability of catalyst, and operational simplicity. The developed protocol is quite general as aliphatic amines, cyclohexylamine and benzylamine were converted to corresponding urea efficiently and selectively (Scheme 1.4).



Scheme 1.4. Conversion of urea from amine catalyzed by task specific IL.

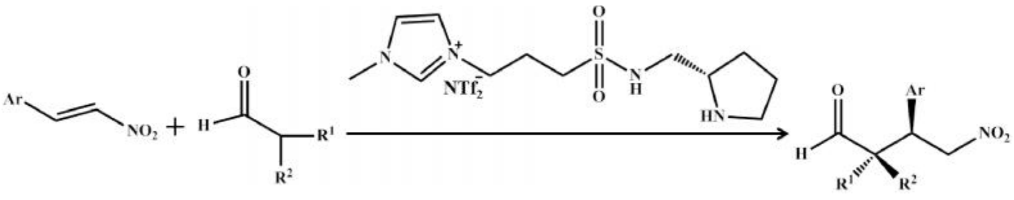
As Organocatalysts

In the last few years a renewed interest in the use of organic compounds as catalysts has begun to appear. ILs have the potential to have a huge impact in this area [206-209].One of the promising approaches to organocatalysis is through hydrogen bonding interactions, and the reactions to which this has been most often applied are Diels-Alder cycloadditions and their derivatives. Luo and coworkers used a functionalized chiral IL as an efficient reusable organocatalyst for asymmetric Michael addition of ketones/ aldehydes with nitroalkenes(Scheme 1.5) [210].



Scheme1.5. OrganocatalysisofasymmetricMichael addition reaction by a functionalized chiral IL.

Pyrrolidine-based chiral IL has been developed by Ni and coworkers [211]. This chiral IL has been found to catalyze the Michael addition reaction of aldehydes and nitrostyrenes to give moderate yields, good enantioselectivities, high diastereoselectivities and recyclability (Scheme 1.6).



Scheme1.6. Organocatalysisof Michael addition reactionof an aldehyde and nitrostyreneby a chiral IL.

Though ILs are green solvents, they are synthesized from the materials which use fossil fuels as their resource. Synthesizing ILs from renewable raw materials will add to the green attributes of ILs. Sugars are suitable, abundantly available raw material for the synthesis of ILs. Also the presence of hydroxyl groups in the ILs derived from sugars makes them highly coordinating solvents thus enabling them to be used in stereoselective and metal catalyzed reactions [212].Imidazolium acetate has been successfully used as organocatalysts for benzoin condensation, hydroacylation and oxidation of alcohols using carbon-dioxide and air [213].

Catalysis in ILs is an exciting and growing area of research which holds considerable potential for industrial applications. The use of ILs as reaction media for catalytic transformations or as the catalyst itself can have a profound effect on activities of reactants and selectivity of products. The IL could be readily recycled [114]. They provide a medium for performing clean reactions with minimum waste generation.In this work, the application of binary systems of PILs and AIL as reaction medium and catalyst in organic synthesis has been investigated where Michael addition reaction has been chosen as a model reaction.

1.3. Michael Addition Reaction

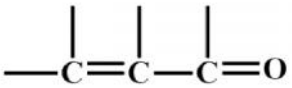
The Michael addition reaction of acyclic active methylene compounds and carbonyl compounds is an ideal model reaction for kinetic investigations. The nucleophilic addition of enolate anions (or analogous) to the carbon-carbon double bond of α,β-unsaturated ketones, aldehydes, nitriles or carboxylic acid derivatives is a process known as Michael addition reaction.

Arthur Michael in 1887 first built up important synthetic methods for the nucleophilic addition to carbon-carbon double bond in conjugation with electron withdrawing groups such as >CO, -COOH, -CN, _NO$_2$, -CONH$_2$, -SO$_2$R, -COOR. Although a carbon-carbon double bond gives an electrophilic addition, the presence of electron withdrawing groups in conjugation with double bond not only lower its reactivity towards electron seeking reagents but at the same time activate towards reagent that are electron rich.

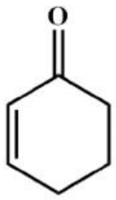
Michael reaction is one of the most efficient carbon-carbon bond forming reactions in organic synthesis. This reaction is usually carried out under acid or base catalysis. These would lead to environmentally hazardous residues and undesirable side products. To avoid typical disadvantages resulting from the presence of such catalysts, a large number of alternative strategies have been developed using Lewis acids, basic clays KF/Al$_2$O$_3$, guanidine, microwave irradiation, alumina, zeolite, bismuth nitrate and enzymes. Unfortunately many of these procedures require long reaction times, rigorous reaction conditions and use of toxic solvents such as DMSO or DMF. Thus, the development of a fast and facile protocol that could be performed at ambient temperature for Michael addition becomes particularly fascinating and remains a great challenge.

Michael Acceptor

The unsaturated compounds used in the reaction areoften called Michael acceptors and may include any unsaturated system having a functional group capable of stabilizing the carbanionic intermediate. The acceptor compounds are usually α,β-unsaturated esters, aldehydes, ketones and nitriles. The Michael acceptors may also add a variety of nucleophiles other than enolate anions such as alcohols, thiols and amines. In addition, many α,β-unsaturated ketones which might be used as Michael acceptors (Figure 1.13) undergo self-condensation reaction in presence of bases.



α,β-unsaturatedcarbonyl compound



2-cyclohexene-1-one

Figure1.13. RepresentativeMichael acceptors.

Michael Donor (Active Hydrogen Compounds)

Michael donors are compounds that contains a -CH_2- group and –CH- group flanked by two electron withdrawing groups (-CN, C_2H_5COO-, >CO etc.). Since they can increase the activity of hydrogen and stabilize the conjugate base, they are also known as active hydrogen compounds (Figure 1.14).

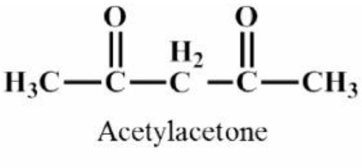


Figure1.14. Representative Michael donors.

Mechanism of Michael Addition Reaction Catalyzed by Base

Generally organic bases (piperidine, puridine,triethylamine, KOH, NaOH, NaOEt etc.) are used as catalysts and the reaction is carried out in the presence of a protic solvent (water or alcohol). The mechanism for the base catalyzed Michael addition reaction between acetylacetone and cyclohexenone is given in Figure 1.15.

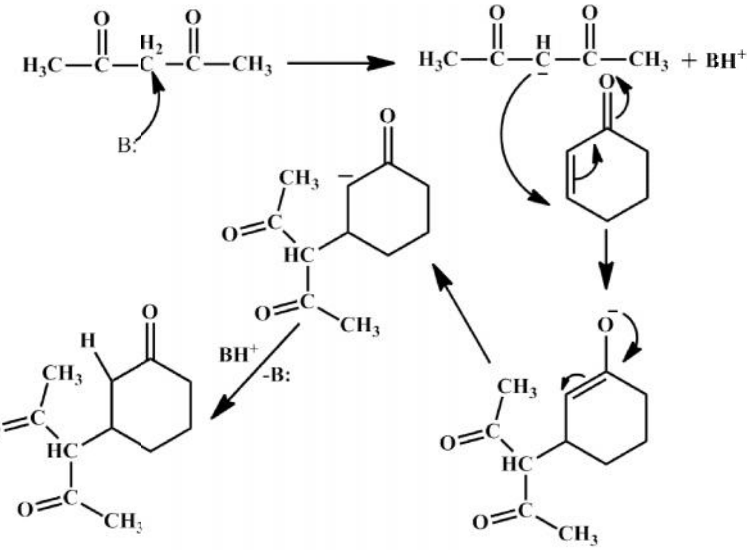


Figure1.15. Mechanism of Michael Addition Reaction (base catalyzed).

The function of the base is to abstract a proton from acetylacetone and to generate the corresponding carbanion, which then acts as a nucleophilic reagent and attacks the α,β-unsaturated system. The base, which generates the enolate ion, is regenerated, so usually only a catalytic amount of the base is required.

There are several techniques to follow the reaction progress like ultra-violet spectrophotometry, chromatography, polarity, conductivity and so on. In this work, thin layer chromatography (TLC) was used as the technique since it is easy, less expensive and convenient with the process and very small amount of solvent is required to develop the TLC plates. The following section describes the salient features of TLC.

1.4. Thin Layer Chromatography

Chromatography is a separation process. It is the best and modern separating technique. Different components in a sample can be differentiated and quantitatively determined by this technique.

In chromatography, two immiscible phases are brought into contact wherein one phase is stationary and the other is mobile. The sample mixture introduced into the mobile phase undergoes a series of interactions with stationary and mobile phase. Interactions exploit differences in the physical and chemical properties of the component in the sample. These differences govern the rate of migration of the component under the influence of the mobile phase through the stationary phase. The least retarded component elutes first and most strongly interacted component elutes last.

When the stationary phase remains in the form of a thin layer adhering to a suitable form of backing material over which the mobile phase is allowed to ascend by capillary action, the technique is called thin layer chromatography (TLC). The most commonly used stationary phases, which are available in different grades, specially prepared for TLC; include silicagel, alumina, kieselguhr and cellulose powders.

1.5 Literature Review

The study of physicochemical properties of ILs is very useful as different combination of cations and anions possess different sets of physical and chemical properties [105,107**]**. Thus, physicochemical properties of ILs may be controlled by varying the structures [225-226]. There are numerous reports available in the literature on physicochemical properties of ILs [217-222]. Most of them explain viscosity, density, refractive index, speed of sound at different temperatures for pure ILs. But reports on the study for binary systems of ILs are very limited. Refractive indices and deviations in refractive indices for the binary systems of trifluoromethanesulfonate-based ILs with water were studied by Vercher et al [223]. Density and viscosity data were measured and corresponding excess molar volumes and the viscosity deviations were calculated for the binary mixture of water with 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [BMIm][NTf$_2$] over the whole mole fraction range [224]. For several binary mixtures of ILs with water, density, isobaric molar heat capacity, and excess molar enthalpy were determined [225]. The effect of water on the viscosities and densities of 1-butyl-3-methylimidazolium dicyanamide and 1-butyl-3-methylimidazolium tricyanomethane were studied at atmospheric pressure. The conductivity of binary systems of ILs was found to be higher than pure ILs [226]. The strength of IL-water interaction was studied by investigation of physicochemical properties of the IL-water binary systems [227]. The change in physicochemical properties and interactions of ILs with molecular solvents was also studied [228] which would help in tuning binary systems for task-specific applications.

For a wide variety of substances like organic, inorganic, organometallic, polymer compounds, biomolecules and metal ions; ILs show promising solvation behavior. Some ILs are immiscible with organic solvents, thus they can be a nonaqueous-polar alternative for two-phase systems [229]. ILs can also be immiscible polar phases with water. They are used in high vacuum systems due to their negligible volatility which characterizes them as green solvents. Therefore, ILs can replace conventional volatile organic solvents which eliminate major environmental problems. ILs can control reaction chemistry, either by participating in the reaction or stabilizing the ionic transition states [4], thus ILs can be good catalysts.

ForFridel-Crafts sulphonylation of benzene, [BMIm][Cl-AlCl$_3$] was used as reaction medium which exhibited increased reaction rate with high yield [230]. In displacement of benzylic chloride with KCN, [BMIm][PF$_6$] was used as solvent and catalyst that eliminated the use of volatile organic solvents and hazardous catalyst disposal and gave high yield [231]. For Michael addition reaction, [BMIm][OH] served as catalyst and medium to give bis addition product in presence of methyl acrylate with high yield [5]. In all cases pure ILs were used as solvent and/or catalyst which makde the process expensive. Moreover storage and handling of pure ILs are expensive and difficult. Therefore, it has been very crucial to understandthe physicochemical properties of pure ILs as well as their binary systems with molecular solvents to explore the potential of ILs as solvents and catalysts in organic synthesis. The systematic study of physicochemical properties may reveal interactive features in the binary systems for the application as solvent and/or catalysts in organic synthesis.

1.6. Objectives of the Work

Binary systems of ILs with molecular solvents may be very promising as the advantageous properties of both ILs and molecular solvents may be exploited. The properties of ILs may be controlled by changing the anion, cation and the alkyl chain length of the cation. Addition of molecular solvents influences the properties of ILs and reduces the cost. Moreover the combination of ILs with molecular solvents can improve or eliminate few limitations of pure ILs, like high viscosity, water and air sensitivity etc. Thus, the studies of physicochemical properties of IL containing binary systems is useful which would help tuning the systems for task specific applications as catalysts and media in organic synthesis.

The work aims at accomplishing the following objectives-

- To envisage the structural change and aggregation behavior of ILs induced by incorporation of molecular solvents of varying composition.
- To explore the possibility of utilizing binary IL-molecular solvents as catalyst and reaction medium for organic synthesis.

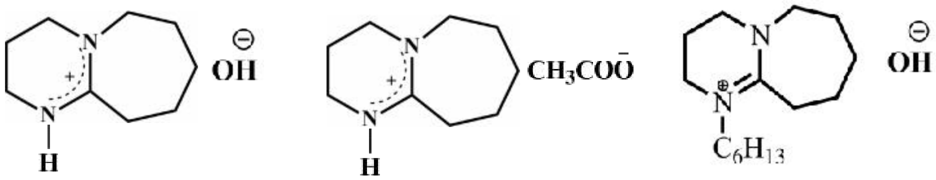
- To understand the influence of the effect of binary IL-molecular solvents as catalyst and reaction medium, on organic synthesis.

Emphasis will be given to optimize properties of binary IL-molecular solvent systems by varying composition and develop economically viable process for use of the systems as catalysts and medium for green synthesis.

1.7. Present Work

In this work, PILs and an AIL based on DBU (Scheme 1.7) have been synthesized and characterized. The prepared ILs were characterized by thermogravimetric and differential thermal analysis (TG-DTA) and spectral analyses by FTIR and NMR have been carried out. Density functional theory (DFT) - based computations have performed for the AIL to optimized the structure and predict the H-bonding in cations and anions by analyzing calculated bond distance, bond angles, atomic charges etc. FTIR, ^{1}H NMR, and ^{13}C NMR spectra have also been calculated computationally and correlated with the experimental spectra of the AIL.Physicochemical properties of different PILs, [DBU][OH] and [DBU][CH_3COO]and AIL [C_6DBU][OH] have been studied in detail. The major focus has been on the binary mixtures of ILs with molecular solvents to find efficient means to tune properties suitable for use as a catalyst and a medium for a model reaction, Michael addition reaction.

The mixture of IL and water is important due to the hygroscopic nature of ILs and the effect of water as an impurity. In addition many ILs are completely miscible with water and therefore it is worth studying the interaction of ILs withwater. Molecular level insight provides clues to improving properties and performance of ILs for specific applications. The excess property is the change in property from the two pure components (water and IL) to the mixture. Thus it involves the disruption of interactions in the neat solvents and the establishment of interactions in the mixture. In cases where the neat solvents have strong like-like interactions but the excess property is the difference in the strength of interactions between unlike species (IL/water) compared to like species (IL/IL and water/water). In this work, binary mixtures of prepared ILs with water, DBU, acetic acid have been prepared in the wide composition range. For studying physicochemical properties, density, viscosity, refractive index, TG-DTA, FTIR, conductivity, solvatochromism have been carried out. Excess properties are reported for binary systems of AIL with water.



[DBU][OH] **[DBU][CH_3COO]** **[C_6DBU][OH]**

Scheme 1.7. The structure of the DBU based ILs.

In this work an attempt has been made to make a comprehensive investigation of the kinetics of, a model reaction of organic synthesis, Michael addition reaction of acyclic active methylene compounds, acetylacetone, and carbonyl compound, 2-cyclohexan-1-one by using the ILs and their binary systems as reaction medium and catalyst. The kinetic results in pure ILs have been compared with the kinetic results of the reaction in binary systems of the ILs with water, acetic acid and DBU. The physicochemical properties of the pure ILs and their binary systems with molecular solvents have been correlated with the kinetics of the reaction. The kinetic results using PILs and AIL as catalysts and reaction medium have also been compared. The ultimate goal has been to understand the structure and arrangement of ions of ILs in pure and the mixtures with molecular solvents and to understand the mechanism of catalysis of the reaction at molecular level.

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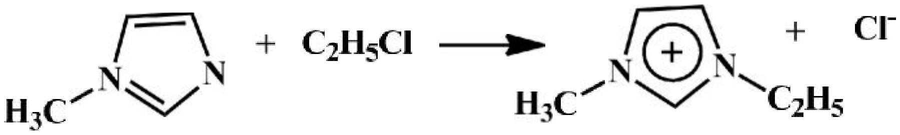
Abstract

Protic ionic liquids (PILs), 1,8-diazabicyclo[5.4.0]-undec-7-ene-8-ium hydroxide ([DBUH][OH]) and 1,8-diazabicyclo[5.4.0]-undec-7-ene-8-ium acetate ([DBUH][CH_3COO]) were prepared by the neutralization reaction of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) with water and acetic acids as weak acids.The ionic liquids, [DBU][OH] and [DBU][CH_3COO] were formed where the protonated DBU is the cation and OH^- and CH_3COO^- are the anions. Synthesis of aprotic ionic liquid (AIL)wascarried out by alkylation of a base followed by metathesis. [C_6DBU][Cl] wasformed in the alkylation step where hexyl-DBU is the cation and the chloride is the anion. Finally metathesis reactionwas carried outusing NaOHto replacechloride ion by hydroxyl ion. Both protic and aproticILs were characterized by thermalanalysis using thermogravimetric-differential thermal analysis (TG-DTA) and spectral measurementsusing Fourier transform infrared (FTIR), Proton-1 nuclear magnetic resonance (^{1}H NMR) and Carbon-13 nuclear magnetic resonance (^{13}C NMR). Computational analyses were performed to explain the arrangement of anions and cations in the AIL and to support the experimental results.

2.1 Introduction

As described in Chapter 1 (section-1.1),ILs are molten salts having melting point below 100 ^oC and are composed of cations and anions.Salts of this kind contrast classical salt e.g.NaCl,KBr, etc. which require molecular solvents for their dissociation into cations and anions. ILs are self-dissociated and do not require any solvent to dissociate into cations and anions. The cations of ILs are organic, whereas anions can be inorganic or organic entities[1-2]. The suitable combination of ions results in an IL with desirable properties [3-4]. Thus ILs show potential technological importance as an alternate solvent to conventionally used volatile organic solvents. The field of ILs is growing at a very fast rate, as the many beneficial properties of these liquids are identified and utilized.

Most research on ILs has focused on AILs. These are generally salts consisting solely of cations (alkyl cations, which are not protonated) and anions. Examples are [C_2MIm][BF_4], [C_4MIm][NTf_2], and so on [5]. The alkyl cations of many ammonium, imidazolium, pyridiniumandphosphonium ILs are prepared by alkylation of a suitable precursor, a nucleophile, using an alkylating agent such as halogeno-alkane or a dialkyl sulfate (Scheme-2.1).



Scheme2.1. Synthesis of [C_2MIm][Cl].

Many ILs are synthesized in a two-step process. First, the halide salt with the required cation is prepared by alkylation (Scheme 2.1). The halide anion is then exchanged with the required anion, typically by anion metathesis. In anion metathesis, anions are exchanged between an organic salt and an inorganic anion source such as a group-I metal salt or asilver salt (Scheme 2.2).

$$[C_4MIm]Cl + Li[NTf_2] \rightarrow [C_4MIm][NTf_2] + LiCl$$

Scheme2.2. Metathesis process for synthesis of aprotic ILs.

Another subset of ILs is PILs, which are easily produced through the combination of a Brønsted acid and Brønsted base. The key properties that distinguish PILs from other ILs is the proton transfer from the acid to the base, leading to the presence of proton-donor and proton–acceptor sites, which can be used to build up a hydrogen-bonded network. PILs have a number of unique properties compared to other ILs, with the exception of some Brønsted acidic ILs. As mentioned in Chapter 1(Section-1.2.4), PILs are formed through the transfer of a proton from a Brønsted acid to Brønsted base, according to scheme 2.3. This gives distinct features to differentiate PILs fromAILs. In fact all PILs have a proton available for hydrogen bonding. More often theyhave non-negligible vapor pressure, and some are distillable media, where their boiling point occurs at a temperature lower than the degradation temperature.

$$B: + AH \rightarrow HB^+ + A^-$$

Scheme 2.3. PIL formation through proton transfer from a Brønsted acid, AH to a Brønsted base, B**:** (e.g. Formationof EAN, $CH_3CH_2NH_2$+ HNO_3 → $CH_3CH_2NH_3^+$ NO_3^-).

The proton-transfer process can be improved through the use of stronger acids and/ or stronger bases, hence leading to greater driving force for the proton transfer. The pK_a values of acids and bases may be considered as an indication of how strongly a proton will be transferred from the acid to a base, though it must be noted that the pK_a's are usually considered for aqueous solutions [6-7] and may not be appropriate for the non-aqueous PILs.

Most of the ILs are structurally based on imidazole which is inert for many organic reactions. Therefore, to expand the scope of organic synthesis the need for the developments of novel task-specific ILs is ever increasing.

DBU is a class of amidine compounds andhas found applications in organic synthesis as a catalyst and as a non-nucleophilic base. Because of its strong alkaline nature, the use of DBU in organic synthesis has been investigated extensively [8-12]. ILs based on DBU were developed to address the issues associated with the use of DBU in organic synthesis [13-15].In fact, DBU was found to be superior to other tertiary amines as catalyst, base or promoter. Hence DBU has the necessary potential to serve as an amine to develop a new class of task-specific DBU-derived ILs which would not only serve as a reaction medium but also as a catalyst or a promoter.

Research to date includes numerous attempts to synthesis ILs by using different methods. The first non-chloroaluminate room temperature acidic IL, such as SO_3H-functionalized IL, was prepared by Forbes and co-workers [16]. It is flexible, nonvolatile, and immiscible with many organic solvents, especially with CH_2Cl_2. This feature has been exploited for synthesis ofporphyrinin a Forbes' IL/CH_2Cl_2 biphasic system [17]. Another acidic IL, 1-butyl-3- methylimidazolium hydrogen sulfate ([BMIm][HSO_4]) prepared by ion exchange between [BMIm][Cl] and H_2SO_4 or $NaHSO_4$was used in esterification [18]and alkylation [19]. Furthermore, some inorganic or organic acids, such as HCl, HBF_4, and CF_3COOH, could react directly with *N*-alkylimidazoles to form a new class of PILs, which bear an acidic proton on N-3 of the imidazolium ring. Itis worth noting that on the basis of PILs, the manufacturer, BASF has commercialized a process under the name BASIL [20]. Recently, the PILs have been used as acidic catalysts for the esterification [21], protection reaction of aldehyde carbonyls [22], Mannich reaction [23], Biginelli condensation [24], and Friedlander annulation [25].

ChloroaluminateILs have already gained increasing attention in replacement of the conventional mineral and solid acid catalysts [36]. Nevertheless, chloroaluminateILs are very sensitive to hydrolysis [27-28]. Trace amounts of water can change the composition of the salt and the concentration of protons. As a result, it is difficult to accurately control the acidity of these ILs. ILs prepared from protonated imidazole and bis(trifluoromethanesulfonyl)amide could be used as non-aqueous proton-conducting electrolytes in fuel cell devices. However, the main disadvantages of imidazolium-based ILs are their relatively high cost and toxicity. Therefore, the development of low cost and low toxicity room temperature ILs is highly desirable.

Although the first IL (EAN) is a protic IL, the study of the structure-property relationships of these materials has newly been initiated and remains in the developmental stage [29]. The important characteristic that differentiates PILs from other ILs is the transfer of a proton from the acid to the base, to make proton donor and proton acceptor sites [30]. PILs are in general proton conducting and electrolytes of this kind proved themselves beneficial owing to various possible applications such as in fuel cells, as an electrolyte in aqueous batteries, in double layer capacitors, in actuators or in dye-sensitized solar cells. There are numerous potential new fields of application for PILs [31]. To date based on IL studies there is limited literature available on PILs. However, this family of ILs has several suitable properties and potential applications due to their protic nature [32].

DBU can serve as a non-nucleophilic base. As a strong base, DBU can grab proton from very weak acids even from water (amphoteric in nature) and become positively charged (protonated DBU) with an anion (conjugated base of the acid). Hence DBU can develop a new class of task-specific DBU-derived ILs. In the proton transfer process the ΔpK_aplays an important role for acids and bases. For base DBU, the value of $\Delta pK_a$is 13.4 [33] and to ensure sufficient proton transfer for the production of highly ionized PILs, the value of $\Delta pK_a > 10$ is required [34]. The ΔpK_a value of 4 has been sufficient for complete proton transfer [35]. The DBU-based ILs have been attractive due to the ability of proton conduction and unique physicochemical properties.

Synthesis of several PILs based on DBU has been reportedand applications of the synthesized ILs in organic synthesis have been investigated [36-39]. The PILs synthesized based on DBU have been successfully applied as catalyst in Knoevenagel condensation reaction [40].Thermophysical properties of AILs based on DBU have been studied along with the synthesis of the AILs [41].Although synthesis of PILs and AILs based on DBU has been reported, the useful data on synthesis of DBU based ILs is limited. This impedes utilizing them for various applications in which the conventional solvents are not suitable.

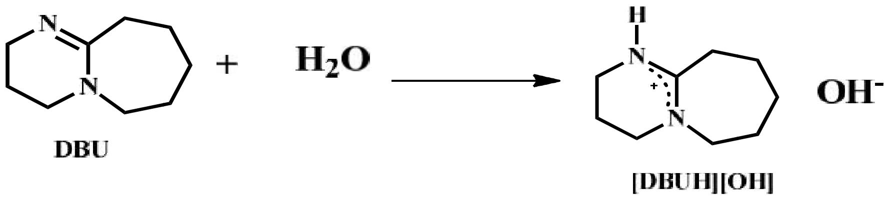
Despite numerous studies, there is still the need for synthesis of new DBU based PILs and AILs for their potential use in manifold applications or exploit the advantageous properties of already know DBU-based ILs. In this work, it is especially focused on the synthesis of functionalized basic ILs for useas a catalyst and a reaction medium in organic synthesis.An attempt has beenmade to synthesizeand characterizeDBU based protic and aprotic ILs.The prepared ILs were characterized by spectral (FTIR, ^{1}H and ^{13}C NMR) and thermogravimetric analyses. The presence of functional groups wasconfirmed by spectral analysis while thermogravimetric analyzer provided information regarding thermal stability of the ILs. An attempt has also been made to study the structure of the novel AIL computationally. From the computational study the ionic geometry (shape of the ion, bond angles, bond length, and dihedrals), energies of ions, and chemical reactivity (where the electrons are concentrated, where they want to move, and where reagents will attack) has predicted. Moreover, IR and NMR spectra have been calculated and correlated with the experimental spectra.

2.2 Experimental

2.2.1 Materials and Methods

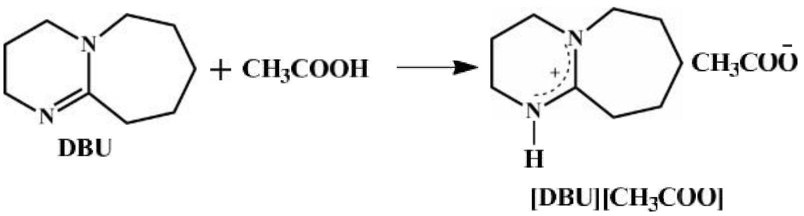
DBU (Sigma), glacial acetic acid (RCI Labscan), 1-chlorohexane (Sigma), NaOH (Merck), DCM (Merck)were used as received without further purification. Double distilled de-ionized water (conductivity: 0.055μScm^{-1} at 25.0 ^{o}C) from HPLC grade water purification system (BOECO, Germany) was used for neutralization reaction.

Calculated amount of DBU (6.569 mmol) and Water (6.569 mmol) were taken in a vial kept in an ice bath and sonicated for 30 min to prepare the PIL, [DBUH][OH] (Scheme 2.4).



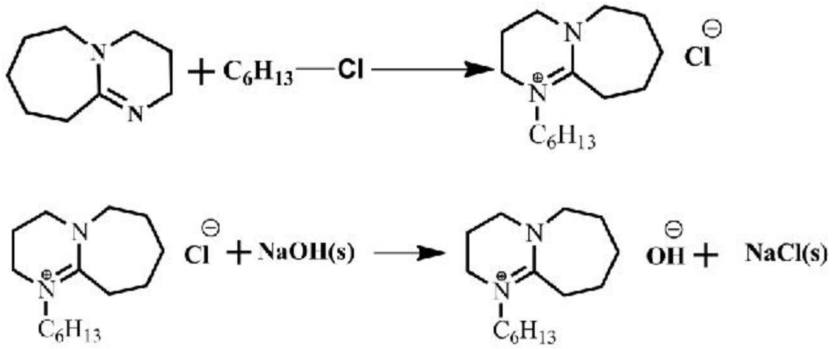
Scheme 2.4. Neutralization reaction between DBU and water.

Similarly, calculated amount of DBU (6.569 mmol) and acetic acid (6.569 mmol) were taken in a vial kept in an ice bath and sonicated for 30 min to prepare the PIL, [DBUH][CH_3COO] (Scheme 2.5).



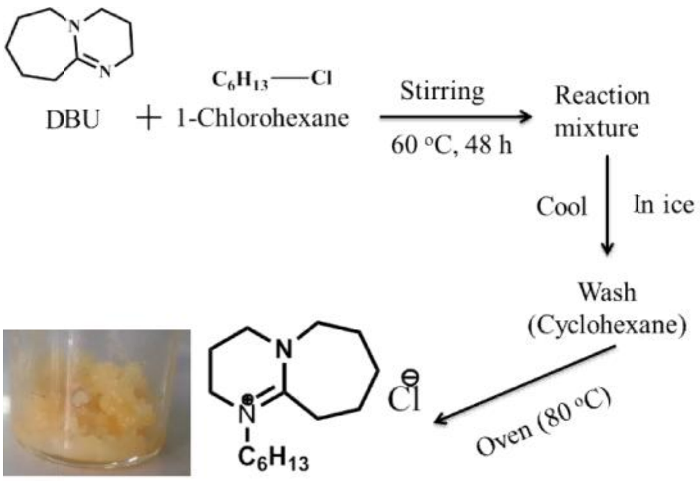
Scheme 2.5. Neutralization reaction between DBU and acetic acid.

AIL based on DBU was synthesized by alkylation of DBU by 1-chlorohexane at room temperature. hexyl-1,8-diazabicyclo-[5.4.0]-undec-7-ene-8-ium chloride ([C_6DBU][Cl]) is produced. The anion halidewasreplaced by appropriateanion through metathesis (Scheme 2.6).



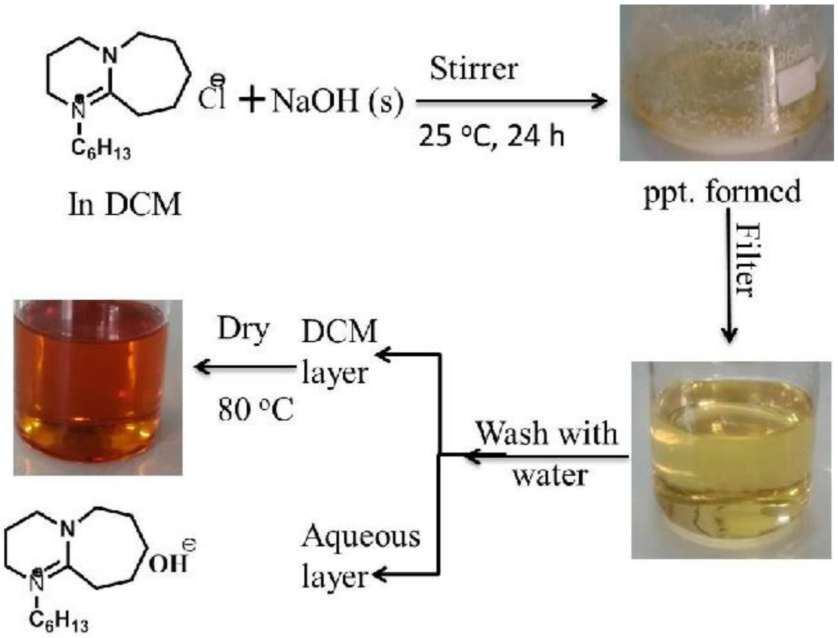
Scheme 2.6. Chemical reaction for synthesis of AIL, [C_6DBU][OH] from DBU.

The AILs derived from DBU were prepared in two steps. In step-1 [C_6DBU][Cl] was prepared by alkylation of the DBU with 1-chlorohexane. At room temperature the product [C_6DBU][Cl] was formed which was wax like solid (Scheme 2.7).



Scheme 2.7. Synthesis of halide salt [C_6DBU][Cl] from DBU.

In step-2 the prepared [C_6DBU][Cl] was converted to [C_6DBU][OH] by metathesis reactionusing solid sodium hydroxide pellet. The product, [C_6DBU][OH] was liquid at room temperature, brown in color (Scheme 2.8) and more viscous than its components.



Scheme 2.8. Synthesis of [C_6DBU][OH] from [C_6DBU][Cl] by metathesis process.

FTIR spectra were recorded with a Perkin Elmer FTIR spectrometer (Frontier)in the spectral wavenumber range from 4000 to 400 cm^{-1}.KBr in the pellet form were usedand microdrops of liquid samples were added on the pellet by micropipettefor recording FTIR spectra.Raw spectra were smoothened and deconvoluted into Gaussian profiles. Each spectrum was subjected to baseline correction before deconvolution and co-efficient of determination (R^2) value of 0.9991 was reached for each peak fitting.

The thermal degradation temperature (T_d) of the ILs was measured using a thermogravimetric differential thermal analyzer (TG-DTA) (a Hitachi instrument, TG-DTA 7200). Samples were heated from 30 °C to 500 °C inan Al-pan under a nitrogen atmosphere. The heating rate was 10 °C min^{-1}.The onset degradation temperature, T_d, can be determined from the point of intersection of the tangents of the TGA curve (Figure 2.1).

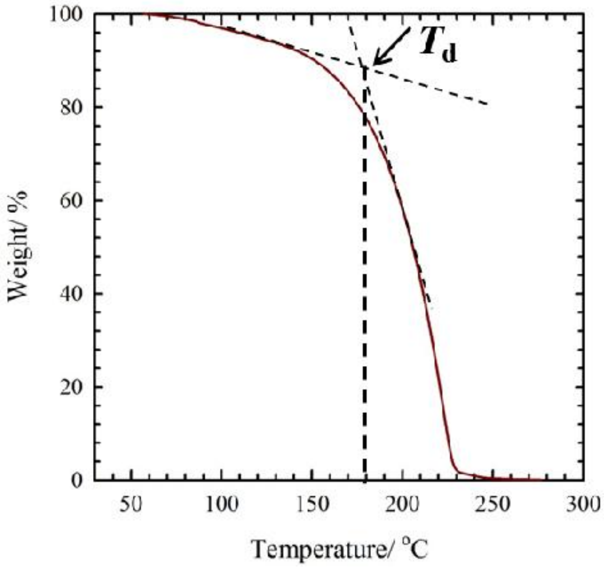


Figure 2.1. Determination of onset degradation temperature from TGA curve.

NMR measurements were carried out on a BRUKER, Ascend 400 spectrometer using a frequency of 400 MHz at 298K using deuterated chloroform ($CDCl_3$) as solvent and tetramethylsilan (TMS) as standard.

Density functional theory (DFT) - based computations were performed using Gaussian09 sets of codes [42]. First, the cation was fully optimized at dispersion-corrected WB97X-D/6-31+G(d,p) level of theory; the OH^- ion was deliberately placed in between the cage-like cavity formed by the rings and the alkyl chain of the cation and the ion-pair monomer was fully optimized at same level of theory. Vibrational frequencies were computed at the same level of theory to generate gas-phase infra-red spectra of the molecule and also for ensuring that the optimized structure resides at the potential energy surface minima by confirming the absence of any negative frequencies. Natural bonding orbital (NBO) analysis was carried out using Gaussian09 to obtain natural charges of the atoms, orbital occupancies and properties related to charge transfer interactions among the lone-pair and anti-bonding orbitals [43]. Absolute chemical shielding of H-atoms and ^{13}C NMR spectra have been computed with the same sets of code- within SCRF-GIAO approximations at WB97X-D/6-311+G(d,p) level of theory [44].

2.3.Results and Discussion

2.3.1. Synthesis of PILs and AIL from the Base DBU

PILs were prepared by neutralization reactions by the constituent acids and bases without using any solvent (Scheme 2.4 and 2.5).Equimolar amount of acid and base were mixed and the mixture was kept in an ice bath as the reaction is exothermic. Miranet al. also reported the preparation of similar PILs without using any solvent [45]. In presence of the strong base, DBU, water behaves as an acid as water is amphoteric in nature. The neutralization reaction between the DBU and water was not completed as the ionization of water is very small and showed the presence of unreacted water (5-10%). The yield of the [DBU][OH] was higher than 90% and [DBU][CH_3COO] was higher than 95%. It The yield of [DBU][CH_3COO] was higher than that of [DBU][OH since the proton donating ability of acetic acid is higher than water although acetic acid is also a weak acid. The yield of the prepared PILs was not 100%. This is not surprising as the neutralization reaction was incomplete. AIL, [C_6DBU][OH] was synthesized by alkylation of DBU followed by anion metathesis (Scheme 2.6). Lethesh et. al reported similar scheme for synthesis of AILs based on DBU [41]. The yield of the [C_6DBU][OH] was higher than 84%. The prepared PILs and AIL were characterized by thermogravimetric analyses and spectral analyses.

2.3.2. Characterization of the Prepared [DBU][OH] and [DBU][CH_3COO]

2.3.2.1.Thermogravimetric and DifferentialThermal Analysis (TG-DTA) of the Prepared [DBU][OH] and [DBU][CH_3COO]

The protic ILs derived from DBU were prepared by mixing the base, DBU with weak acids, water and acetic acid. The obtained mixers were colorless and more viscous than the precursors. The thermal stability of the prepared ILs was checked. Figure 2.2shows thermogravimetric curves of DBU, water and [DBU][OH], at heating rate of 10 $^{o}Cmin^{-1}$ using Al-pan under N_2 atmosphere and the temperature range was 30-300 ^{o}C.

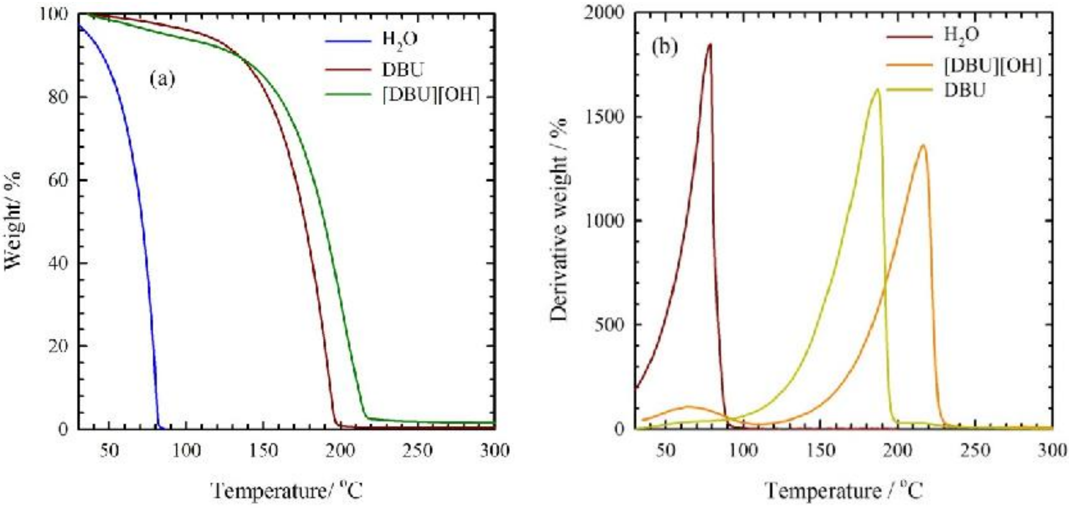


Figure 2.2. Thermogravimetric analyses of water, DBU and prepared [DBU][OH] at the heating rate of 10 $^{o}C/min$ under N_2 atmosphere using Al-pan. (a)thermogravimetric (TG)curve and (b) differential thermogravimetric (DTG) curve.

Thermograms for water, DBU and [DBU][OH] showed progressive loss in weight. The curve for [DBUH][OH] exhibits higher thermal stability (Figure 2.2) compared to its constituents. This is consistent with literature [46]. In fact, water is stabilized by salt formation with its counter parts, DBU became positively charged by getting one proton from water leaving one OH^- anion[46]. The electrostatic attraction between positively charged $DBUH^+$ and OH^- is strong; , therefore[DBUH][OH] exhibited higher (more than 20 ^{o}C) temperature for degradation compared to pure DBU. In fact PILs with strong N-H bonds were reported to show highthermal stability[47]. The fact that [DBUH][OH] showed weight loss from the beginning may correspond to the presence of free water due to incomplete proton transfer in spite of super strong basicityin other words, high proton accepting ability of DBU.

Figure 2.3 shows the differential thermal analysis (DTA) curve for DBU, water and [DBU][OH] under same condition done for TG and DTG curves. The DTA curve (Figure 2.3) exhibited two endothermic peaks. The sharp endothermic peak indicates phase changes (evaporation) of unreacted water below 100 °C. The broad endothermic peaks below 100 °C are obtained from dehydration of the systems and the broad endothermic peaks at higher temperature (> 200 °C) are accompanied by degradation of [DBU][OH] and DBU.The endothermic peak for [DBU][OH] shifted to higher temperature compared to that for DBU is consistence with the TG and DTG curve.

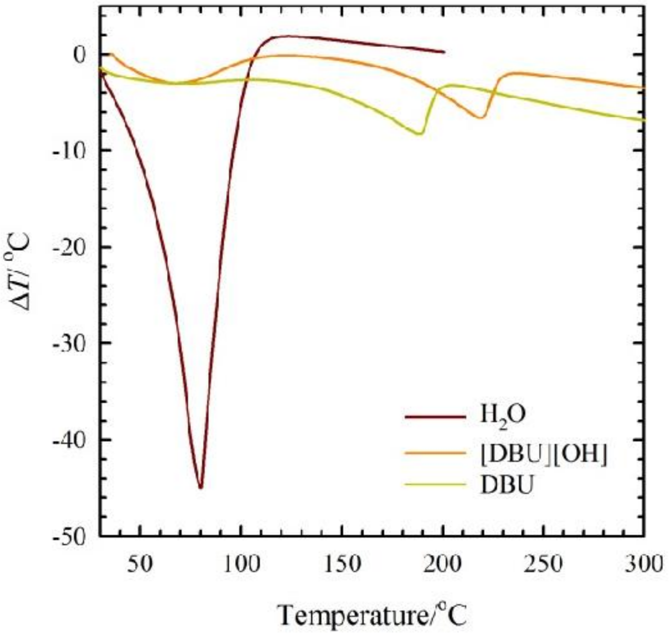


Figure 2.3. DTA curve for H_2O, DBU and [DBU][OH].

The PIL, [DBU][CH_3COO], synthesized from the neutralization reaction of DBU and acetic acid, was a viscous liquid and colorless at room temperature. Figure 2.4 shows thermogravimetric analyses of DBU, acetic acid and [DBU][CH_3COO] under N_2 atmosphere at heating rate of 10 °C min^{-1} using an Al-pan with the temperature range 30-300 °C.

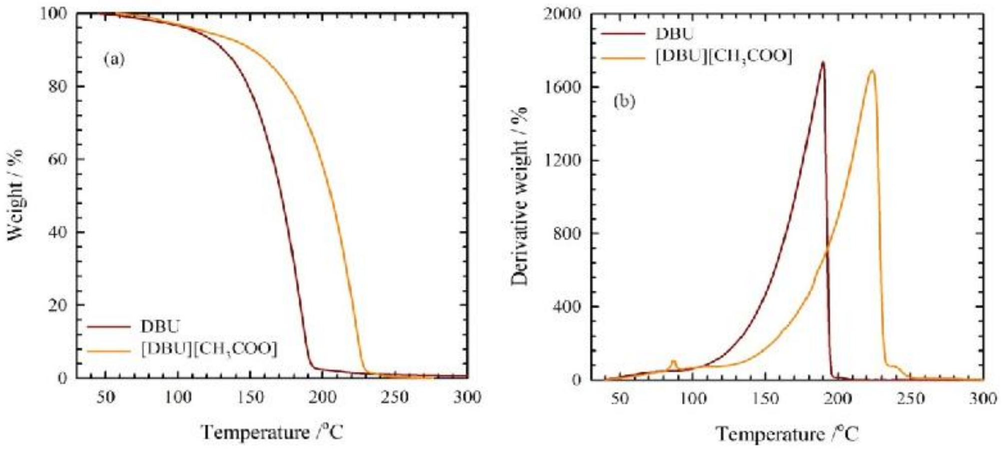


Figure 2.4. Thermogravimetric analyses of DBU and prepared [DBU][CH_3COO] in N_2 atmosphere at heating rate of 10 ^oC/min using Al-pan; (a) TG curve and (b) DTG curve.

Thermograms for DBU and [DBU][CH_3COO] showed progressive loss in weight (Figure 2.4). [DBU][CH_3COO] shows higher thermal stability compared to pure DBU which is consistent with literature [46]. Here acetic acid is stabilized by salt formation with the base DBU through neutralization. In fact, DBU became protonated and positively charged. On the other hand, the CH_3COO^- anion is formed from acetic acid by leaving one H^+ to the base DBU. The strong electrostatic attraction between protonated DBU and CH_3COO^- made [DBU][CH_3COO] more thermally stable (more than 30 ^oC) compared to pure DBU. Moreover, the strong N-H bond in [DBU][CH_3COO] showed high thermal stability [47]. The initial weight loss is very small as the acetic acid is stronger than water and the proton giving ability is higher than that of water. The thermogram for pure acetic acid is absent here as the glacial acetic acid is volatile and it is difficult to keep its weight stable.

Figure 2.5 shows DTA curves for DBU and [DBU][CH_3COO]. The curve for pure DBU shows two endothermic peaks. The broad endothermic peak at about 80 ^oC is for evaporation of free water present in the DBU (98% pure)and the sharp peak at 190 ^oC is for the degradation of DBU. The curve for [DBU][CH_3COO] also shows two endothermic peaks where the broad peak at 100 ^oC is for the evaporation of unreacted acetic acid and the sharp peak at 235 ^oC is for the degradation of [DBU][CH_3COO]. The peak for [DBU][CH_3COO] shifted (more than 45 ^oC) to higher temperature compared to that for DBU. This behavior also correlated well with the TG and DTG curve (Figure 2.4).

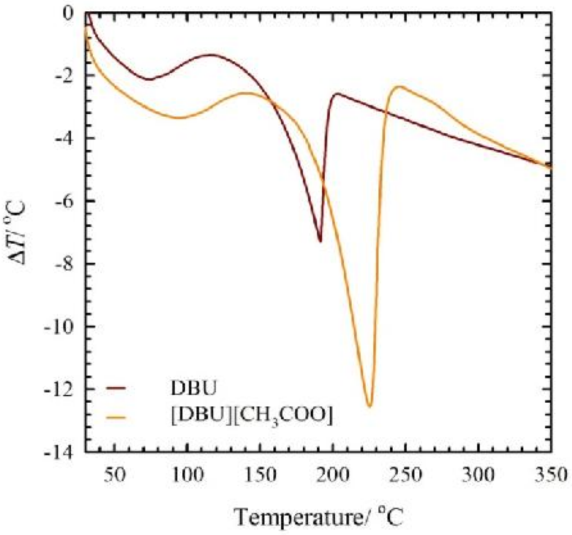


Figure 2.5. DTA curve for DBU and [DBU][CH_3COO] at the heating rate of 10 °C/min in N_2 (100 mL/min) atmosphere.

2.3.2.2 Spectral Analysis of the Prepared [DBU][OH] and [DBU][CH_3COO]

FTIR Spectrum

Figure 2.6 shows the FTIR spectrum of [DBU][OH] in the 400-4000 cm^{-1}range where the bending vibration of N-H can be identified at 1644 and 1510 $cm^{-1}$and stretching vibration at 3262 cm^{-1}. A weaker band appeared at 3100 cm^{-1} which is attributed to a Fermi resonance overtone of the 1550 cm^{-1} band.

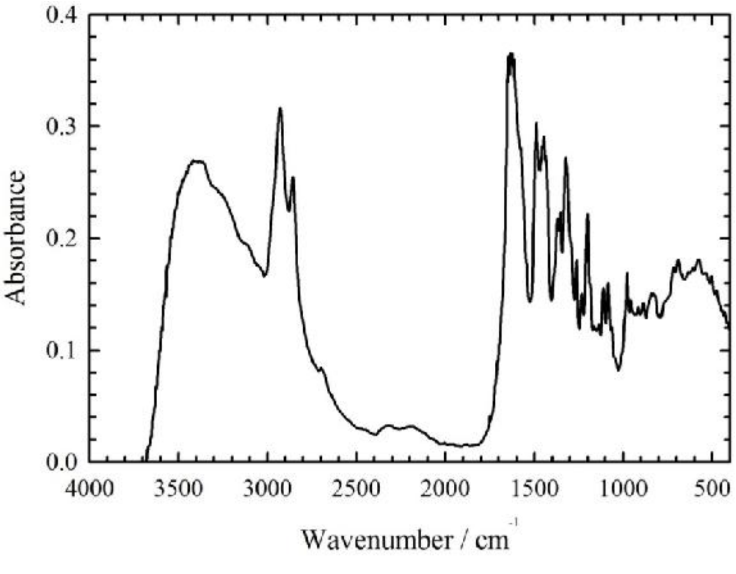


Figure 2.6. FTIR spectrum for [DBU][OH].

Due to the overlapping of different stretching bands in the region of 3050-3580 cm^{-1}, the spectrum has been deconvoluted(Figure 2.7) into several Gaussian peaks (R^2 = 0.9991) for the analysis of the presence of N-H bond in [DBU][OH] where the peaks at 3262 and 3100 cm^{-1} appeared clearly. The peaks in the region 3300-3600 cm^{-1} is for OH$^-$ stretching.

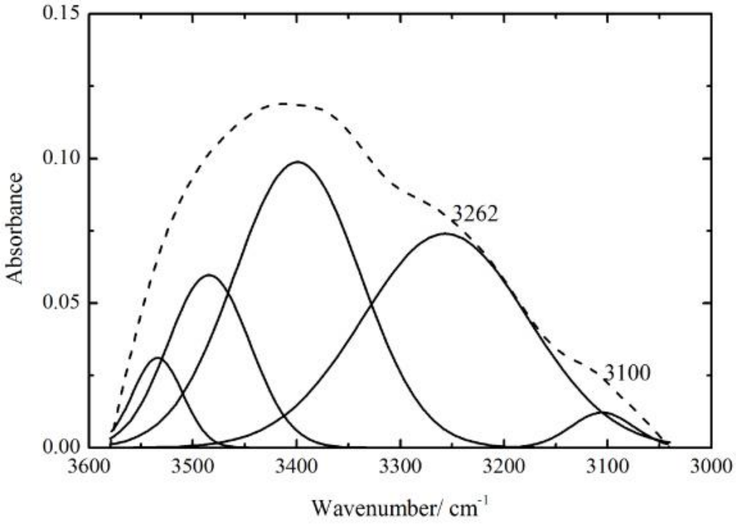


Figure 2.7. Deconvoluted spectrafor [DBU][OH] in the region of 3050-3580 cm^{-1}.

Similarly the FTIR spectrum (Figure 2.8) of [DBU][CH_3COO] in the 400-4000 cm^{-1} shows the band arising from the bending vibration of N-H at 1644 and 1554 cm^{-1}and stretching vibration at 3362 cm^{-1}. A weaker band appeared at 3109 cm^{-1} which is attributed to a Fermi resonance overtone of the 1554 cm^{-1} band.

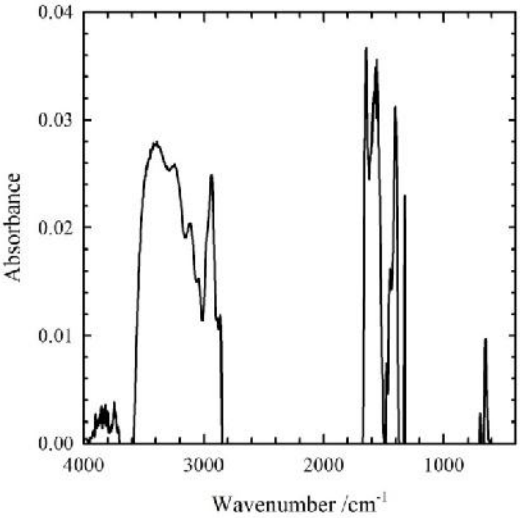


Figure 2.8. FTIR spectrum for [DBU][CH_3COO].

Different stretching bands overlapped in the region of 3025-3500 cm^{-1} and therefore, the spectrum has been deconvoluted into four Gaussian peaks (Figure 2.9) where the peaks at 3109 and 3362 cm^{-1}appeared more clearly. The peaks at about 3233 cm^{-1} is for OH-stretching present in DBU as impurity.

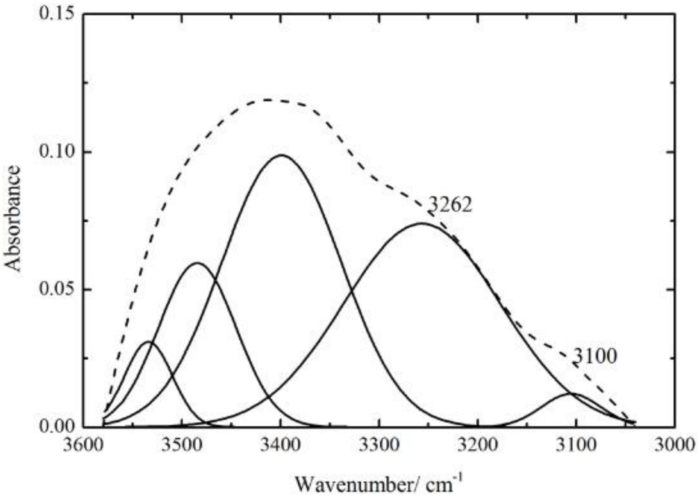


Figure 2.9. Deconvoluted spectra for [DBU][CH_3COO] in the region of 3025-3500 cm^{-1}.

NMR Spectra

^{1}H and ^{13}C NMR Spectra of [DBU][OH]

In order to confirm the structure of [DBU][OH], ^{1}H NMR and ^{13}C NMR analysis were performed.The ^{1}H NMR spectrum of DBU was measured in $CDCl_3$(Figure 2.10).As water is used to prepare [DBU][OH] in the neutralization reaction,the use of D_2O was avoided so that protons from water would be detectable. The signal appeared at δ value of 1.362-1.391 as a multiplet for six protons at position 3,4,5 (Figure 2.10). The signal for two hydrogen at position 10 appeared at 2.070-2.097 δ value as a multiplet. The signal appeared at 2.209-2.242 δ value was interpreted for two protons at position 6. The two protons attached to ring carbon having nitrogen atom on one side appeared at 2.916-2.940 δ. Similarly the four protons at C-9 and C-11 appeared at 3.202-3.054 δ.For hydroxyl proton broad singlet should be appeared at high field (0.5-1 ppm) which is not seen clearly in the spectrum due to overlap with some other signals in this region [48]. All the values were in good agreement with reported data [49].

The signals for protons are briefly described as follows -

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.289 (s, 1H, N_8), 3.202-3.054 (m, 4H, $CH_{2(9,11)}$), 2.916 – 2.940 (m, 2H, $CH_{2(2)}$), 2.209 – 2.242 (m, 2H, $CH_{2(6)}$), 2.070 – 2.097 (m, 2H, $CH_{2(10)}$), 1.362 – 1.391 (m, 6H, $CH_{2(3,4,5)}$).

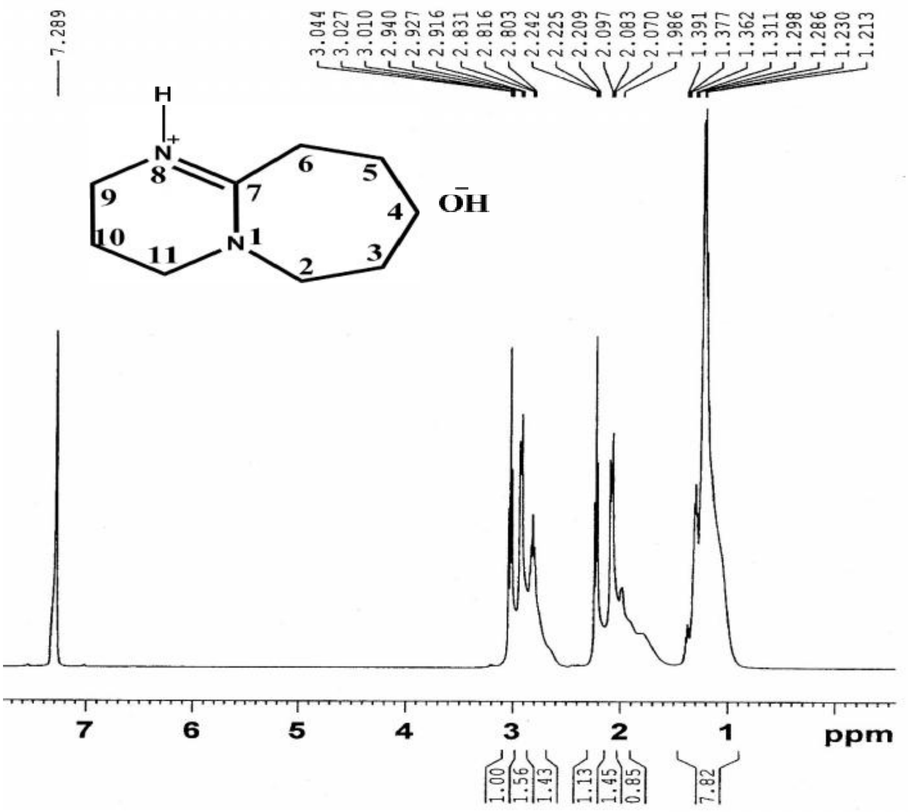


Figure 2.10.^{1}H NMR spectrum of [DBU][OH] in $CDCl_3$at 400 MHz.

The spectrum showed a singlet at 7.289 ppm suggesting that the DBU was protonated at the amidine nitrogen. The ^{1}H NMR spectrum of pure DBU also showed a singlet at 7.303 (less intense) which might be due to the presence of trace water in it.

^{13}C NMR spectrumshowed signals at 21.834-52.487 for eight carbons (2, 3, 4, 5, 6, 9, 10, 11) (Figure 2.11). One signal at 161.536 δ stands for the carbon at 7. Another signal at 175.457 δ stands for carbonyl carbon present in the structure due to the contamination by air.

NMR spectrum for nine carbons is summarized as-

^{13}C NMR (400 MHz, $CDCl_3$): δ 175.457 (CO), 161.536 (C_7), 54.487 – 21.834 ($CH_{2(2,3,4,5,6,9,10,11)}$).

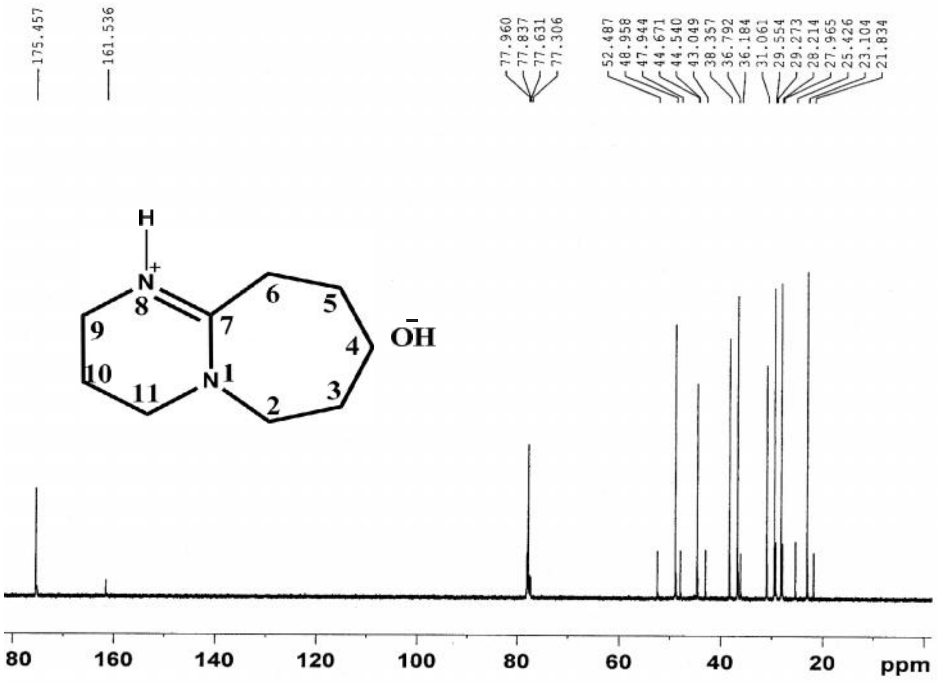


Figure 2.11.^{13}C NMR spectrum of [DBU][OH] in CDCl$_3$at 400 MHz.

The ^{13}C NMR spectrum of [DBU][OH] in CDCl$_3$ showed that the bridgehead carbon (C-7 using the numbering shown in the structure below) appears at 161.536 ppm instead of 160.721 ppm for unreacted DBU [50]. The shifting of C-7 signal from 160.721 to 161.536 is due to the interaction between C-7 and anion as C-7 is more electropositive because of the presence of two electron withdrawing N-atoms . The ^{1}H and ^{13}C NMR data are entirely consistent with the protonated DBU and anion.

^{1}H and ^{13}C NMR Spectra of [DBU][CH$_3$COO]

^{1}H NMR and ^{13}C NMR analyses were performed for explaining the structure of [DBU][CH$_3$COO] clearly. The signal for three protons of CH$_3$ group appeared as a singlet at 1.399 δ value (Figure 2.12). The signal appeared at 1.548-1.672 δ value as a multiplet for six protons at position 3,4,5. The signal for two hydrogen at position 10 appeared at 2.083-2.163 δ value as a multiplet. The signal appeared at 2.459 δ value was interpreted for two protons at position 6. The two protons attached to ring carbon having nitrogen atom on one side appeared at 2.817 δ. Similarly the four protons at C-9 and C-11 appeared at 3.054-3.202 δ. The spectrum showed a singlet at 7.290 ppm suggesting that the DBU was protonated at the amidine nitrogen.

The signals for other protons are briefly defined as follows -

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.290 (s, 1H, N_8), 3.054 – 3.202 (m, 4H, $CH_{2(9,11)}$), 2.817 (s, 2H, $CH_{2(2)}$), 2.459 (s, 2H, $CH_{2(6)}$), 2.083 – 2.163 (m, 2H, $CH_{2(10)}$), 1.548 – 1.672 (m, 6H, $CH_{2(3,4,5)}$), 1.399 (s, 3H, CH_3).

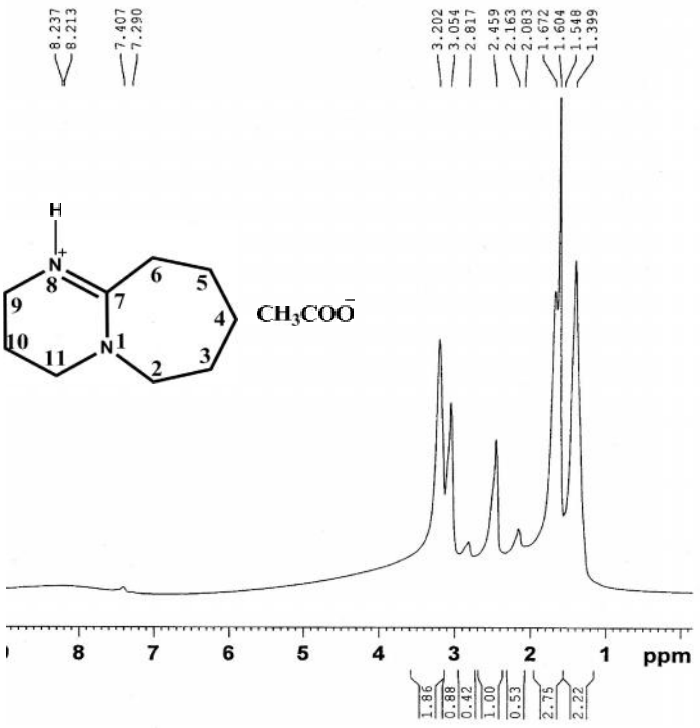


Figure 2.12.^{1}H NMR spectrum of [DBU][CH_3COO] in $CDCl_3$at 400 MHz.

^{13}C NMR spectrum showed nine signals in aliphatic region at 19.275-53.900. Two signals at 165.695 and 176.102 δ stand for the carbon at 7 (Figure 2.13) and carbonyl carbon respectively present in the structure.

NMR spectrum for eleven carbons is summarized as-

^{13}C NMR (400 MHz, $CDCl_3$): δ 176.102 (CO), 165.695 (C_7), 53.900 – 19.2795 (CH_3, $CH_{2(2,3,4,5,6,9,10,11)}$).

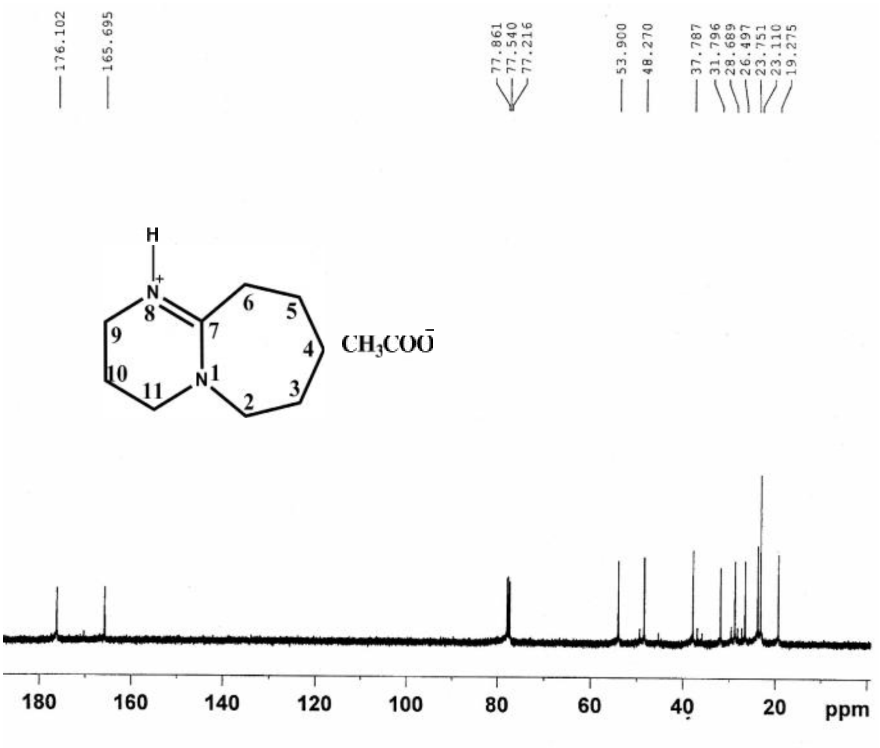


Figure 2.13.^{13}C NMR spectrum of [DBU][CH$_3$COO] in CDCl$_3$ at 400 MHz.

The ^{13}C NMR spectrum of [DBU][CH$_3$COO] in CDCl$_3$ showed that the bridgehead carbon (C-7 using the numbering shown in the structure) appears at 165.695 ppm instead of 160.721 ppm for unreacted DBU [50]. This shifting (from 160.721 to 165.965) is due to the interaction of C-7 with the anion as the C-7 is more electropositive because two N-atoms are bonded to it. The ^{1}H and ^{13}C NMR data are entirely consistent with the protonated DBU and anion.

2.3.3. Characterization of the Prepared [C$_6$DBU][OH]

2.3.3.1.Thermogravimetric (TG) Analysis of the Prepared [C$_6$DBU][OH]

Figure 2.14 shows thermogravimetric analyses for DBU, 1-chlorohexane, [C$_6$DBU][Cl] and [C$_6$DBU][OH] at heating rate of 10 ^{o}Cmin^{-1}under N$_2$ atmosphere.

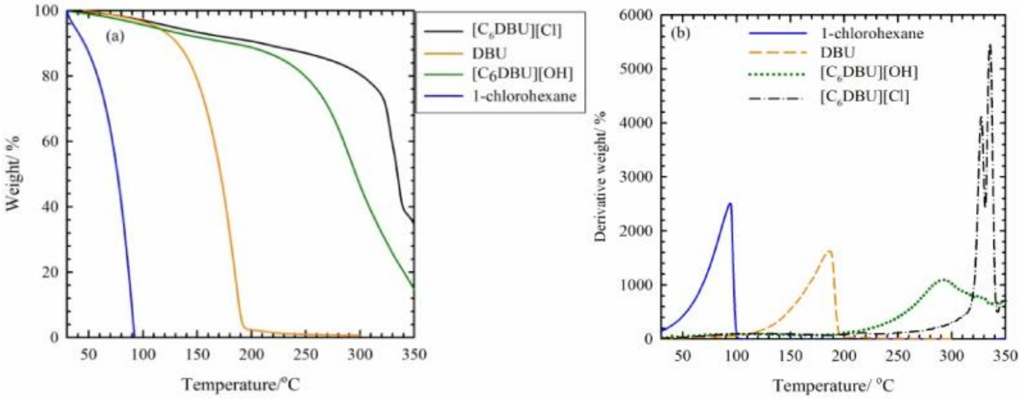


Figure 2.14. Thermogravimetric analysis of [C_6DBU][OH] and [C_6DBU][Cl] with the starting materials, DBU and 1-Chlorohexane under N_2 atmosphere using an Al-pan at heating rate of 10 ^{o}C; (a) TG curve and (b) DTG curve.

Thermogramsfor DBU, 1-chlorohexane, [C_6DBU][Cl] and [C_6DBU][OH] showed progressive loss in weight(Figure 2.14). The curve for [C_6DBU][Cl] and [C_6DBU][OH] showed higher thermal stability compared to pure DBU and 1-chlorohexane.The hydroxide salt, [C_6DBU][OH] has lower thermal stability compared to the chloride salt, [C_6DBU][Cl]. It may be due to the higher nucleophilicity of the hydroxide anion which in turn lowersthe thermal stability by decomposing the cationic core via bimolecular substitution (SN_2) reaction of the easily accessible alkyl group [51]. The higher thermal stability of the chlorideIL can be attributed to itslargersize and the less nucleophilic nature. Diop et al. reported that the thermal stability of the DBU based ILs with chloride anion is below 300 °C, which is in good agreement with our results [52]. The difference in the thermal degradation temperature of the same cation with different anions is due to the difference in the basicity or the nucleophilicity of the anions [53].

2.3.3.2.Spectral Analysis (FTIR, ^{1}H and ^{13}C NMR) of the Prepared [C_6DBU][OH]

Figure 2.15 shows the FT-MIR spectrum of the prepared AIL, [C_6DBU][OH] in the 400-4000 cm^{-1} region where the C-N stretching at 1194 cm^{-1}, C=N stretching at 1652 cm^{-1} and C-H stretching at 2942 cm^{-1} can be identified. Due to the overlapping of the different bands in the region of 2750-3016 cm^{-1}, the spectrum was deconvoluted into several Gaussian peaks for the analysis of different C-H stretching in the AIL.

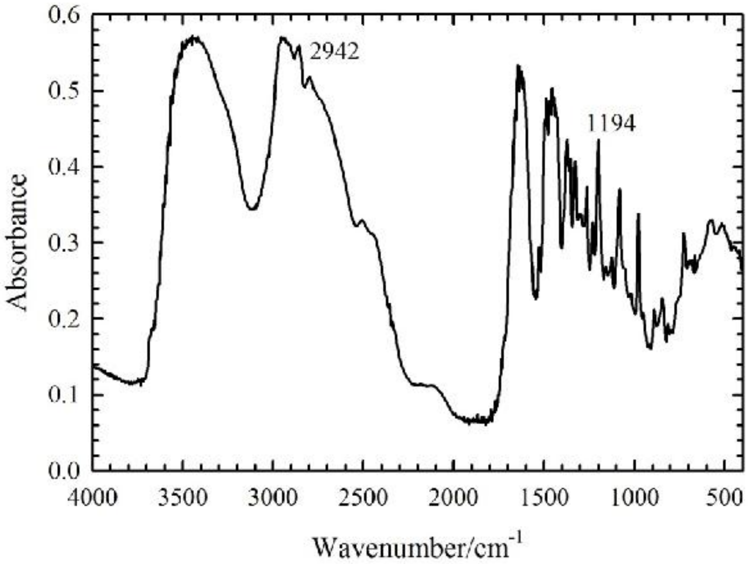


Figure 2.15. FTIR spectrum of [C$_6$DBU][OH].

Figure 2.16 shows the deconvoluted spectrum of the [C$_6$DBU][OH] where the broad band has been fitted to four Gaussian peaks. The C-H stretching is split into two bands at 2961 cm^{-1} for asymmetric and 2882 cm^{-1} for symmetric mode. The bands at 2771 and 2700 cm^{-1} appeared mainly due to the C-H attracted by the oxygen of the anion probably by formation of hydrogen bonds.

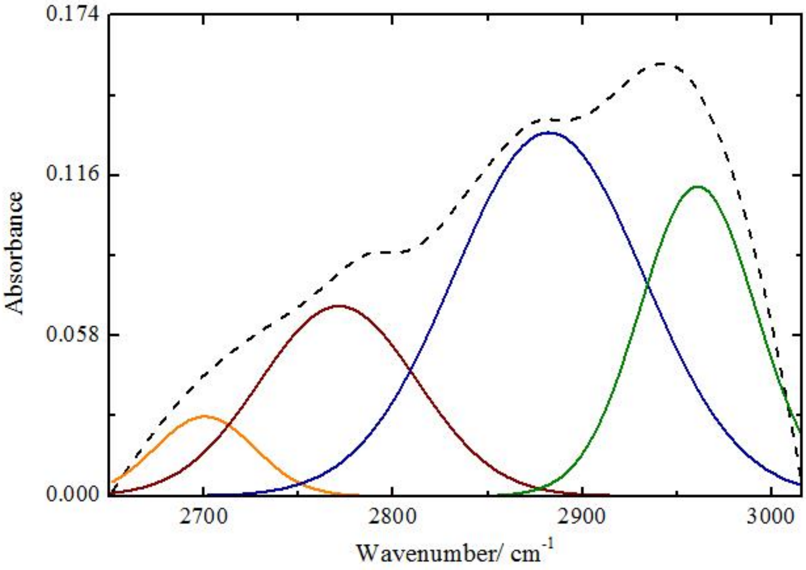


Figure 2.16. Deconvoluted spectra of [C$_6$DBU][OH] in the region of 2650-3015 cm^{-1}.

^{1}H and ^{13}C NMRSpectra of [C_6DBU][OH]

^{1}H NMR and ^{13}C NMR analyses of the prepared AIL, [C_6DBU][OH] gave information which confirm the structure of it. The signal for three protons of CH_3 group appeared at 0.506-0.539 ppm. The signal appeared at 0.939-0.960 ppm as a multiplet for four protons at position c, d (Figure 2.17). The signal for four hydrogens at position b, e appeared at 1.305-1.315ppm as a multiplet. The signal appeared at 1.377-1.480 ppm was interpreted for four protons at position 3, 10.The signal appeared at 1.715-1.835 ppm was interpreted for four protons at position 4, 5. The ten protons at 2, 6, 9, 11, and f attached to carbon adjacent to nitrogen atom appeared at 2.146-2.262, 2.532-2.600, 3.098-3.136, 3.248-3.275, and 3.318-3.347 ppm respectively. These protons appeared at low field as they are deshielded due to the presence of more electronegative N-atoms. A broad singlet appeared at 5.041δ for the hydroxyl proton (hydrogen bonded) [48].

The signals for other protons are briefly described as follows -

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.041 (s, 1H, -OH), 2.146 – 3.347 (m, 10H, $CH_{2(2,6,9,11,f)}$), 1.715 – 1.835 (m, 4H, $CH_{2(4,5)}$), 1.377 – 1.480 (m, 4H, $CH_{2(3,10)}$), 0.939 – 1.315 (m, 8H, $CH_{2(a,b,c,d)}$), 0.506 – 0.539 (m, 3H, CH_3).

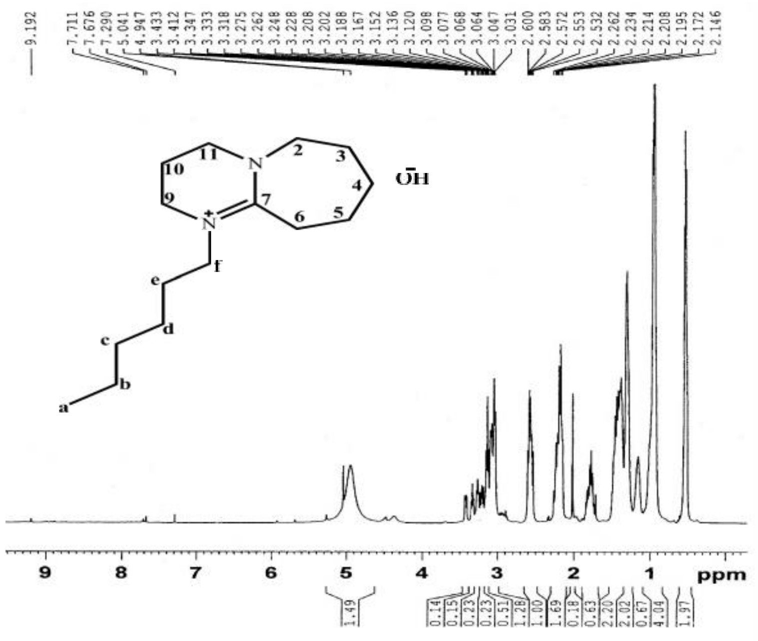


Figure 2.17.^{1}H NMR spectrum of [C_6DBU][OH] in $CDCl_3$ at 400 MHz.

^{13}C NMR spectrum showed a singlet at 13.752 ppm for the carbon of CH_3. Nine aliphatic carbons appeared at 19.918-28.417 for b, c, d, e, 3, 4, 5, 6, and 10 positions. The four deshielded carbons due to the presence of N-atom appeared at 44.959-57.132. Two signals at 166.079 and 175.691 stand for the carbon at 7 (Figure 2.18) and carbonyl carbon respectively.

NMR spectrum for fifteen carbons is summarized as-

^{13}C NMR (400 MHz, $CDCl_3$): δ 175.691 (CO), 166.079 (C_7), 44.959 – 57.132($CH_{2(f,2,9,11)}$), 19.918 – 28.417 ($CH_{2(b,c,d,e,3,4,5,6,10)}$), 13.752 ($CH_3$).

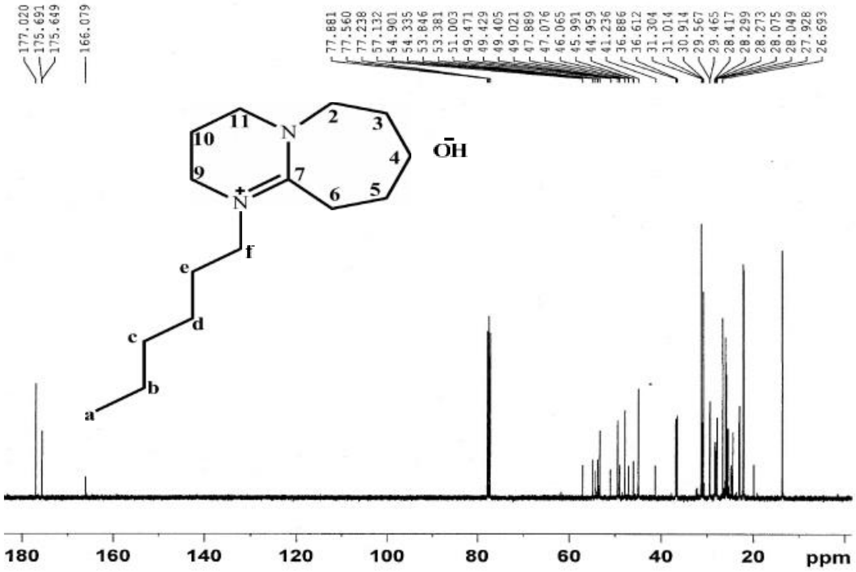


Figure 2.18.^{13}C NMR of [C_6DBU][OH] using $CDCl_3$ as solvent at 400 MHz.

2.4. Computational Study

2.4.1. Optimization of the structure of [C_6DBU][OH]

H-bonding plays an important role in ILs to determine the structure and physical parameters. Computational methods help to understand the nature of the H-bonds in ILs. Usually, H-bond form between a H-bond donor (C-H) and a H-bond acceptor, typically with a lone pair of electrons (such as O). On the other hand, H-bond forms between the partial positive charge on H atom and partial negative charge on electron donor. H-bond is single, shows linear interaction (180^o) and is ionic in nature. In ILs, networks of H-bonds form and these are not one donor-one acceptor type H-bonds. Eventually these are bifurcated (2 acceptor and 1 donor H), trifurcated (3 acceptor and

1 donor H) and chelating (1 acceptor and 2 donor H) H-bonds and these can be disordered with vacant H-bonding sites [54].The optimized structure exhibits the cation and the anion positioning themselves with respect to each other in a fashion that multiple C-H···O H-bonding can be observed. In particular, H-atoms attached to the C^{39}, C^3 and C^1 atoms form moderate to moderately strong H-bonds with the O^{47} atom the OH^- moiety (Figure 2.19).

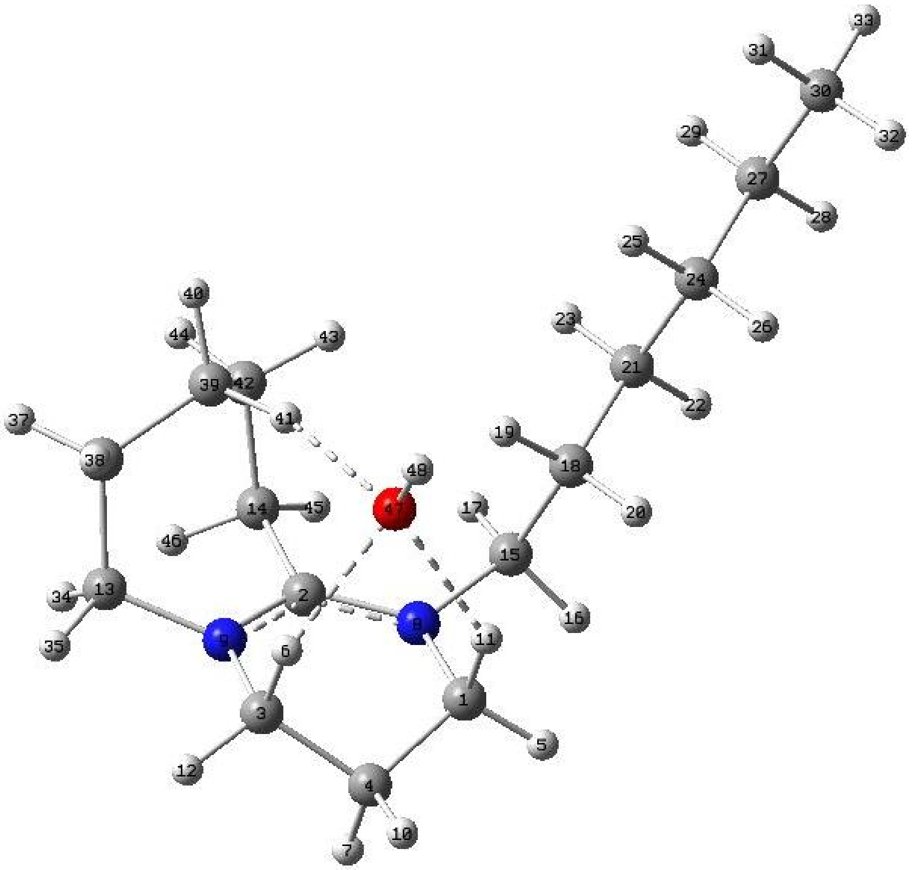


Figure 2.19.WB97X-D/6-31G+(d,p) level optimized geometries of [C_6DBU][OH]; color code: blue=nitrogen atoms, red=oxygen atom, grey=carbon atoms and white=hydrogen atoms; dashed lines representing H-bonds and solid lines representing covalent bonds.

Table 2.1 lists the prospective C-H···O H-bond distances and angles, which shows that combination of at least three moderate to moderately strong H-bonds results in an accepting trifurcated type interionic H-bonding. The bond angles also support the notion, as all the bond angles lie above 110 ^{o}- which is a prerequisite for defining a particular non-covalent interaction as H-bond.

Table 2.1. Selected C-H···O bond distances and bond angles corresponding to the optimized structure of [C_6DBU][OH] at WB97X-D/6-31G+(d,p) level of theory

Atoms	Bond Distances (Å)	Bond Angles (°)
C^{39}–H^{41}···O^{47}	3.075	166.512
C^{3}-H^{6}···O^{47}	2.871	132.242
C^{1}-H^{11}···O^{47}	2.853	131.967
C^{18}-H^{19}···O^{47}	3.255	136.150

Relative strength of the H-bond can be understood by NBO analysis- which have been a powerful tool to interpret various types of H-bonding in terms of perturbation in orbital hybridization, second order perturbation energy, delocalization of natural charge and the NBO generated Frontier orbital scheme [43]. Here the relative strength of the C-H···O bondshas been analyzed by computing the second-order perturbation energy (E2). E2 energy values of the H-bond acceptor or the lone-pair donor atom, or the O^{47} atom, and the H-bond donor or lone-pair acceptor groups, which are the anti-bonding C-H sigma orbitals (σ*C-H), are given in Table 2.2. O^{47} of the OH^- ion has three lone pair (lp) electrons and all the lp electrons contribute as H-bond donor to a more or less extent. In particular, σ* C^{39}-H^{41} participates in stronger H-bond with all three lp electron densities ($O_{lp(1)}$, $O_{lp(2)}$ and $O_{lp(3)}$), which is manifested by the more positive E2 energy values, as higher E2 values correspond to energetically more favorable H-bond formation. σ* C^{39}-H^{41} is involved in stronger H-bond formation with $O_{lp(1)}$ and $O_{lp(3)}$ compared to the $O_{lp(2)}$. σ* C^{3}-H^{6} orbital forms strong H-bond with the $O_{lp(2)}$ but σ* C^{18}-H^{19} binds, in general, weakly with the $O_{lp(1)}$ and $O_{lp(3)}$ and does not interact with the $O_{lp(2)}$ at all; E2 energy values corresponding to C^{18}-H^{19}···O^{47} H-bond correlates well with the fact that the bond distance is much larger compared to the other C-H···O H-bonds.

Table 2.2. Second order perturbation energy (E2) for the charge transfer within the donor-acceptor NBOs

Donor NBO	Acceptor NBOs	E2 Energy Values (Kcalmol^{-1})		
		O_{lp1}	O_{lp2}	O_{lp3}
O^{47}	σ^* C^1-H^{11}	6.47	0.56	8.42
O^{47}	σ^* C^{18}-H^{19}	4.30	-	0.42
O^{47}	σ^* C^{39}-H^{41}	3.03	8.12	8.52
O^{47}	σ^* C^3-H^6	0.28	9.72	3.18

NBO charge distribution map, as given in Figure 2.20, of [C_6DBU][OH] shows that the C^2 atom is the most positive one with a partial charge +0.602 atomic unit (a.u.). Natural charges of selected atoms are provided with in Table 2.3. The positive charge of the C^2 atom is related to the presence of the two most negative N atoms covalently bonded to C^2. Moreover, O47 is directed to the C^2 atom and the distance between these two atoms is 3.170 Å.

Table 2.3. Natural (NBO) charges on selective atoms of the optimized structure of [C_6DBU][OH]

Atom	**Natural Charges (a.u.)**
C^1	-0.30535
C^2	+0.60238
C^3	-0.29814
C^{18}	-0.52409
C^{39}	-0.54717
N^8	-0.42101
N^9	-0.43368
O^{47}	-1.34232

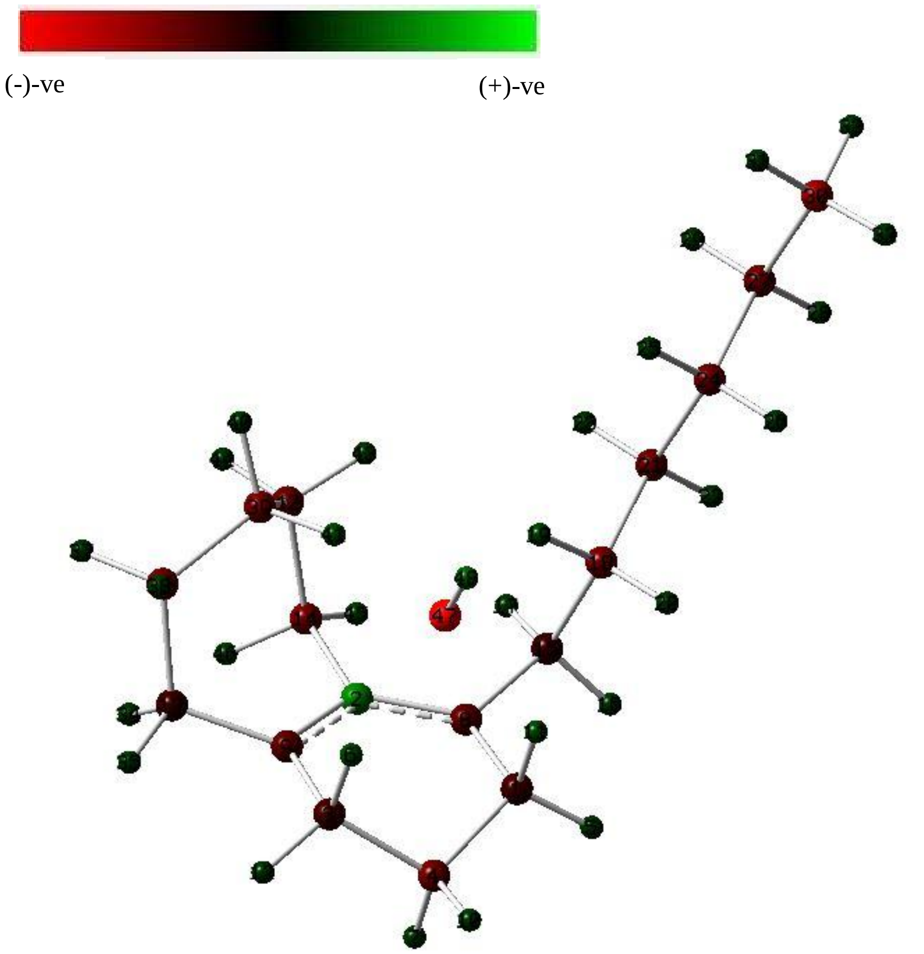


Figure 2.20. Natural charge distribution map of the optimized geometry of [C_6DBU][OH].

2.4.2. Experimental and Calculated FTIR Spectra of [C_6DBU][OH]

FTIR spectra of [C_6DBU][OH] (experimental and calculated) is shown in Figure 2.21 at the wavenumber range of 2600-3100 cm^{-1}. The calculated spectra showed the presence of asymmetric stretching of C-H at 2961 cm^{-1} and symmetric stretching at 2882 cm^{-1}. The hydrogen bonded C-H (carbon 1, 3, and 39) with the oxygen of the anion appeared at 2771 cm^{-1} also present in the calculated spectra, which matches fairly well with the experimental wavenumber corresponding to the same stretching assignment.

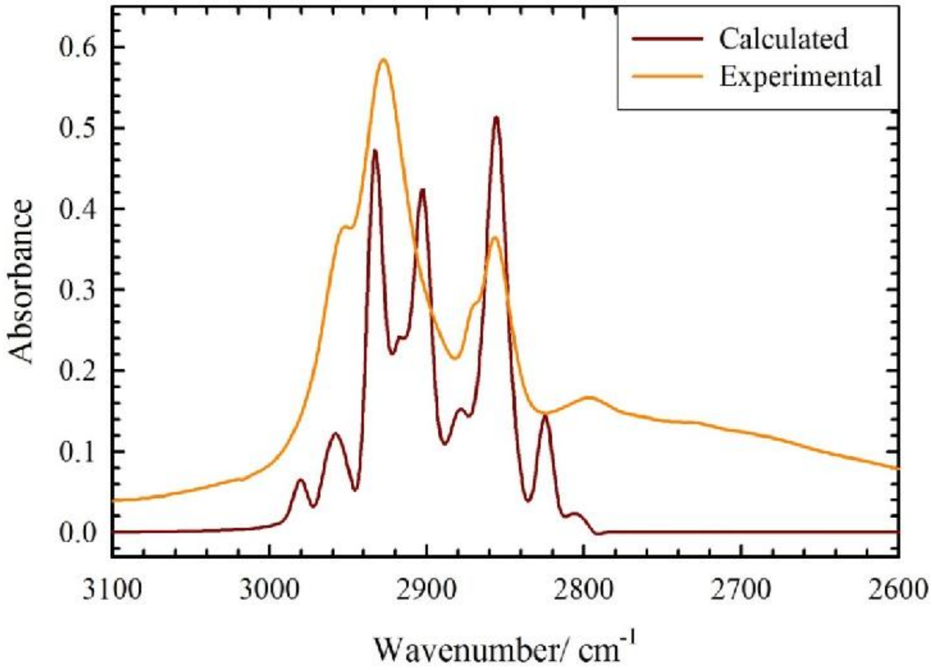


Figure 2.21. Comparison between experimental and theoretical FTIR spectra of [C_6DBU][OH] in the range of 2600 to 3100 cm^{-1}.

2.4.3. Experimental and Calculated ^{1}H NMR and ^{13}C NMR spectra of [C_6DBU][OH]

^{1}H NMR Spectra

Figure 2.22 shows the theoretical absolute chemical shift of the protons of [C_6DBU][OH]. Since this is an absolute chemical shift, the H-atom of OH$^-$ ion is seen to appear at very low field (33 ppm). This alone does not signify anything but when the theoretical NMR spectrum is compared to the experimental ^{1}HNMR spectra, as shown in Figure 2.17, it is observed that the H-atom of the OH$^-$ ion is at the most downfield chemical shift- indicating that the H-atom of the OH$^-$ is the most deshielded H-atom of the structure and O^{47} is involved in the formation of H-bonding.

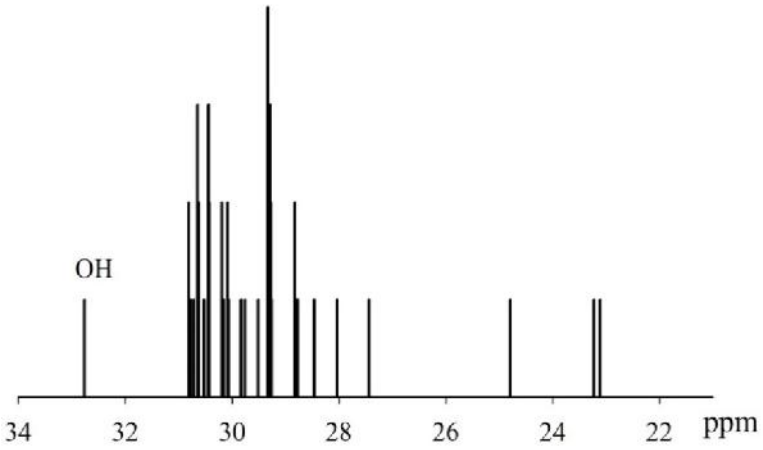


Figure 2.22. Theoretical ^{1}H NMR spectra of [C_6DBU][OH].

^{13}C NMR Spectrum

The calculated ^{13}C NMR spectrum of [C_6DBU][OH] is shown in Figure 2.23. The peak for C^7 appeared in the low field at 148 ppm as this carbon is deshielded due to the presence of two N-atoms joined to it. The four carbons (2,9,11,f) also deshielded due to the presence of adjacent N-atom and appeared at low field (34 to 40 ppm). Thus, the calculated ^{13}C NMR spectrum of [C_6DBU][OH] is similar with the experimental spectrum (Figure 2.18) qualitatively.

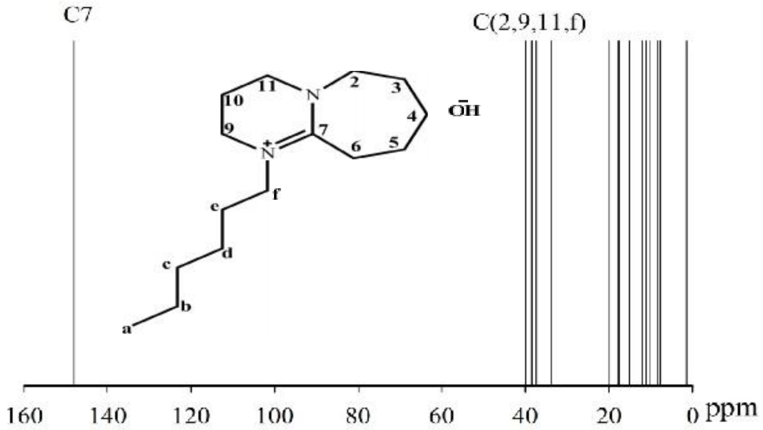


Figure 2.23. Calculated ^{13}C NMR spectrum of [C_6DBU][OH].

2.5. Conclusions

The PILs, [DBU][OH] and [DBU][CH_3COO] derived from a strong base DBU can be successfully synthesized by neutralization reaction in yield higher than 90 %.An AIL, 8-hexyl-1,8-diazabicyclo[5.4.0]-undec-7-ene-8-ium hydroxide ([C_6DBU][OH]), based on a strong base DBU with long alkyl chain can also be successfully synthesized using alkylation of DBU with 1-chlorohexane followed by anion metathesis using solid NaOH giving more than 84 % yield. The FTIR, ^{1}H NMR, and ^{13}C NMR spectral results collectively support the formation of the ILs. The halide salt, [C_6DBU][Cl] and the hydroxide salt, [C_6DBU][OH] exhibit higher thermal stability compared to the precursors to indicate the formation of cations and anions (strong electrostatic interactions). The thermal stability of PILs and the AIL ishigher compared to DBU and are comparable to typical ILs. All prepared PILs and AIL exhibit unique characteristics of ILs.The computational study of the AIL supports well the experimental findings.

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Abstract

Binary systems of PILs and AIL with molecular solvents like water, DBU and acetic acid were prepared at various molar ratios, X_{IL}ranging from 0 to 1.0. Physicochemical properties of pure and binary systems of the ILs have been investigated by measuring conductivity from impedance spectroscopic analysis, density, viscosity, and refractive index. The thermal analysis of the systems was conducted using TG-DTA. Thermal stabilitychanges with increasing concentration of IL observed. ILs have shown higher thermal stability than molecular solvents and the binary systems of ILs. But in all cases there is a minimum value of degradation temperature for the binary system of ILs. The conductivity increases with increasing concentration of ILs and attained a maximum at the mole fraction of the IL, X_{IL}= 0.2 and then decreases to attain a limiting value. The spectral analysis was carried out by Fourier transform infrared spectroscopy (FTIR) which showed the presence of trapped water in the binary systems of IL-rich region for AIL indicating special arrangement of ions and solvent molecules. The particle size of these binary systems were measured by dynamic light scattering method where the size of particles increases with increasing concentrations of AIL and a sudden decrease in the particle size at X_{IL}> 0.4. The density changes with increasing concentrations of the AIL and the variation of excess molar volume as a function of mole fraction of IL shows negative deviation in all the ranges of composition. The viscosity increases uptoX_{IL} = 0.8 and then decreaseswith increasing concentration of AIL. The excess viscosityas a function of mole fraction of AIL showed negative deviation in water-rich region and positive deviation in IL-rich region. The refractive index increases with increasing the mole fraction of AIL and excess refractive index shows positive deviation in the whole of the mole fraction of the AIL.

3.1. Introduction

ILsare liquids composed exclusively of ions and the structure of the cation or the anion may be widely varied to have series of ILs most of which are liquid at room temperature. Physicochemical properties can, therefore, be easily tuned simply by changing the structure of the component ions. The ionic state and ionic mobility influence the physicochemical properties of the ILs directly and may provide microscopic information regarding the physicochemical properties. Comprehensive understanding of the general aspects of properties and their correlation with the structures of the RTILs requires a thorough systematic investigation of a wide variety of ILs by changing the cationic and anionic structures.

The applications of ILs can be further expanded by use of an additional solvent. ILs are not found to be suitable for application as heat-transfer fluid due to high viscosity [1-5]. The combination of IL with molecular solvents can improve or overcome theselimitations. This makes studies on binary mixtures containing ILs interesting. Physicochemical properties and theoretical studies of binary systems containing ILs are required to better understand the molecular interactions existing between ILs and solvents including water. These results can give ideas of various interactions such as solute-solute, solute-solvent, and solvent-solvent interactions. Within molecular solvents manifold forces are involved like hydrogen bonding, ionic/charge-charge, dipolar, and van der Waals interactions. The adequate information about the physicochemical properties of binary mixtures helps in establishing or designing of various applications of ILs [6].

IL-based mixed solvent systems appear to be very promising ones in order to expand the utility and better tune their physicochemical properties. ILs may be combined with other molecular solvents to tailor the physicochemical properties of the IL of interest in a favorable fashion and controlled manner [7]. From the combination of pure ILs with other solvents in binary mixtures, the availability and diversity of the media can be significantly increased. Often in order to increase the efficiency of a process (e. g. separation, extraction, synthesis, etc.), a solvent or mixture of solvents may be tuned by the addition of other solvents. Solvent-modified ILs may alleviate the problem of limited solute solubility associated with many ILsas well as provide affordable solubilizing media with conveniently modified physicochemical properties. This approach has the potential to increase the efficiency and applications of ILs many-fold. In selecting a solvent for IL the toxicity of the solvent is the prime factor that must be taken into account. Subsequently, greener alternatives, such as water, liquid polymers, supercritical fluid, non-aqueous organic solvents and even another IL can be suitable choice as solvents to form potentially mixed green media with ILs [8]. IL-molecular solvent mixed binary systems have found immense industrial, pharmaceutical, and biomedical importance due to their environmentally compatible nature. Reciprocally, properties of molecular solvents may also get modified in favorable manner by addition of an IL to it. The unique physicochemical properties of the ILs, such as negligible vapor pressure, high ionic conductivity, and high thermal, chemical, and electrochemical stability, make them quite distinct from conventional molecular liquids and establish them as unique fluid materials. However the high viscosity and considerably low conductivity of pure ILs make them inadequate for use as electrolytes in commercial electrochemical devices. These can be overcome by addition of polar solvents which lower the viscosity and increases the conductivity significantly [9-14]. In fact, specific reaction media with controlledreaction dynamics can be designed by tuning the polarity of IL-based binary systems by suitable choice of polar solvents. Therefore optimization of the properties to desirable chemistry for a specific task can be achieved by varying the compositions of the binary systems.

In order to understand the behavior of ILs,pure or mixed with other solvents, the experimental determinationof their physical properties and the corresponding excessproperties are of great importance. Moreover, the knowledgeabout the physical properties of ILs may help to find newapplications for these kinds of substances.The physical properties such as melting point, boiling point, density, surfacetension and viscosity are related to the mechanics and engineering componentsassociated with a process. For example, density, viscosity, and surface tensionwill determine important parameters including rates of liquid–liquid phaseseparation, mass transfer, power requirements of mixing and pumping. Otherphysical properties, such as refractive index is related to certain chemicalproperties despite providing a bulk property description. Chemical propertiessuch as the polarity and relative hydrogen bond donating and accepting abilityare more obviously related to the molecular chemistry of their application [15].Due to intermolecular interactions, these parameters measure and the chemicalproperties are believed to play a major role in determining solubility, partitionconstants, and reaction rates.

Although there are numerous reports on the physicalproperties of ILs, pure or mixed with molecular solvents, onlyfew papers contain physical properties data for the ILs [16-21]. Most of them deal with density, speedof sound, viscosity, and refractive index for some pure ILs. References concerning deviations from ideality forbinary systems at different temperaturerange are still very limited.Vercher et al.[22] reported refractive indices and deviations in refractiveindices for several trifluoromethanesulfonate-based ILs inwater and reported that the deviations in refractive index decreases with increasing temperature. They also correlated deviations in refractive index with excess molar volume for the IL + water system.Ge et al. [23] measured densityand viscosity data and calculated the corresponding excessmolar volumes and the viscosity deviations, for the binary mixture (water + [BMIm][NTf$_2$])over the whole mole fraction range.García-Miaja et al. [24] experimentally determined excess molar enthalpy at T = 303.15 K,and density and isobaric molar heat capacity for several binarymixtures (water + IL). And Carvalho et al. [25] studied the effect ofwater on the viscosities and densities of 1-butyl-3-methylimidazoliumdicyanamide and 1-butyl-3-methylimidazolium tricyanomethaneat atmospheric pressure.

The study of physicochemical properties ofbinary system containing ILs might helpto better understand the molecular interactionsexisting between ILs and solvents [26-32]. This can shedlight onvarious interactions such as solute-solute, solute-solvent and solvent-solvent interactions. DBU is a strong organic base and can accept proton even from weak acid and become positively charged species with an anion (conjugated base of the acid). If the acid is weak the conjugate base or the anion will become a strong base. So, DBU can be used to prepare a new class of task-specific ILs, both PILs and AILs.The ΔpK_a of bases is the major parameter in the proton transfer behavior and for DBU it is 13.4 [33]. The $\Delta pK_a > 10$ is required to ensure adequate proton transfer to produce highly ionized PILs [34]. MacFarlane et al. showed that for the completion of proton transfer, $\Delta pK_a = 4$ is sufficient [35]. The PILs having high ΔpK_a exhibit all characteristic properties of AILs like high thermal stability, high ionic conductivity etc. The ability of proton conduction and unique physicochemical properties make DBU-based ILs attractive.Water may be used as a weak acid to prepare the PIL, [DBU][OH] which will reduce the cost of the ILs. It is very important to study physicochemical properties of ILs, pure or mixed with other molecular solvents for understanding the behavior of ILs like interactions of ions with other ions and molecular species. The study of physical and chemical properties of ILs and their binary systems with molecular solvents will help to find the new applications as solvent and/or catalysts for organic synthetic reactions.

There are reports on thermodynamic properties of binary mixtures containingaprotic or protic ILs with different molecular solventsbut noexperimental study is available on binary mixtures of DBU-based PILsand AILswith water, DBU, and acetic acid.Lethesh et al. [36] alsoreported synthesis and thermophysical properties of DBU-based ILs and reported that there is a lack of information on thermophysicalproperties of DBU based ILs.Physicochemical properties of binary systems ofaDBU based IL, [DBU][OH], [DBU][CH_3COO], and [C_6DBU][OH] with molecular solvents (water, DBU and acetic acid) have been thoroughly investigated in this work.. The results obtained have been interpreted in terms of variousmolecular interactions in the binary systems.The eyes have been pointed on the understanding of how the physicochemical properties ofILs are able to affect organic reactivity as well as how they relyon their structural features.

3.2. Experimental

3.2.1. Materials and Methods

DBU (Sigma) and glacial acetic acid (RCI Labscan) were used as received without further purification. Double distilled de-ionized water (conductivity: 0.055 μScm^{-1} at 25.0 ^oC) from HPLC grade water purification system (BOECO, Germany) was used for preparation of binary systems of the ILs. The PILs and AIL were prepared in the laboratory and characterized and then used for further study.

TG-DTAwas studied by a Hitachi instrument (TG-DTA 7200) in the temperature range of 30–500 ^oC at a heating rate of 10 ^oC per min under N_2 gas (100 $mLmin^{-1}$) atmosphere.

Conductivity was measured by electrochemical impedance spectroscopic (EIS) measurements using AutolabPGSTAT302N – a high performance impedance analyzer with the FRA32M module over a wide frequency range of 10 μHz to 32 MHz. The ionic conductivity (σ) was determined with stainless steel electrodes. The liquid sample (ionic liquid or its binary systems) was filled between two mirror-finished stainless steel electrodes using a Teflon ring spacer and subjected to impedance measurement.

FTMIR spectra recorded with a Perkin Elmer FTIRspectrophotometer (Frontier)in the spectral wavenumber range from 4000 to 400 cm^{-1}.KBr pellets were used and one drop of the liquid sample was added on the pellet using micropipette (5-10 μL)for recording FTIRspectra. Raw spectra were smoothened and deconvoluted into Gaussian profiles. Each spectrum was subjected to baseline correction before deconvolution and regression co-efficient (R^2) of 0.9991 was reached for each peak fitting.

FTNIR spectra were recorded by a Perkin Elmer FTIR spectrophotometer (Frontier) in absorbance mode with 20 scans for each sample in the range 4000-12000 cm^{-1}at 4.0 cm^{-1}resolution. Rectangular quartz cell of path length 1.0 mm was used for measurement of binary systems of AIL with X_{IL} = 0-1.0. Uncertainty is 1% for the measurements by this spectrophotometer. Raw spectra were smoothened and deconvoluted into Gaussian profiles. Each spectrum was subjected to baseline correction before deconvolution and regression co-efficient (R^2) of 0.9991 was reached for each peak fitting.

Density of the ILs and their binary systems was measured with an Anton Paar vibrating tube density meter (Model no. DMA 4500). The accuracy was 0.000005 gcm^{-3} and repeatability was 0.00001 gcm^{-3} of density measurement. The meter was calibrated with nano-pure water and with dry air at atmospheric pressure. A small amount of sample (about 1.5-2.0 mL) was injected to a U-shaped borosilicate glass tube that was being excited to vibrate at its characteristics frequency. This frequency changed with the changing density of the sample. The density of the sample was measured by determination of the characteristic frequency and through a mathematical conversion using the following equation-

$$\text{Density} = KA \times Q^2 \times f_1 - KB \times f_2 \qquad (3.1)$$

where, KA, KB are apparatus constants, Q is quotient of the period of oscillation of the U-tube divided by the period of oscillation of the reference oscillator, f_1, $f_2$are correction terms for temperature, viscosity and nonlinearity.

After each measurement, the U-shaped tube was cleaned with ethanol and nano-pure water and dried well. The temperature of the apparatus was controlled by a built-in Peltier device.

Viscosity of pure ILs and their binary systems with molecular systems was measured with an Anton-Paar falling ball automated viscometer (Lovis-2000M/ME) with an accuracy of $\pm 10^{-6}$mPa.s. A capillary with diameter 1.8 and 2.5 mm and a gold ball were used for the measurements. The supplied standard oil was used to calibrate the capillary and the ball. The measuring angle was maximum 70 ^{o}. Temperature was controlled by means of a built-in Peltier thermostat within ±0.01 K.

Refractive index (RI) was measured by using an Anton-Paar Abbemat-300 automated refractometer with high resolution optical sensor. The temperature was controlled by means of a built-in Peltier thermostat within ±0.01 K. The reflected light was used to measure RI. The sample on the top of the measuring prism was irradiated by anlight emiting diode (LED) from different angles. The incident beam was either refracted into the sample or reflected back into the prism. The reflected beam was detected by a sensor array. From this the critical angle for total reflection was calculated and used to determine RI of the sample.

Diameters of the aggregates of ILs in the binary systems were measured using a particle size analyzer, Zetasizer Nano ZS90 (ZEN3690, Malvern Instruments Ltd, UK) by DLS measurements at different temperatures. A He-Ne laser beam of 632.8 nm wavelength was used as the light source and the measurements were made at a fixed scattering angle of 90^{o}. The scattering intensity data were analyzed to obtain the hydrodynamic diameter (D_h) of the aggregates formed in the binary mixtures. A measuring glass cell of 10 mm diameter was used. The particle size detection limit was about 0.3 nm-5 μm. The accuracy of the D_h determined by DLS measurements was ± 2%. The temperature was controlled by using Peltierthermostat within ±0.01K throughout the experiments. Before starting the measurements the laser light was illuminated for about 30 min to stabilize the system. At least 3 measurements, each of 30 runs were carried out for each sample and the run time was set at 30 s for each sample.

Aliquot of a stock solution of Reichardt'spyridinium*N*-phenoxidebetaine dye (RBD) in ethanol was transferred to a volumetric flask andethanol was allowed to evaporate at room temperature. Then water, [C_6DBU][OH] and its binary systems with water were added to the volumetric flask to preparesolutions with the desired concentration of the probe dye, RBD. Themixtures in all cases were sonicated for about 30 min to ensure homogeneity. The UV-visible spectra of RBD solutions of pure [C_6DBU][OH] and its binary systems with water were recorded.

3.3. Results and Discussion

3.3.1. Preparation of Binary Systems of [DBU][OH] with Water and DBU

Appropriate amounts of DBU and H_2O were mixed at various molar ratio to have compositions varying from an equimolar salt to DBU-rich and H_2O-rich conditions. The mixtures were sonicated for 30 min to ensure homogeneous mixing. The mixture at equivalent molar ratio formed a protic neutral salt of [DBU][OH]. The compositions are given in Table 3.1.

Table 3.1 Preparation of binary systems of [DBU][OH] with water and DBU

	Mole Fraction											
DBU	0.00	0.10	0.15	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
H_2O	1.00	0.90	0.85	0.80	0.70	0.60	0.50	0.40	0.30	0.20	0.10	0.00

3.3.2. Preparation of Binary Systems of [DBU][CH_3COO] with Acetic Acid and DBU

Similarly to prepare binary systems of [DBU][CH_3COO] with DBU and CH_3COOH, appropriate amounts of DBU and CH_3COOH (glacial) were mixed at various molar ratio. The mixtures were sonicatedto ensure homogeneous mixing. The compositions are given in Table 3.2.

Table 3.2. Preparation of binary systems of [DBU][CH_3COO] with acetic acid and DBU

	Mole Fraction											
DBU	0.00	0.10	0.15	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
CH_3COOH	1.00	0.90	0.85	0.80	0.70	0.60	0.50	0.40	0.30	0.20	0.10	0.00

3.3.3. Preparation of Binary Systems of $[C_6DBU][OH]$ with Water

$[C_6DBU][OH]$-H_2O binary systems with compositions varying from H_2O-rich condition to $[C_6DBU][OH]$-rich conditions were prepared at various molar ratio by mixing appropriate amounts of $[C_6DBU][OH]$ and H_2O. As the $[C_6DBU][OH]$ hydrophobic in nature, the mixtures required sonication for at least 1 h to ensure homogeneous mixing. For the system of $X_{[C_6DBU][OH]}$ = 0.9 the mixture took two days to become clear. The detail compositions are given in Table 3.3.

Table 3.3. Preparation of binary systems of $[C_6DBU][OH]$ with water

	Mole Fraction										
$[C_6DBU][OH]$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
H_2O	1.0	0.9	0.3	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0

3.3.4. Physicochemical Properties of the Prepared Binary Systems of [DBU][OH] with Water and DBU

3.3.4.1. Thermogravimetric-Differential Thermal Analysis (TG-DTA)

Thermal properties of [DBU][OH] and its binary systems with water and DBU were studied by using TG-DTAunder N_2 (100 mL/min) atmosphere at heating rate of 10 ^{o}Cmin^{-1}. Figure 3.1(a) shows TG curves for [DBU][OH] and its binary systems with water and DBU.

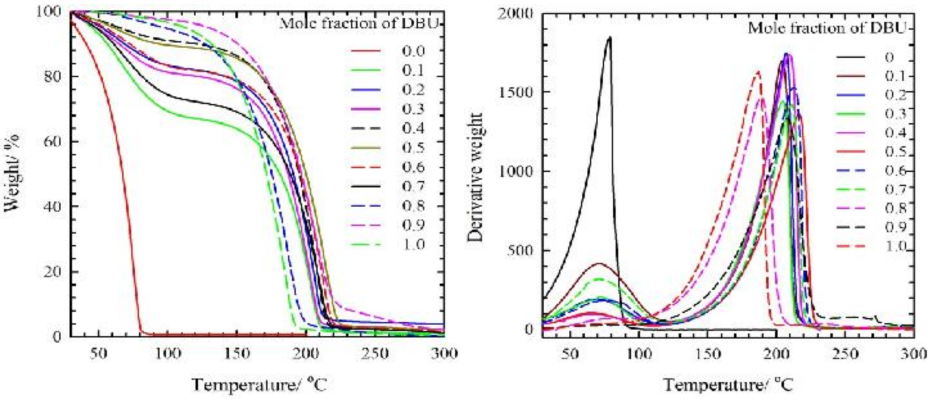

Figure 3.1. Thermogravimetric analysis of [DBU][OH] and its binary systems with DBU and water at heating rate of 10 ^{o}Cmin^{-1}under N_2 atmosphere: (a) TG curve and (b) DTG curve.

The binary systems in the water-rich condition (X_{DBU}< 0.5) showed progressive loss in weight due to the presence of free water. The curve for the [DBU][OH] exhibited higher thermal stability compared to free water and DBU since water and DBU were stabilized by the formation of salt, [DBU][OH] [37]. The binary systems for X_{DBU} = 0.2 and 0.8 showed lower thermal stability as compared to the pure [DBU][OH]. At X_{DBU} = 0.2, water is attracted to the ions of [DBU][OH] with perturbation of the hydrogen bonds in water by the strong electrostatic field of ions of the [DBU][OH] [38]. Due to this attraction between water molecules and ions of [DBU][OH], the network structure of cations and anions started breaking into small cluster and the degradation temperature of this composition decreases.At X_{DBU} = 0.8 in DBU-rich composition, the thermal stability of this system is lower because of the interspecies H^+ exchange between molecular DBU and the $DBUH^+$ which weakens the electrostatic interaction between cations and anions of the [DBU][OH]. Therefore, the degradation temperature at X_{DBU} = 0.8 is lower than that of pure [DBU][OH].

The DTGcurve in Figure 3.1(b)shows that the binary systems of [DBU][OH] with water and DBUundergo two-step weight loss process. These correspond to the evaporation of free water below 100 ^{o}C and the degradation of the salts produced from the neutralization of DBU with water.

The DTA (Figure 3.2) curve for the system also exhibited two endothermic peaks.

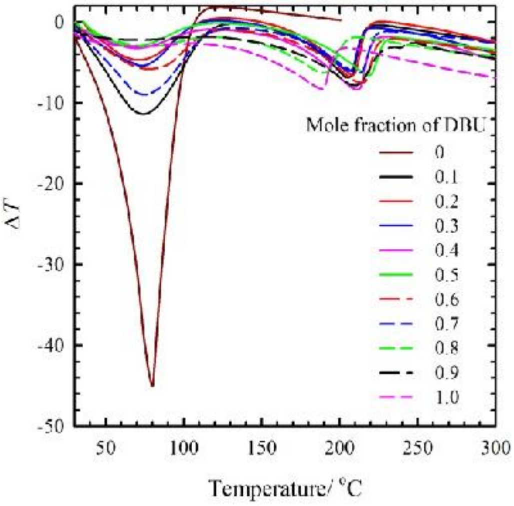

Figure 3.2. DTA curve for [DBU][OH] and its binary systems with water and DBU measured under N_2 atmosphere at heating rate of 10 ^{o}Cmin^{-1}.

The sharp endothermic peak indicates phase changes (evaporation) of unreacted water below 100 ^{o}C. The broad endothermic peaks below 100 ^{o}C are obtained from dehydration of the binary systems and the broad endothermic peaks at higher temperature (> 200 ^{o}C) are accompanied by degradation of [DBU][OH].

3.3.4.2. Conductivity Measurement by Electrochemical Impedance Spectroscopic (EIS) Analysis

Figure 3.3 shows the Nyquist plot for [DBUH][OH] and the binary mixtures of [DBUH][OH] with water and DBU. The Nyquist plot of impedance gives information about the electrochemical impedance behavior. The real component (Z′) represents the Ohmic propertiesand the imaginary component (Z″) stands for the capacitive properties. This study has been carried out in the frequency region 100 Hz to 1 MHz. For an ideal super-capacitor, the Nyquist plot shows three frequency dependent regions. In the high frequency region, it shows behavior like a pure resistor. However, pure capacitive behavior is observed in the low frequency region where the imaginary part sharply increases and a vertical line is observed. In the case of the medium frequency domain, the influence of the electrode porosity can be observed. The electrolyte penetrates deeper and deeper into the porous structure of the electrode when the frequency decreases from the very high frequency and results in more and more electrode surface being available for ion adsorption [39].

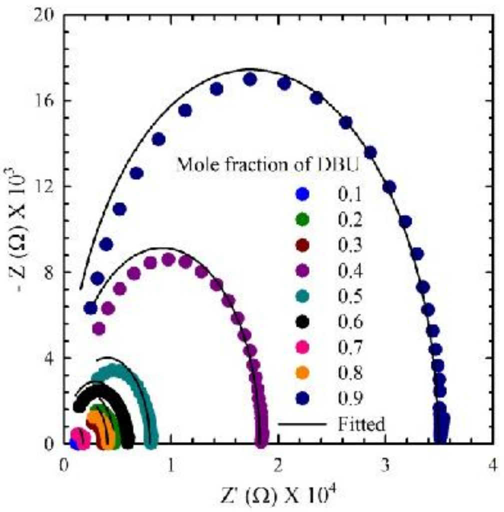

Figure 3.3. Electrochemical impedance spectroscopic analysis for [DBU][OH] and its binary systems with water and DBU.

However, solution resistance (R_s) of these systems can be obtained from the intercepts at the highest frequency of the curves on the real axis. The Nyquist plots were analyzed by fitting the experimental impedance spectra to an equivalent electrical circuit. A suitable circuit for the systems has been schematically demonstrated in Figure 3.4.Semicircle is obtained at high frequency and a straight line is observed at low frequency regions. The conductivityvalues for the IL ([DBU][OH]) and itsbinary systems with water and DBU are given in the Table 3.4.

Table 3.4. Conductivity of binary mixtures of DBU and water

Mole fraction of DBU	**Conductivity ($S\ cm^{-1}$)**
0	1.4×10^{-11}
0.1	1.9×10^{-8}
0.2	5.4×10^{-8}
0.3	3.9×10^{-8}
0.4	3.3×10^{-8}
0.5	3.1×10^{-8}
0.6	4.3×10^{-8}
0.7	5.1×10^{-8}
0.8	6.2×10^{-8}
0.9	4.1×10^{-8}
1.0	1.5×10^{-13}

The IL, [DBUH][OH] exhibits lower conductivity (higher resistance) than its binary systems with water and DBU (x = 0.2 and 0.8). The mobility of ions is higher in binary systems than in the pure IL which is due to the interchange of proton between $DBUH^+$ (cation) and molecular species (DBU/ H_2O). Moreover, the conductivity of the binary mixture, where DBU is in excess (X_{DBU} = 0.8), is higher than that of the binary mixture where water is in excess (X_{DBU}= 0.2). It indicates that the interactions,like hydrogen bonding, ion-dipole interaction etc. between ions of IL and water are stronger than that of with molecular DBU, as water is more polar than DBU.

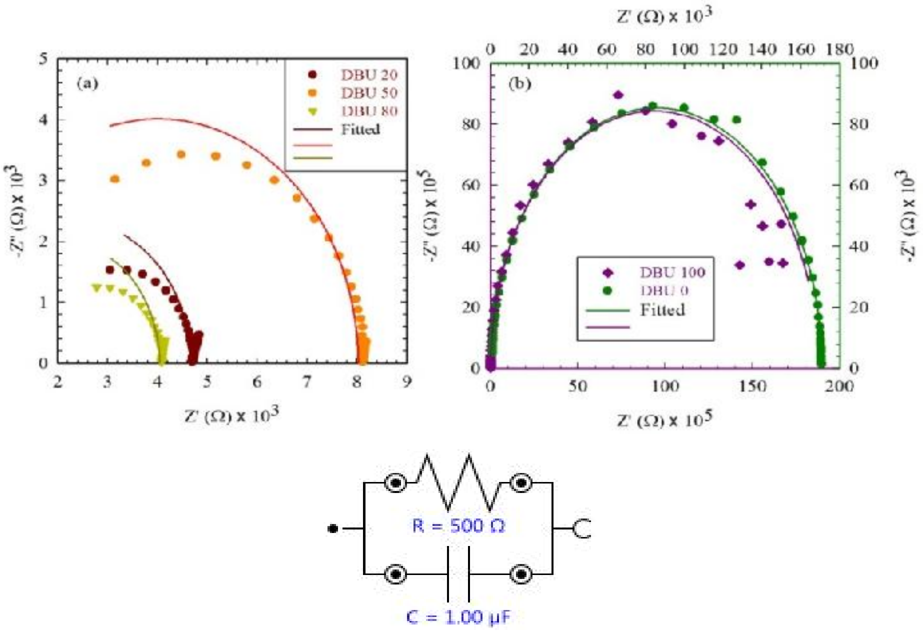

Figure 3.4. Nyquist plots and equivalent electrical circuit used in EIS fitting data for (a) binary systems of [DBU][OH] with DBU and water; (b) DBU and water.

3.3.5. Physicochemical Properties of the Prepared Binary Mixtures of [DBU][CH_3COO] with Acetic Acid and DBU

3.3.5.1. TG-DT Analysis of [DBU][CH_3COO], DBU, and Acetic acid

Thermal properties of [DBU][CH_3COO] and its binary systems with acetic acid and DBU were studied using TG-DTA. Figure 3.5 shows TGA curves for [DBU][CH_3COO] and its binary systems with acetic acid and DBU. The binary systems in the acetic acid-rich composition ($X_{DBU} < 0.5$) showed progressive loss in weight due to the presence of unreacted acetic acid. The curve for [DBU][CH_3COO] exhibited higher thermal stability compared to DBU since acetic acid and DBU were stabilized by the formation of salt, [DBU][CH_3COO] [37].

The binary systems for X_{DBU} = 0.2 and 0.8 showed lower thermal stability as compared to the pure [DBU][CH_3COO]. At X_{DBU} = 0.2, acetic acid may be attracted by the ions of [DBU][CH_3COO] [38] through the formation of hydrogen bonding which weakens the network structure of cations and anions. At this composition, the network structure of the ions breaks into smaller clusters. This is how, the degradation temperature decreases at X_{DBU} = 0.2.At X_{DBU} = 0.8 in DBU-rich condition, the thermal stability of this system is lower because of the interspecies H^+exchange between molecular DBU and the $DBUH^+$ which weakens the electrostatic interaction of the ions of [DBU][CH_3COO].

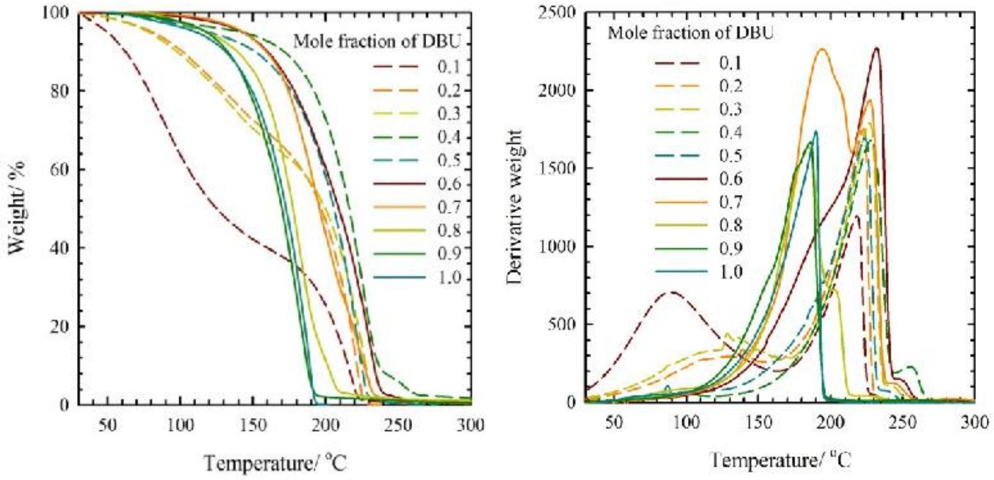

Figure 3.5. Thermogravimetric analysis of [DBU][CH_3COO] and its binary systems with DBU and acetic acid under N_2 atmosphere at heating rate of 10 °C min^{-1}: (a) TG curve and (b) DTG curve.

From the DTGcurve (Figure 3.5) it can be seen that the binary systems of [DBU][CH_3COO] with acetic acid and DBUinvolve two-step weight loss process. These are due to evaporation of free acetic acid below 100 °C and the degradation of the salts produced from the neutralization of DBU with acetic acid.

The DTA (Figure 3.6) curve for the system also exhibited two endothermic peaks.

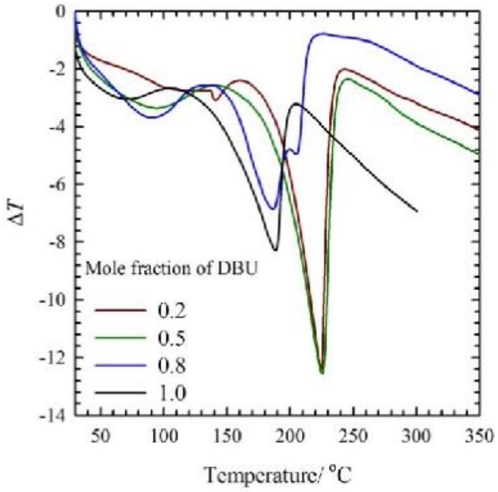

Figure 3.6. DTA curve of [DBU] [CH_3COO] and its binary systems with DBU and acetic acid at heating rate of 10 °C/min in N_2 atmosphere.

The broad endothermic peaks below 100 °C correspond to evaporation of the unreacted acetic acid in the binary systems and the broad endothermic peaks at higher temperature (> 200 °C) is due to by degradation of [DBU][CH_3COO].

3.3.5.2. Conductivity Measurement by Electrochemical Impedance Spectroscopic (EIS) Analysis

Conductivity of [DBU][CH_3COO] and its binary systems with DBU and acetic acid has been studied by EIS analysis. Figure 3.7 shows the Nyquist plot for [DBU][CH_3COO] and its binary systems with acetic acid and DBU. This study has been carried out in the frequency region 100 Hz to 1 MHz.

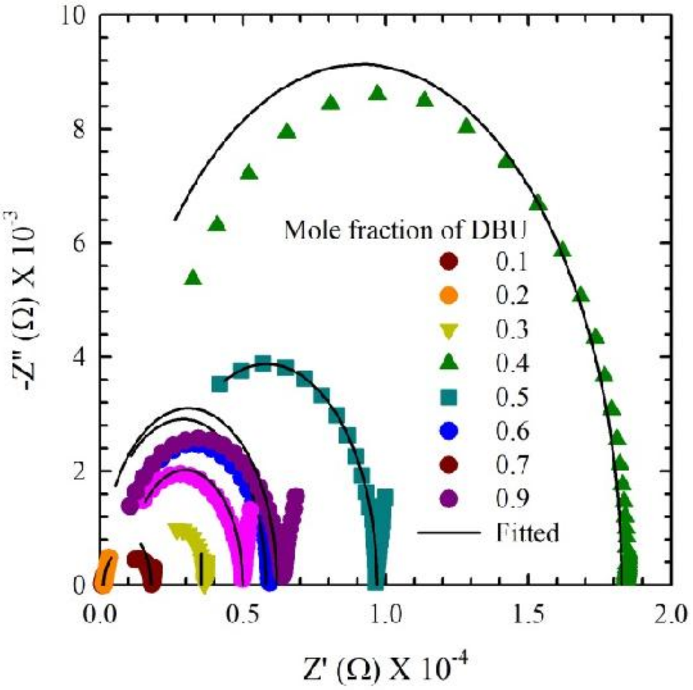

Figure 3.7. Electrochemical impedance spectroscopic analysis for [DBU][CH_3COO] and its binary systems with acetic acid and DBU.

Figure 3.8 shows the Nyquist plot and a suitable circuit for [DBUH][CH_3COO] and its binary mixtures (only selective compositions are shown for clarity)with acetic acid and DBU. From the intercepts at the highest frequency of the curves on the real axis (X-axis), solution resistance (R_s) of the system can be found. The Nyquist plots were analyzed by fitting the experimental impedance spectra to an equivalent electrical circuit. A suitable circuit for the systems has been schematically demonstrated in Figure 3.8. Semicircle is obtained at high frequency and a straight line is observed at low frequency regions. The conductivity values for the IL, [DBU][CH_3COO] and its binary systems with acetic acid and DBU are recordedin Table 3.5

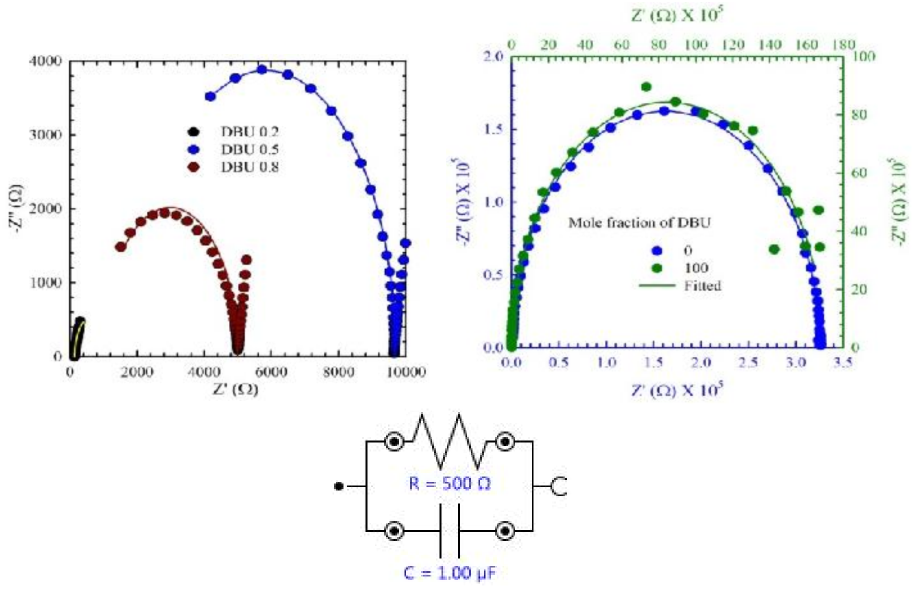

Figure 3.8. Nyquist plots and equivalent electrical circuit used in EIS fitting data for (a) binary systems of [DBU][CH_3COO] with DBU and acetic acid and (b) pure DBU and acetic acid.

Table 3.5. Conductivity of binary mixtures of DBU and acetic acid

Mole fraction of DBU	**Conductivity (S cm^{-1})**
0	2.9×10^{-6}
0.1	11.0×10^{-3}
0.2	5.8×10^{-3}
0.3	3.7×10^{-3}
0.4	1.6×10^{-3}
0.5	0.5×10^{-3}
0.6	1.7×10^{-3}
0.7	1.9×10^{-3}
0.8	3.9×10^{-3}
0.9	2.1×10^{-3}
1.0	1.5×10^{-13}

[DBU][CH_3COO] exhibits lower conductivity (higher resistance) than its binary systems with DBU and acetic acid (*x* = 0.2 and 0.8). Theconductivity of the binary systems of [DBU][CH_3COO] with DBU and acetic acid is higher because of the presence of molecular species (DBU and acetic acid) which helped breaking the large network structure into smaller clusters. Moreover, mobility of ions is higher in binary systems than in the pure IL due to the interchange of proton between $DBUH^+$ (cation) and molecular DBU andanion,CH_3COO^-which weakens the ionic interaction of ions in [DBU][CH_3COO]. Thus, the conductivity of pure IL, [DBU][CH_3COO] is lower than its binary systems with DBU and acetic acid.

3.3.6. Physicochemical Properties of the Prepared Binary Mixtures of [C_6DBU][OH] with Water

3.3.6.1. FTIR Spectroscopic Analysis of [C_6DBU][OH] and its Binary Systems with Water

3.3.6.1.1. FTMIR Spectroscopic Analysis

The FTIR spectroscopy is an important tool for determining the extent of the hydrogen bonding present and thus reflects some structural information. Free and hydrogen-bonded species have molecular vibrations at different IR frequencies [40]. Generally, solubilized water molecules have three distinct states: trapped water, bound water, and free water.The trapped water,with the O-H stretching vibration at about 3600 cm^{-1}, is regardedas the water species dispersed among the long hydrocarbonchains of the ILs [41]. This trappedwater exists as monomers (or dimers) and has nohydrogenbondinginteractions with the surroundings. Furthermore, asmall amount of water dissolved in a nonpolar/hydrophobic solvent isalso considered to be trapped water [42].These water molecules are either justmechanically trapped within the micellar structure or thermodynamicallybound to the polar region of the ILs through intermolecularhydrogen-bonding interactions. Amongst the mechanicallytrapped water molecules, some are intermolecularlyhydrogen bonded with them and some are free [43]. As the trapped water molecules are matrix-isolateddimers or monomeric in nature, they absorb in the high-frequencyregion [41].

The bound water molecules form hydrogen-bonding interactions with the polar headgroups of the ILs, thus resulting in absorption in the low-frequencyregion of the IR spectrum. For the binary systems of [C_6DBU][OH] with water, the O-H stretching vibration of the bound water appeared at 3400 cm^{-1}[44].

Apart fromthese two types of water species, the free water molecules,which occupy the core of the self-association of the ILs with long chain hydrocarbon, havestrong hydrogen-bonding interactions amongst themselves,that is, they have similar bulk-water properties, thus shiftingthe O-H stretching band to a lower frequency of 3200 cm^{-1}.

FTIR spectroscopic analysis of the binary systems of [C_6DBU][OH] with water was carried out (Figure 3.9).

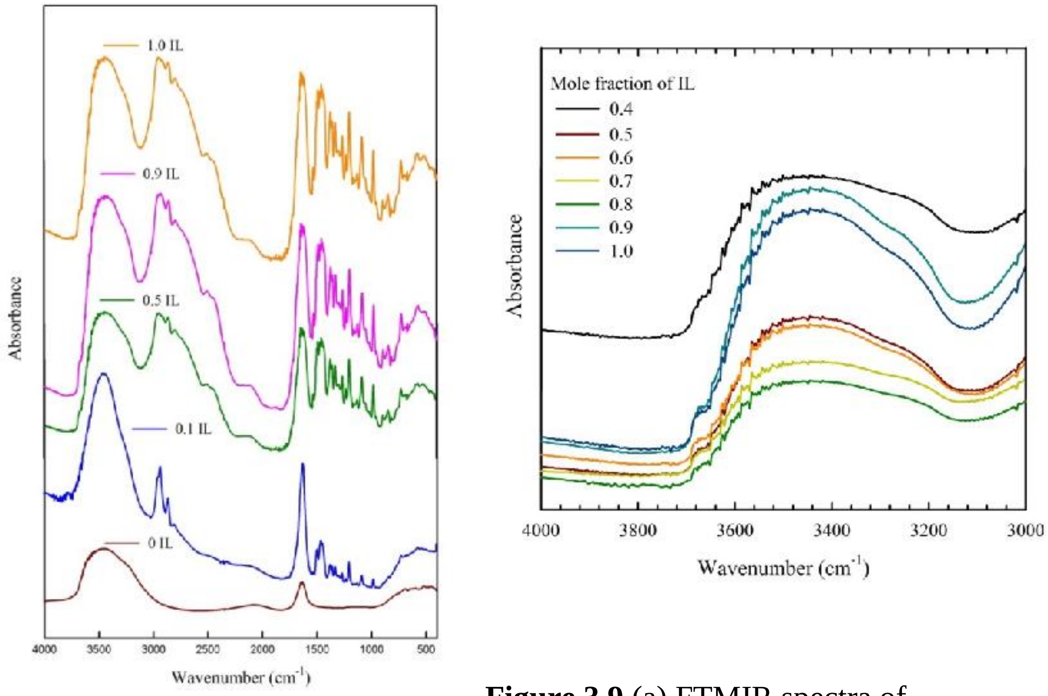

Figure 3.9.(a) FTMIR spectra of [C_6DBU][OH] and its binary systems with water, (b) magnification of the spectrum in the frequency range from 3000 to 4000 cm^{-1}.

Only the bandsof O-H stretching (3200–3600 cm^{-1}) and C-H stretching (3090–3160 cm^{-1}) change significantly withadded water. The O-H stretching bands appearat 3400 and 3200 cm^{-1}, which are due to the bound and free water respectively. After that, the wavenumber of the O-H stretching band remains almost unchanged when the

[C_6DBU][OH] content reached up to $X_{[C_6DBU][OH]}$ = 0.4; but when the content of [C_6DBU][OH] exceeds $X_{[C_6DBU][OH]}$ = 0.4 the O-H stretching band appears at 3680 cm^{-1} along with the free and bound water (Figure 3.9). A possible reason for this behavior is that when water is added to the [C_6DBU][OH], the water molecules are either mechanically trapped in the core of the self-association of the [C_6DBU][OH] or thermodynamically bound to the polar region of the free cations or/and anions by hydrogen-bonding interactions.

In addition, when the water content is $X_{[C_6DBU][OH]} < 0.5$ the wave number of the C-H stretching moves to a low frequency region (2943 to 2927 cm^{-1}), which is caused by the electrostatic attraction of the electronegative oxygen atoms of the water molecules with the polar region of the cation [45].

3.3.6.1.2. FTNIR Spectroscopic Analysis

NIR spectroscopy is a spectroscopic method that uses the near IR region of the electromagnetic spectrum (12000-4000 cm^{-1}). Absorptions in the NIR region are generated from fundamental vibrations by two processes; overtones and combinations. Overtones can be thought of as harmonics. So every fundamental will produce a series of absorptions at multiples of the frequency. Combinations are rather more complex. NIR absorptions are at a higher state of excitement so they require more energy than a fundamental absorption. Combinations arise from the sharing of NIR energy between two or more fundamental absorptions. While the number of possible overtones from a group of fundamental absorptions in a molecule is limited to a few, a very large number of combinations will be observed. The effect of all these absorptions combines to make many NIR spectra to look rather uninteresting and to consist of only a few rather broad peaks. These combination and overtone bands correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Since each different material is a unique combination of atoms, no two compounds produce the exactly same NIR spectrum. Therefore, NIR spectroscopy can result in a positive identification of each different materials. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms and statistical treatments, NIR spectroscopy is an excellent tool for quantitative analysis, offering a practical alternative to time-consuming wetchemical methods and liquid chromatographic techniques.

Figure 3.10 shows the FTNIR spectra of [C_6DBU][OH]-water binary systems of different compositions in the 4000-8000 cm^{-1} region where the combination band arising from the symmetric, antisymmetricstretching,and bending vibration of water molecules can be identified. Due to the overlapping of different combination bands, the spectrum has been deconvoluted into several Gaussian peaks for the analysis of different water species in the binary systems. There are several ways that ionic species in water affect NIR spectra. These effects include (1) decreasing concentration of water, (2) ion-dipole interaction between ions of IL and water molecules affecting the hydrogen-bonding of water, (3) the presence of OH^- ions, (4) the presence of another NIR-active functional groups and conditions by which some ions produce OH^- and H^+ through hydrolysis [46].

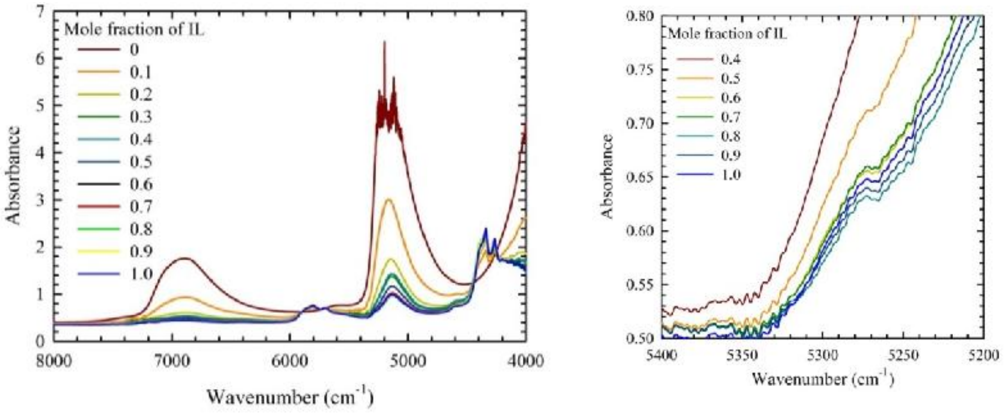

Figure 3.10.(a) FTNIR spectra of [C_6DBU][OH] and its binary systems with water, (b) amplification of the spectrum in the frequency range from 5200 to 5400 cm^{-1}.

The salt lowers the intensity of the water peak and also shifts it to the left, toward higher frequencies indicating less hydrogen bonding. Different ions have somewhat different effects, depending on their size and electronic characteristics. Differences in the intensities of changes to the NIR spectra have been attributed to the charge-to-radius ratios of cations or anions. The ionic hydroxyl group in water has its own specific absorption band with first overtone band at 7040 cm^{-1}. As the hydroxide concentration is increased, the intensity of the water peaks at 6900 cm^{-1}decreases. The absorption band at about 6660 cm^{-1} is for overtone and combination of symmetric and anti-symmetric stretching modes. The strong 5150 cm^{-1} peak is a combination of the asymmetric stretching and bending modes of the water molecule. The band at 5275 $cm^{-1}$for the [C_6DBU][OH]-water binary system indicates that its position depends on the dominant species in which water is trapped [47].

Figure 3.11. shows the deconvoluted spectrum of [C_6DBU][OH]-water binary system with 0.9 mole fraction of IL where the broad band has been fitted to eight Gaussian peaks. The 7080-7400 cm^{-1} region was assumed to arise from the CH vibrations of imidazolium cation [48]. The band at 7020 cm^{-1} is the combination band of -OH in water molecule bonded to [C_6DBU][OH] as the absorbance rises significantly in this region with increasing amount of water. Water mainly remains in monomeric form in IL-rich region and interacts with anions [49].

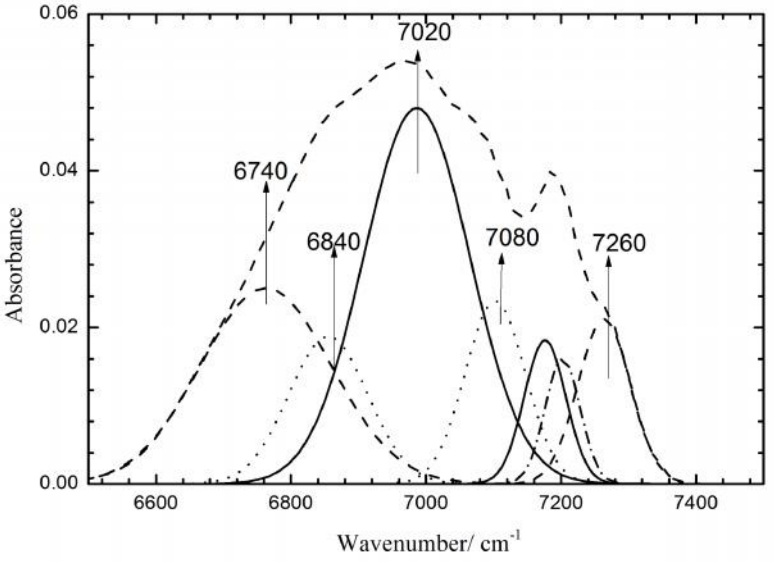

Figure 3.11. Deconvoluted spectrum of [C_6DBU][OH]-water binary mixture with $X_{[C_6DBU][OH]}$ = 0.9.

The smaller peaks at 6740, 6840 cm^{-1} originate from the hydrogen bonded water clusters. The peaks for associated water appears at lower wave number region than the peak for water bounded to [C_6DBU][OH] as the hydrogen bonds between water molecules are much stronger than that between water and anions [50].

3.3.6.2. Particle Size Analysis by DLS Measurements

DLS measurements have been carried out to analyze the size of the aggregates formed in the [C_6DBU][OH]-water binary systems (Figure 3.12). The technique measures the time-dependent fluctuations in the intensity of scattered light from a suspension of particles undergoing random Brownian motion. Analysis of these intensity fluctuations allows for the determination of the diffusion coefficients, which in turn yield the particle size through the Stokes-Einstein equation.

In [EMIM][BF_4]-water binary systems, formation of chain like aggregates was indicated instead of self-organized structures at X_{IL} = 0.05 [51]. The absence of self-organized aggregation is due to the small length of alkyl chain in the imidazoliumring [52]. For aqueous solution of [BMIM][BF_4] vesicle-like hollow spherical shape aggregates with hydrodynamic radius of 243.4 nm at 1.0 mol $L^{-1}$is observed in which water is bonded with anions (BF_4) surrounding the macrocations [53].

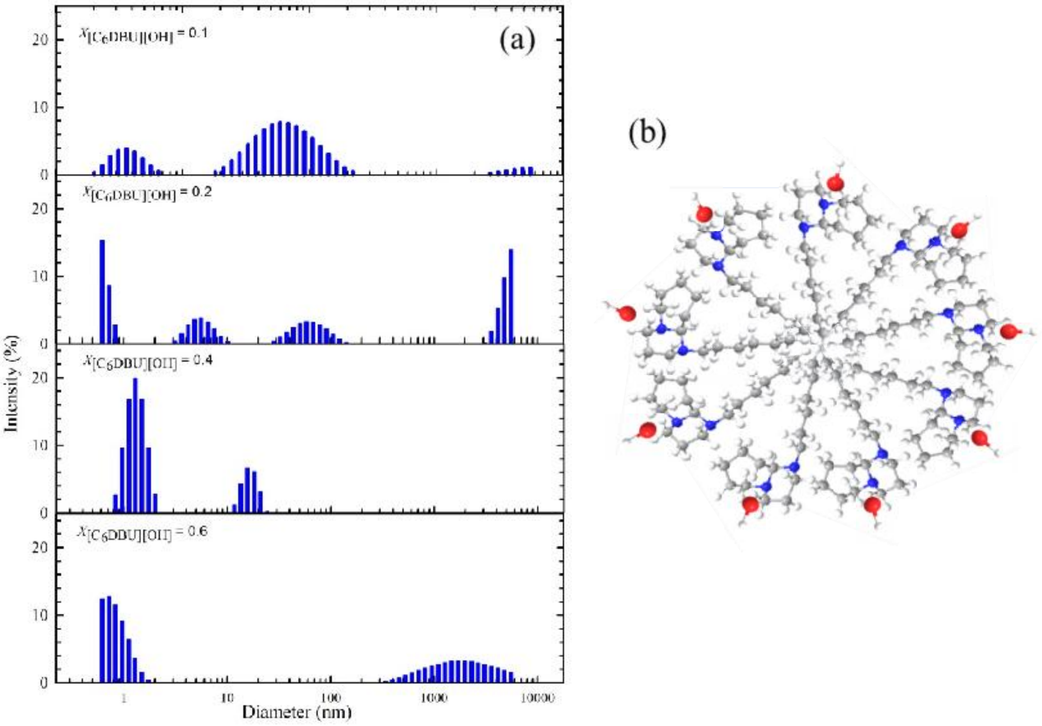

Figure 3.12.(a) Particle size distribution in [C_6DBU][OH] and its binary systems with water at $X_{[C_6\text{DBU}][\text{OH}]}$ = 0.1 to 0.6, (b) Micelle-like aggregation of [C_6DBU][OH] in water-rich region.

For [BMIM][BF_4]-water binary systems, the aggregate size determined from DLS measurements was reported to be larger than 1000 nm at low temperature e.g.about 4 ^{o}C [54]. In the present study, DLS measurements show that, (Figure 3.12.) with increasing concentration of [C_6DBU][OH], $X_{[C_6\text{DBU}][\text{OH}]}$ = 0.1-0.4, the size of the aggregates increase. At $X_{[C_6\text{DBU}][\text{OH}]}$ = 0.5, the aggregates show a narrow distribution. With furtherincrease in concentration of [C_6DBU][OH] (at $X_{[C_6\text{DBU}][\text{OH}]}$= 0.6-1.0), the aggregates size increases again.

The increase in size of the aggregates with addition of [C_6DBU][OH] to water is observed for solutions with $X_{[C_6\text{DBU}][\text{OH}]}$ = 0.1-0.4 and 0.6-1.0. As the [C_6DBU][OH] is hydrophobic and contains a long alkyl hydrocarbon chain (hexyl) in the cation,formation of vesicle like aggregates may be feasible. In water-rich region with $X_{[C_6\text{DBU}][\text{OH}]}$ = 0.1-0.4, it might be micelle-like and in [C_6DBU][OH]-rich region with $X_{[C_6\text{DBU}][\text{OH}]}$ = 0.6-1.0, it might be reverse micelle-like aggregation.

Figure 3.13.shows the DLS measurement for [C_6DBU][OH]-water binary systems at the compositions of $X_{[C_6\text{DBU}][\text{OH}]}$ = 0.6 to 1.0. Peak broadening is observed for [C_6DBU][OH]-rich condition which indicates the presence of aggregates of various sizes.

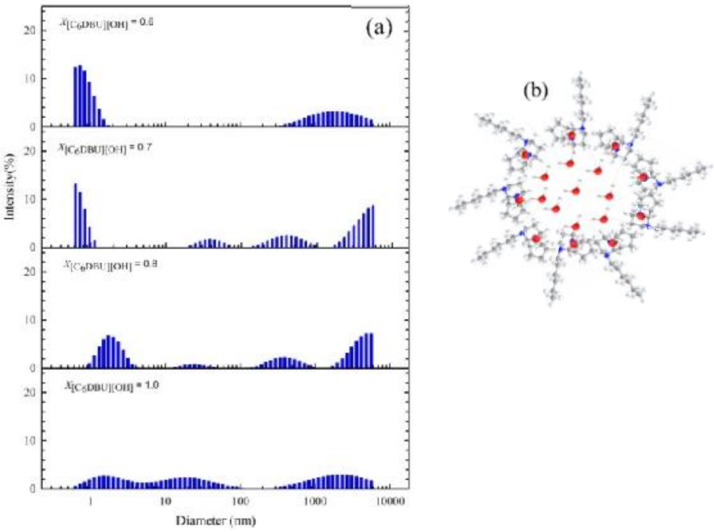

Figure 3.13.(a) Particle size distribution in [C_6DBU][OH]-water binary systems at $X_{[C_6\text{DBU}][\text{OH}]}$ = 0.6 to 1.0, (b) Reverse micelle-like aggregation of [C_6DBU][OH] in [C_6DBU][OH]-rich region.

These polydispersity results from the association of smaller aggregates with the increased amount of [C_6DBU][OH] in the binary systems with water.

The variation of average aggregate size with temperature at $X_{[C_6\mathrm{DBU}][\mathrm{OH}]}$ = 0.5 is shown in Figure 3.14. All systems showed a similar trend. The aggregate size decreases with increasing temperature. This may due to the breaking of vesicle-like aggregation with increasing temperature.

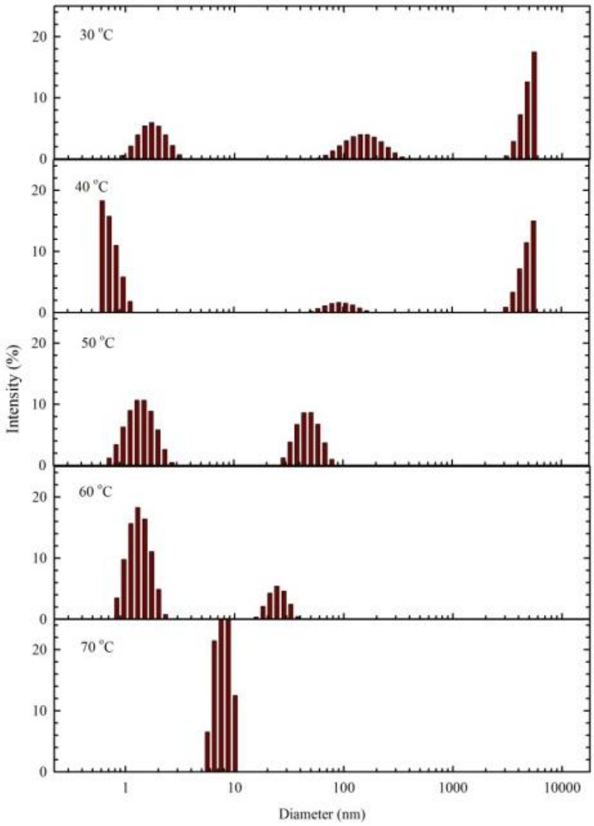

Figure 3.14. Particle size distribution of [C_6DBU][OH]-water binary system at $X_{[C_6\mathrm{DBU}][\mathrm{OH}]}$ = 0.5 by DLS at different temperatures.

3.3.6.3. TG-DT Analysis of [C_6DBU][OH] and its Binary Systems with Water

Thermal properties of [C_6DBU][OH] and its binary systems with water were studied using TG-DTA. Figure 3.15(a) shows TG curves for [C_6DBU][OH] and its binary systems with water. The binary systems showed progressive loss in weight due to the presence of free water.

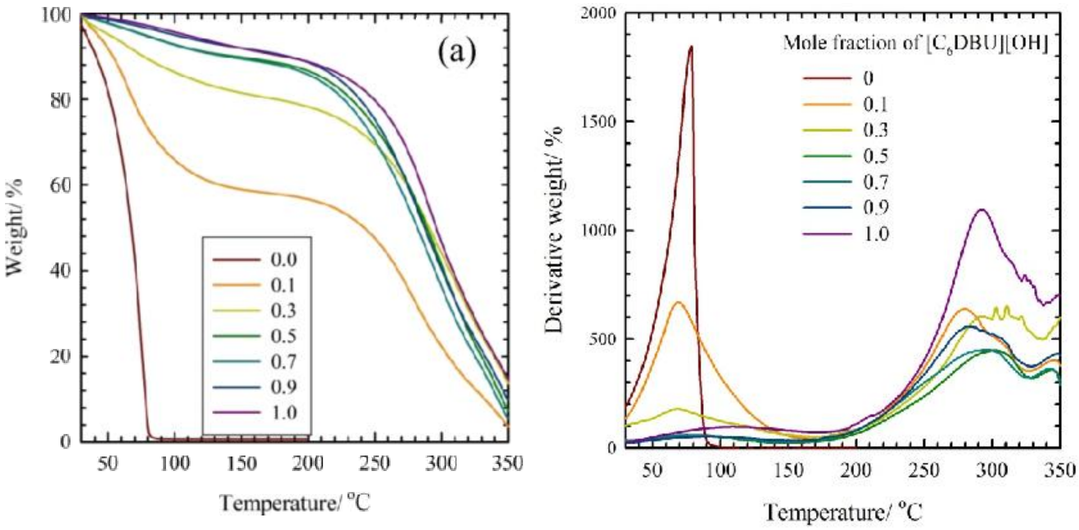

Figure 3.15. Thermogravimetric analysis of [C_6DBU][OH] and its binary systems with water at heating rate of 10 ^{o}C min^{-1}under N_2 atmosphere; (a) TG curve and (b) DTG curve.

The DTG curve in Figure 3.15 (b) shows that the binary systems of [C_6DBU][OH] with water ($X_{[C_6DBU][OH]}$< 0.5) undergo two-step weight loss processes. These are due to the evaporation of free water below 100 ^{o}C and the degradation of the residual system of [C_6DBU][OH] with water above 200 ^{o}C.

If the interaction of the water molecule with the anion of IL is considered, it is suggested that the miscibilityof an IL with water is mostly determined by theassociated anion [49, 55-56]. The crystallographic and spectroscopic data revealed that the anion might be involved in an attractive hydrogen-bonding interaction [57]. There are a variety of ways in which the water molecules can interact with the anion species. Different hydrogenbonded complexes of water molecules with the anions wereconstructed and pre-optimized using density functional theory at the B3LYP/ 6-31G* level which suggested that they are true minimum energy structures. The large negative interaction energies of these complexes indicate that they are stable structures [58].

The experimental results show that the hydrophobicILs can also absorbsome water from air [49]. The cations are in fact responsible for this.There are different interaction patterns between the cation and water molecule and the interaction between the cation and the water is secondary.The NMR spectral resultsindicate that the water moleculecould form hydrogen bonds with the cation involving Imidazolium ring protons H2, H4, and H5 [59].All three C-H can form stable complexes with the water molecules. The presence of the two N atoms and the positive charge in theimidazolium ring makes an acidic C2-H bond between them.Therefore, the [C2-H---O] interaction possesses a more negative interaction energy [58].

Though [C_6DBU][OH] is hydrophobic in nature, the attractive hydrogen-bonding of anion may lead to the formation ofcomplex structure with water. In the cation, there are two N-atoms and the positive charge in the DBU ring makes the C2-H more acidic which creates a suitable environment to form hydrogen bonds with water molecules.

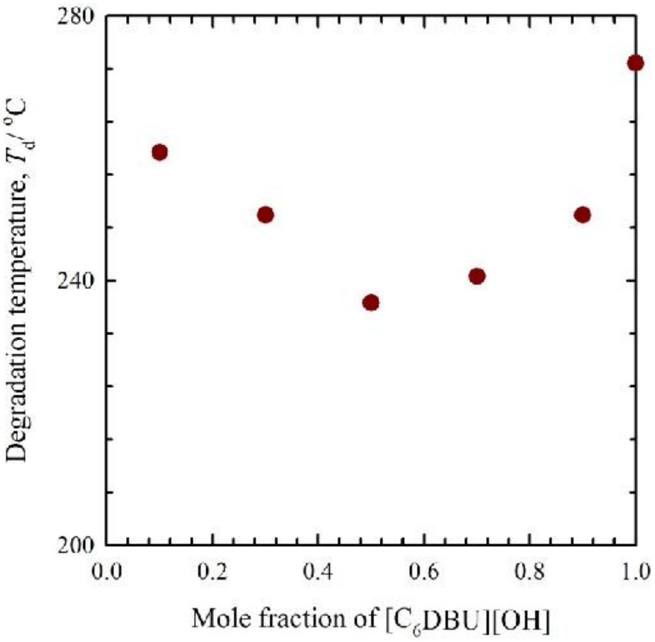

Figure 3.16. The variation of degradation temperature with mole fraction of [C_6DBU][OH] for the binary systems of [C_6DBU][OH] with water.

The curve (Figure 3.16)at $X_{[C_6DBU][OH]}$< 0.5 showed decrease in the degradation temperature with addition of [C_6DBU][OH]. This is due to the fact thatwith decrease inwater content,the interaction between water and cation decreases. Moreover with decreasing water degradation temperature decreases, which is possibly due to decrease in the aggregation (micelle-like) of [C_6DBU][OH] and water.

At $X_{[C_6DBU][OH]}>$ 0.5, the curvesin Figure 3.16 exhibited increasing degradation temperature with increasing concentration of [C_6DBU][OH]. This may due to the formation of reverse micelle-like aggregation in thissurfactant-like hydrophobic IL, [C_6DBU][OH]. But the curve at $X_{[C_6DBU][OH]}$ = 0.5 showed the lowest degradation temperature. This may possibly due to the transition between micelle-like aggregations to reverse micelle-like aggregations.

The DTA (Figure 3.17) curve for the system also exhibited two endothermic peaks. The sharp endothermic peak indicates phase changes (evaporation) of unreacted water below 100 °C. The broad endothermic peak below 100 °Ccorrespond to evaporation of water bound to [C_6DBU][OH] and the broad endothermic peak at higher temperature (near 300 °C)is due to the degradation of [C_6DBU][OH].

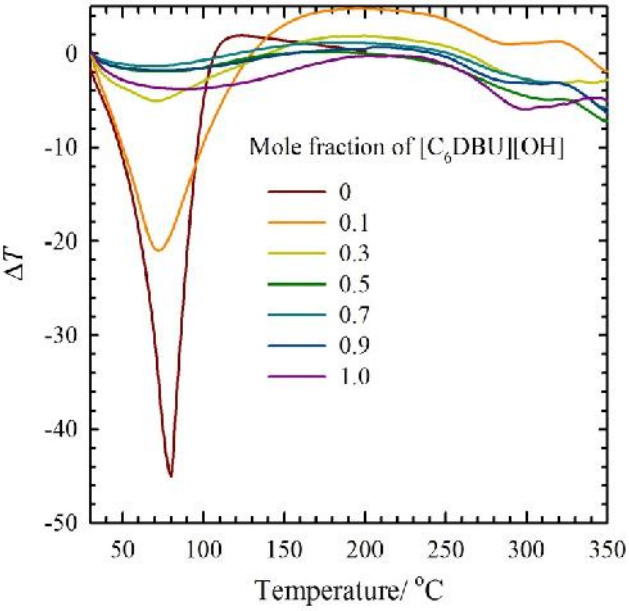

Figure 3.17. DTA curve for [C_6DBU][OH] and its binary systems with water.

3.3.6.4. Impedance Spectroscopic Analysis

Figure 3.18. shows the Nyquist plot and a suitable circuit for [C_6DBU][OH] and the binary mixtures of C_6[DBU][OH] with water and DBU. The Nyquist plot of impedance gives information about the electrochemical impedance behavior. The real component (Z′) represents the Ohmic properties. On the other hand, the imaginary component (Z″) stands for the capacitive properties.

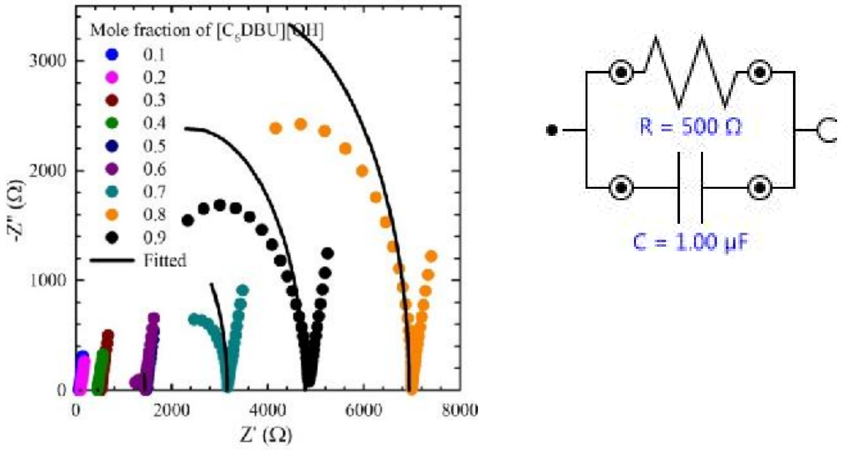

Figure 3.18. Impedance spectroscopic analysis for [C_6DBU][OH] and its binary systems with water.

The measurements were carried out in the frequency range of 100 Hz to 1 MHz. Solution resistance (R_s) of the system was obtained from the intercepts at the highest frequency of the curves on the real axis. The Nyquist plots were analyzed by fitting the experimental impedance spectra to an equivalent electrical circuit. Thus, a suitable circuit for the systems has been schematically demonstrated in Figure 3.18. It is seen that semicircle is obtained at high frequency and a straight line is observed at low frequency regions. The conductivityobserved for [C_6DBU][OH] and its binary systems with water are given in the Table 3.6.

Ionic conductivities of the binary systems of [C_6DBU][OH] with water are graphically represented in Figure 3.19. It is remarkable that ionic conductivities of the mixtures are higher than the pristine compounds (pure water and pure [C_6DBU][OH]) [60-61]. The plot can be divided in two parts which are separated by the maximum of the graphs. In fact, ionic conductivity of ILs can be increased by adding a polar molecular co-solvent, such as water, alcohols, acetonitrile, ketones, etc.[62-67]. A dependence of ionicconductivity on solvent molar fraction exhibits a maximum which is located below 20 mol % IL [68-70].

Table 3.6. Conductivity of binary mixtures of [C_6DBU][OH] and water

Mole fraction of DBU, X_{DBU}	**Specific conductivity (mS cm^{-1})**
0	5.8
0.1	13704.5
0.2	10079.2
0.3	1806.9
0.4	2104.1
0.5	653.6
0.6	676.2
0.7	304.7
0.8	138.4
0.9	201
1.0	35.87

At high IL concentrations, ionic conductivities have lower values due to the fact thatthe viscositiesof the mixtures arelarge. When small amountof water isadded the viscosity decreases and the mobility of the charge carriers rises, consequently the ionic conductivity continuously increases until it reaches its maximum. After the maximum, ionic conductivity decreases upon addition of further water. In mixtures with low IL concentration the number of charge carriers was reported to besmaller since aggregation becomes the dominant effect in this region [71-72].

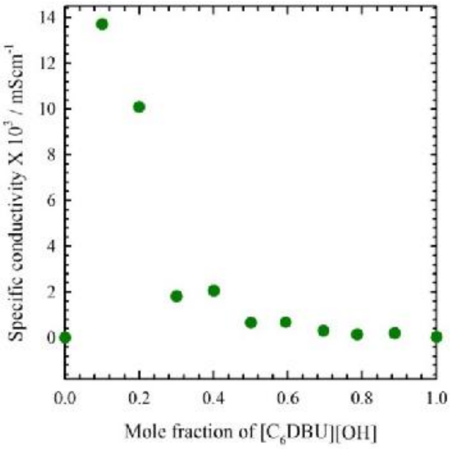

Figure 3.19. Change in conductivity with mole fraction of [C_6DBU][OH] and its binary systems with water.

The ionic conductivity (Λ) and viscosity (η)are related to each other through the Walden rule [73] as noted in Chapter 1-

$\Lambda.\eta$ = constant (3.2)

The equation is derived from the Stokes-Einstein equation and the Nernst-Einstein equation and is mainly applied to solutions, even though it can be applied to pure ILs [74]. Depending on the position in the Walden plot, binary systems are defined in different categories. The position of the ideal line corresponds to a 0.01 M KCl aqueous solution which is fully dissociated and its ions have the same mobility. Thus Walden plot appears as a qualitative tool for evaluating ionicity in ionic liquids.Most ILs fall below the line, suggesting that full ionization is not complete in those cases. Ionic liquids lie as close to the ideal line, are considered to have high ionicity [75].

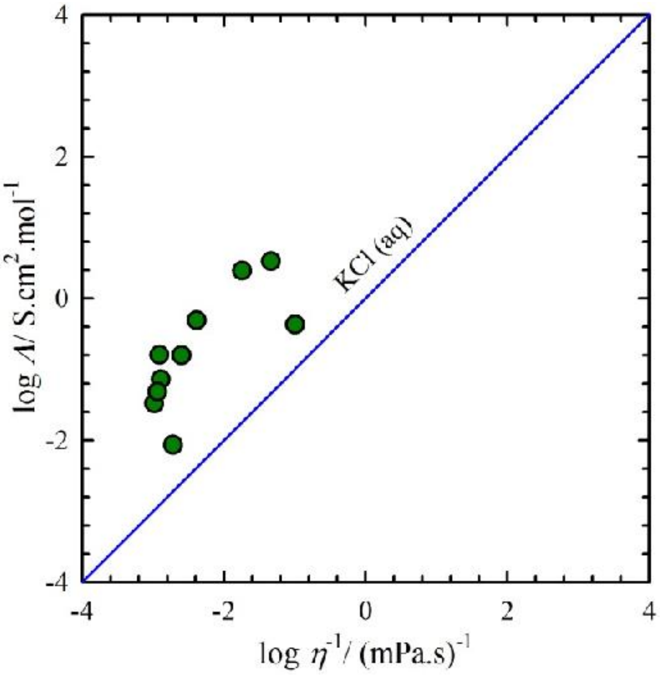

Figure 3.20. Walden plot for binary systems of [C$_6$DBU][OH] with water at 298 K. Walden plot for binary systems of [C$_6$DBU][OH] with water at 298 K (Figure 3.20) shows that all the mixtures analyzed are located over the ideal line and close to the line. Thus they showedgood ionicity.

3.3.6.5. Density

Figure 3.21. shows the effect of concentration of water on the density of the AIL, [C_6DBU][OH] in the temperature range from 293 K to 318 K. The density decreases as the temperature is increased (Figure 3.21 b). But the change in density with mole fraction of [C_6DBU][OH] was rather scattered (Figure 3.21 a).

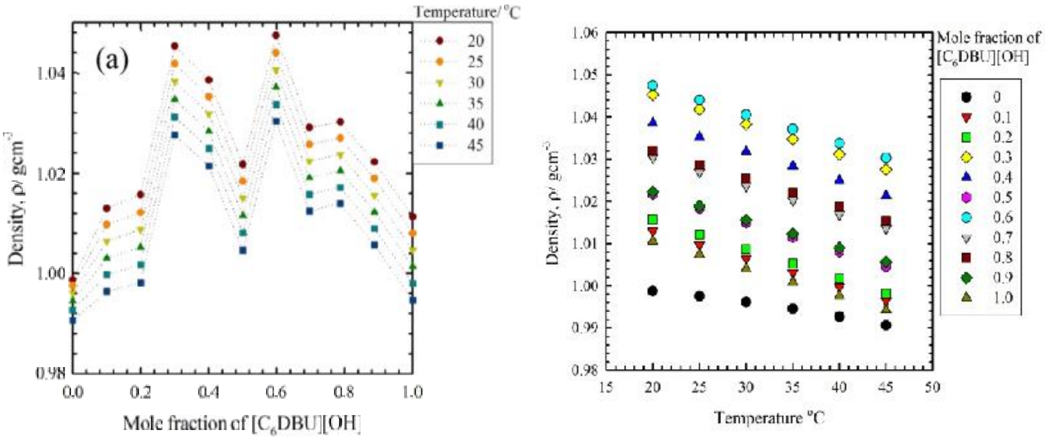

Figure 3.21. Change in density with increase in (a) mole fraction of [C_6DBU][OH] and (b) temperature.

To investigate the molecular interaction between water and [C_6DBU][OH] excess molar volume, V_m^E, has been evaluated from experimental density using equation (3.3). The excess molar volume, V_m^E, and many other thermodynamic properties of a binary liquid mixture prepared with chemical substances1 and 2 at fixed temperature *T* and pressure *p*, are frequently described using the Redlich-Kister equation (3.4). Its original form leads to

$$V_m^E = \frac{x_1M_1 + x_2M_2}{\rho_m} - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right) \qquad (3.3)$$

Wherex_1 and x_2 are the mole fractions calculated from mass fractions, M_1 and M_2 are molar masses, ρ_1 and ρ_2 are densities of pure components 1 and 2 respectively, ρ_m is the density of the mixture.

$$\Delta Y = x_1x_2 \sum_{k=1}^{n} A_k\,(2x_1 - 1)^{k-1} \qquad (3.4)$$

wherex_1 and x_2 are mole fractions, A_k ($k = 0 – n$) are adjustable coefficients and n is the order of the polynomial expansion.

Figure 3.22 shows the fitted curve of excess molar volume of the binary systems of water and [C_6DBU][OH] at T = 293, 298, 303, 308, 313, and 318 K. The excess molar volume is negative over the entire composition range for the system. The negative excess molar volume can be attributed to the strong interactions between unlike molecules through hydrogen bonding and ion-dipole interaction.

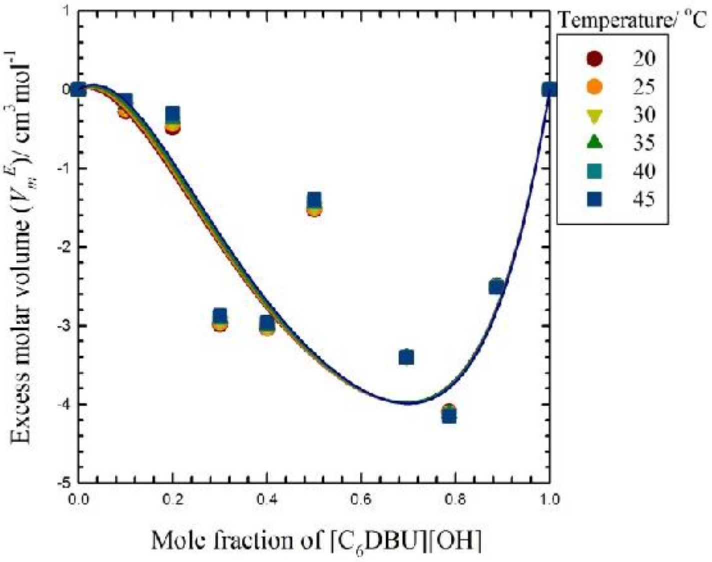

Figure 3.22. Excess molar volume with mole fraction of [C_6DBU][OH] in its binary systems with water.

3.3.6.6. Viscosity

Viscosity can provide an important macroscopic property of ILs and reflects the microscopic characteristics determined by numerous interrelated parameters like molar mass, shape and size of the ions, and intermolecular and inter-ionic forces such as Coulombic interactions, hydrogen bonding or van der Waals interactions.

To investigate the molecular interaction between water and [C_6DBU][OH] viscosity deviation, $\Delta\eta$, has been evaluated from experimental viscosity using equation (3.5).

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \tag{3.5}$$

where x_1 and x_2 are the mole fractions calculated from mass fractions, η_1 and η_2 are the viscosities of pure components 1 and 2 respectively, η_m is the viscosity of the mixture.

Figure 3.23. shows the effect of concentration of water on the dynamic viscosity of the aprotic and hydrophobic IL, [C$_6$DBU][OH] in the temperature range of 293 K to 318 K. The viscositydecreases as the temperature is increased. But the viscosityincreases with the increasing mole fraction of [C$_6$DBU][OH] upto $X_{[C_6\mathrm{DBU}][\mathrm{OH}]}$ = 0.8 and then decreases to pure [C$_6$DBU][OH]. The viscosity of ILswas reported to increase with the length of alkyl chain [76].It is expected that the overall strong electrostatic interaction weakens with an increase in side chain length. However, contribution of weaker and non-associating, dispersion forces also enhances the viscosity. The larger non-polar part of the cations results in higher viscosity. This is due to the fact that the increase in the van der Waal's interactions due to the presence of a long alkyl chain leads to higher viscosities [77]. Sometimes hydrogen bonding suppression, due to the absence of acidic proton in the cation, lowers viscosity [78]. With the addition of water the viscosity of [C$_6$DBU][OH] reduces. Water may therefore be termed as a viscosity reducer for ILs. Thus, the hydrophobic ILs which are immiscible with water, are also affected by the presence of small amounts of water [79].

The presence of aggregates in pure ILs has been supported by computer simulations suggesting the aggregation of alkyl tails through van der Waals attraction. On the other hand, the ionic head groups and the anions are distributed more homogeneously forming a continuous network of ionic channels. Upon addition of water in pure ILs, these aggregates begin to dissociate into free cations and anions. Cations and anions are free in the water-rich mixtures than in the water-poor regions. This is probably the reason of sharp decline in the viscosity of pure ILs when water is added. Water molecules with high relative permittivity weaken electrostatic forces operating between ions.

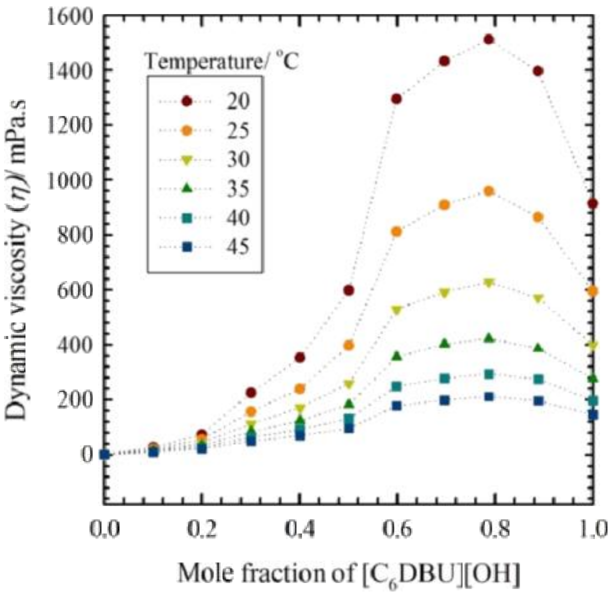

Figure 3.23. Variation of dynamic viscosity with mole fraction of [C_6DBU][OH] for its binary systems with water.

It has been reported that the temperature affects the viscosity of both pure ILs as well as ILs saturated with water [80]. The effect of water on the viscosity of pure IL, [C_6DBU][OH] has been found to be less prominent at higher temperatures (Figure 3.24).

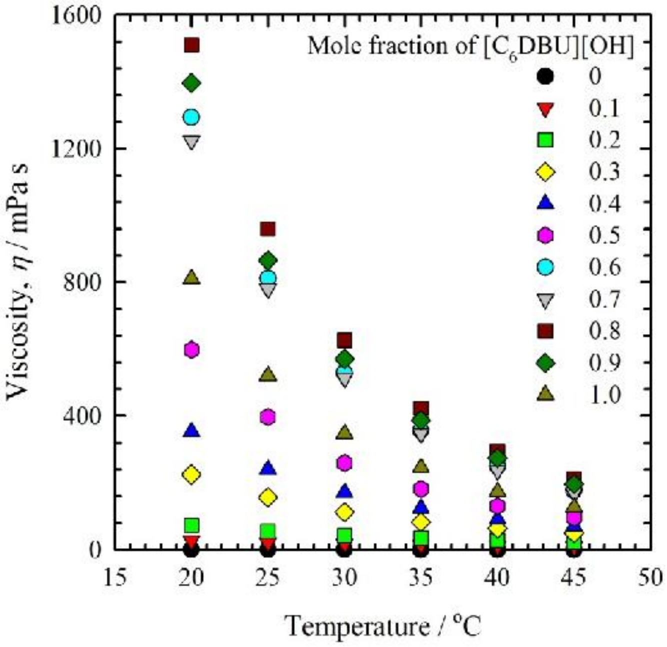

Figure 3.24. Change in viscosity with temperature for [C_6DBU][OH] and its binary mixtures with water.

Figure 3.25. showsviscosity deviation of the binary systems of water and [C$_6$DBU][OH] at T = 293, 298, 303, 308, 313 and 318 K.

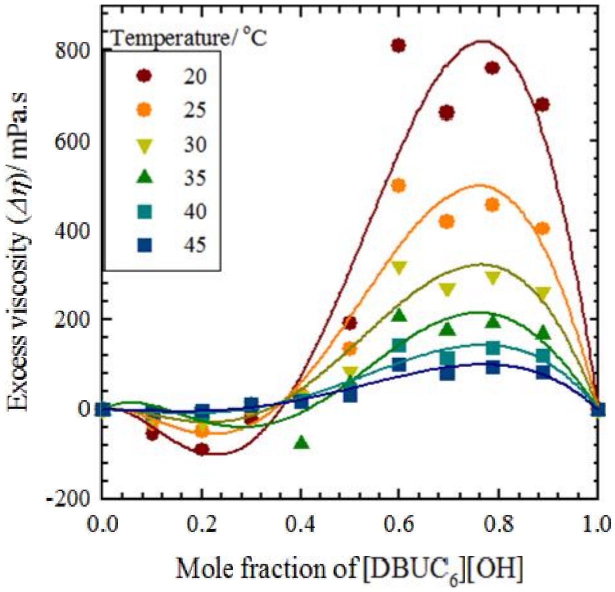

Figure 3.25. Excess viscosity as a function of mole fraction of [C$_6$DBU][OH].

For viscosity deviations, the excess viscosity is negative at $X_{[C_6DBU][OH]} < 0.5$ and positive at $X_{[C_6DBU][OH]} > 0.5$ (Figure 3.25). The negative values of viscosity deviation of the system suggested that viscosities of associates formed between unlike molecules are relatively less than those of pure components. The $\Delta\eta$ decrease as the number and strength of H-bonds are decreased. This indicates that H-bonding in the IL is more dominant in determining the viscosities than in typical polar protic molecular solvents [81]. The negative $\Delta\eta$ obtained for this system suggests that there may be a reduction in the number and strength of H-bonds upon mixing. It should be noted that the negative viscosity deviation may also occur where dispersion forces are dominated for the systems having different molecular sizes [82].

The positive $\Delta\eta$ are discussed in term of ion dipole interaction between the cation of the ILs and molecular solvents. The positive values of viscosity deviation of the system suggested that viscosities of associates formed between unlike molecules are relatively more than those of pure components. The $\Delta\eta$ increases as the number and strength of H-bonds are increased.

3.3.6.7. Refractive Index (*n*)

The refractive index or index of refraction,*n* of a material is a dimensionless number that describes how light propagates through that medium. It is defined as

$$n = \frac{c}{v} \tag{3.6}$$

where *c* is the speed of light in vacuum and *v* is the phase velocity of light in the medium. For example, the refractive index of water is 1.333, meaning that light travels 1.333 times faster in a vacuum than it does in water. The refractive index determines how much light is bent, or refracted, when entering a material.

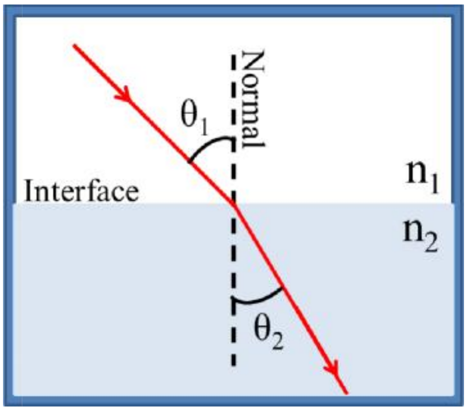

Figure 3.26. Refraction of light between two different media.

The refractive index determines how much light is bent, or refracted when the light passes from one medium to another medium (Figure 3.26). The refractive index (n_1 and n_2) is the ratio of angle of incident (θ_1)light to the angle of refraction (θ_2) and it is described by

$$n_1 \sin\theta_1 = n_2 \sin \theta_2 \tag{3.7}$$

If the light is passed from less dense to denser medium it is refracted toward normal to form angle of refraction which is less than angle of incident.

Figure 3.27shows the change in refractive index with mole fraction of [C_6DBU][OH] for [C_6DBU][OH] and its binary systems with water at different temperatures. It has been shown that the refractive index of [C_6DBU][OH] and its binary systems gradually increase with increasing mole fraction of [C_6DBU][OH].

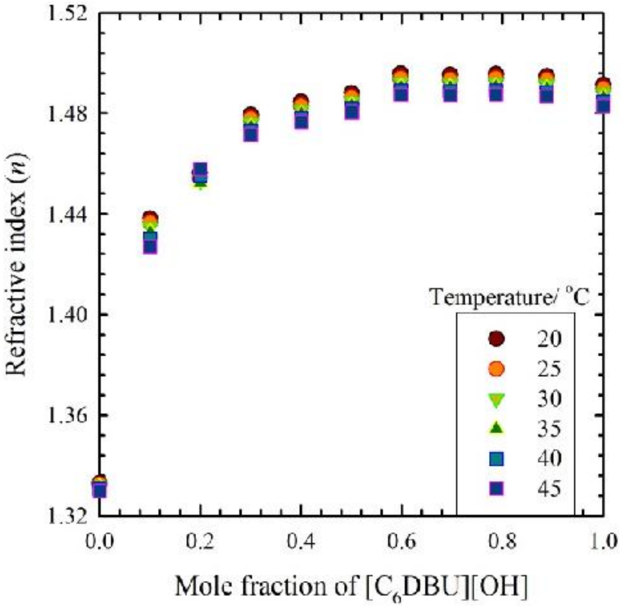

Figure 3.27. Variation of refractive index with mole fraction of [C_6DBU][OH] for [C_6DBU][OH] and its binary systems with water.

The refractive index can provide information about the behavior of light. When light passes through the different substances its velocity decreases withincreasing refractive index of these substances. The light is an electromagnetic wave and it's phase velocity is lowered in a material since the electric field creates a disturbance in the charges of atoms of the material. As the binary systems of [C_6DBU][OH] with water contain ionic species (cations and anions) the electric field of these ions will interact with the electric field of the light. With increasing the mole fraction of [C_6DBU][OH] in the binary systems with water, the interaction with the light increases. Thus, angle of refraction becomes smaller compared to the angle of incident and RI of the systems increases.Also in the most substrates, the refractive index decreases by increasing of the temperature (Figure 3.28). The interaction between molecules decreases as the temperature increases [83].

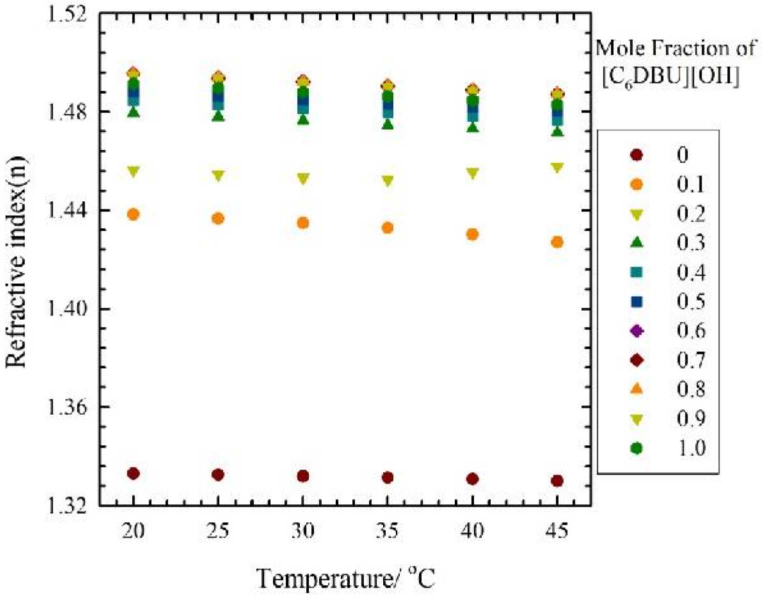

Figure 3.28. Refractive index as a function of temperature for [C$_6$DBU][OH] and its binary systems with water.

From the experimental data of refractive index (n), excess refractive index (Δn) was calculated using equation-3.8 and fitted with Redlich-Kisterpolynomial equation (Figure 3.29).

$$\Delta n = n - (x_1 n_1 + x_2 n_2) \qquad (3.8)$$

The excess refractive index for [C$_6$DBU][OH] and its binary systems with water is positive over the entire composition range. With the increasing mole fraction of [C$_6$DBU][OH] in its binary systems with water the refractive index increases. This is due to the fact that with increasing mole fraction of [C$_6$DBU][OH] the density of the medium increases (Figure 3.21) and the light is refracted toward normal (axis perpendicular to the interfacial plane between the two media). The angle of refraction became smaller and the light passing through the medium becomes slower than that in the air. This is due to the interaction between the light and the different particles present in the medium.Generally refractive indices increase withincreasing density of the medium [84].

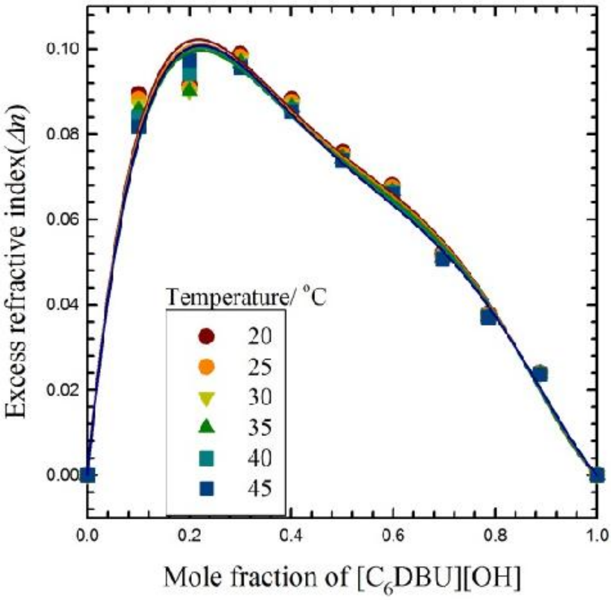

Figure 3.29. Change in excess refractive index with mole fraction of [C_6DBU][OH] for [C_6DBU][OH] and its binary systems with water.

3.3.6.8. Polarity Measurement by Solvatochromic Method

Solvent polarity, as recommended by the IUPAC, isthe sum of all possible, non-specific and specific, intermolecular interactions between the solute ions or molecules and solvent molecules, excluding such interactions leading to definite chemical alterations of the ions or molecules of the solute[85]. Sincethese manifold intermolecular forcesinclude Coulomb interactions, directional interactions betweendipoles (and quadrupoles or higher multipole moments),inductive, dispersive, hydrogen-bonding, and charge-transferforces, as well as solvophobic interactions, not surprisinglysingle macroscopic physical parameters (*e.g.*, dielectric constants,dipole moments, refractive indices) or functions thereofcannot adequately describe solvent polarity. This inadequacy,coupled with the lack of comprehensive theoretical expressions,has led to the introduction of empirical solvent polarity scalesbased on solvent interactions with a reference solute [86].

But the direct measurement of dielectric constant of IL-based binary systems is not possible because of the high conductivity. Therefore, an alternative method, solvatochromic methodusing Reichardt'spyridinium*N*-phenoxidebetaine dye (RBD) as solvatochromic probe (Figure 3.30), has been useful for estimation of polarity for IL and IL-based systems.

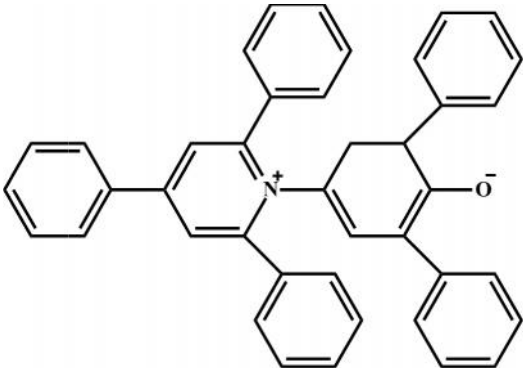

Figure 3.30. Structure of Reichardt'spyridinium*N*-phenoxidebetaine dye (RBD).

The $E_T(30)$ scale, based on the large negative solvatochromicshift of the long-wavelength intramolecularπ–π* chargetransfer(CT) absorption band of Reichardt'spyridinium*N*-phenoxidebetaine dye (historically, the dye numbered 30 in thefirst publication by Dimroth, Reichardt*et al.*), is one of the mostpopular empirical solvent polarity scales which is based onequation (3.9)

$$E_T(30)(kcal/mol) = 28591 / \lambda_{max} \quad (3.9)$$

The λ_{max} i.e. the wavelengthmaximum of the charge transfer band has been used to compare the polarity of differentmedia based on the empirical scale of solvent polarity, the $E_T(30)$ scale [87].Shift in wavelength corresponding to absorption maximum (λ_{max}) of RBD in UV-visible absorption spectrum has been verified for water, [C$_6$DBU][OH], and its binary systems with water. The concentration of RBD solutions in these solvents was 1.9× 10^{-4} M. Figure 3.31 shows the absorption spectra of RBD in different solvents. The absorption maxima for the band 400-700 nm changed with change in the solvents.

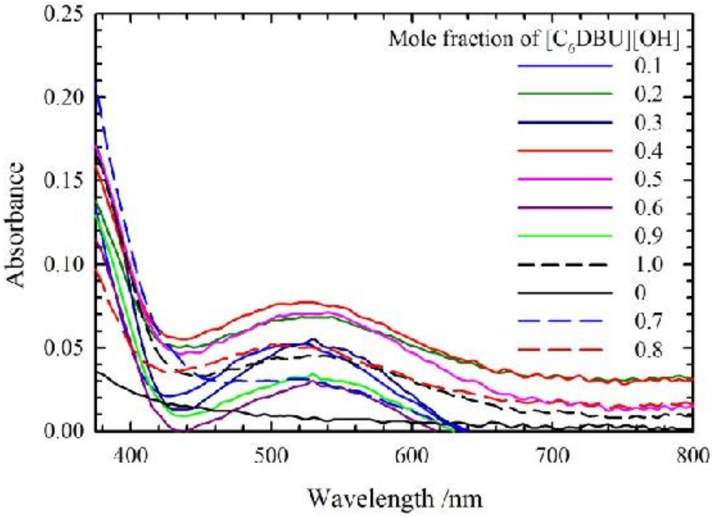

Figure 3.31. Absorption spectra of 1.0 x 10^{-4} M RBD in different binary systems of [C_6DBU][OH] with water.

According to $E_T(30)$ scale the value of $E_T(30)$ increases with increasing solvent polarity. The $E_T(30)$ for different solvents has been evaluated and plotted against mole fraction of [C_6DBU][OH] (Figure 3.32).

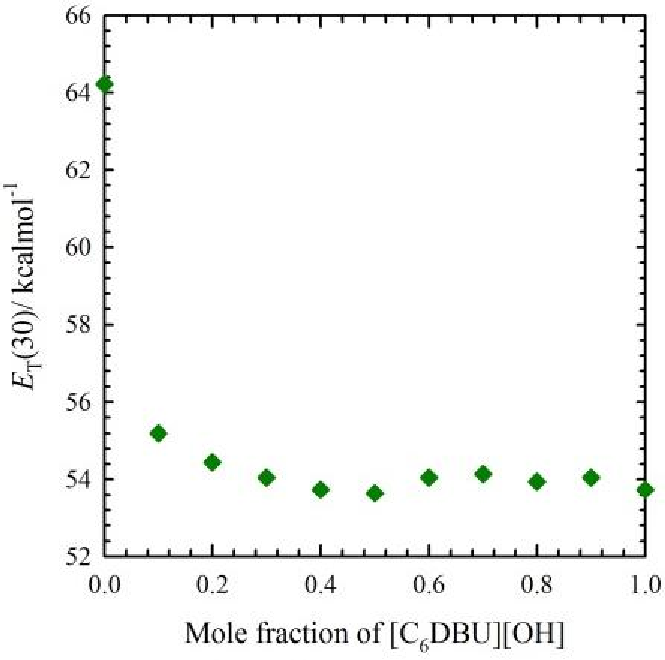

Figure 3.32. Variation of $E_T(30)$ with mole fraction of [C_6DBU][OH] for the binary systems of [C_6DBU][OH] with water.

The results in Figure 3.32 indicate higher $E_T(30)$ values for polar solvent water(i.e.lower λ_{max}) compared to less polar pure IL(i.e. higher λ_{max}). Thisagrees well with the concept of solvatochromism of RBD. If the ground state is morepolar than excited state it is better stabilized by polar solvent and its energy is lowered.Therefore, the energy gap between ground state and excited state becomes larger (Figure 3.33).Thus the charge transfer transition will occur at a shorter wavelength. Consequently, therewill be hypsochromic shift (blue shift) with increasing solvent polarity.

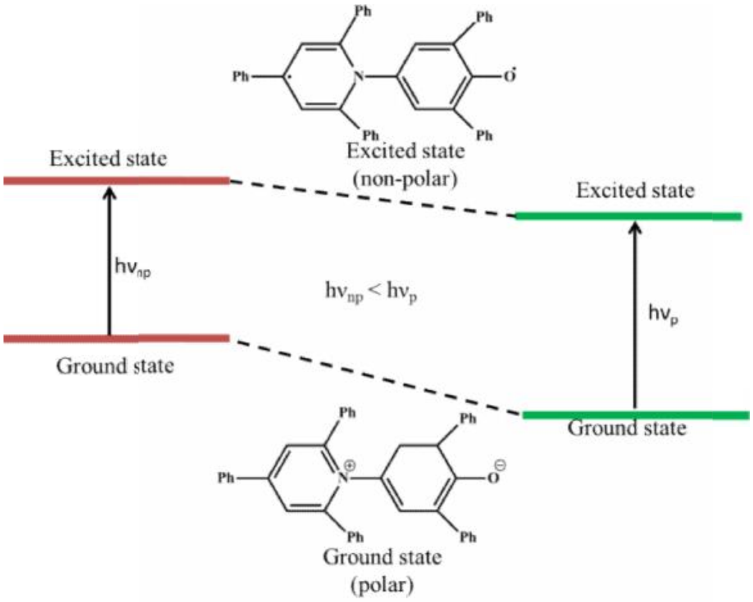

Figure 3.33. Solvatochromic shift of RBD.

Since RBD is polar in ground state, it follows the negative solvatochromism and blueshift occurs. Thus water is the most polar and pure IL is the least polar among the systemsstudied in this work. Polarity scalebased on $E_T(30)$ values may therefore serve the purpose of estimation of polarity of awide variety of solvents and in fact, this is considered to be reliable method for thedetermination of solvent polarity of most of the solvents.

Molecular electronic transitions take place when electrons in a molecule are excited from one energy level to a higher energy level. The energy change associated with this transition provides information on the structure of a molecule and determines many molecular properties such as color. The molar transition energy for charge transfer absorption [*i.e.*, $E_T(30)$] isinfluenced approximately equally by the solvent hydrogenbonddonating (HBD) ability and the solvent polarizability. TheE_T(30) is a good indicator of the HBD ability of ring hydrogenof the cation to the phenoxide group on the RBD [88]. TheE_T(30) value in this work shows that added water has significant effect on the polarity of the IL and can enhance the polarity of the binary systems than the pure IL.

3.4. Conclusions

Physicochemical properties of pure ILs ([DBU][OH], [DBU][CH_3COO], and [C_6DBU][OH]) and their binary systems with molecular solvents (water, acetic acid, and DBU) change with composition of these systems. PureILs have variety of attractive interactions like van der Waals force, dispersion, Coulombic, hydrogen bonding, etc. The lower thermal stability of the binary systems of the prepared ILsindicates the disturbance of Coulombic interactions between ions of ILs by the formation of hydrogen bonding and ion-dipole interactionwith solvent molecules. The specific conductivities of the binary systems of the PILs ([DBU][OH] and [DBU][CH_3COO])are high. Formation of hydrogen bonding between the ions and solvent molecules causes disruption of the electrostatic interaction between the ions ofPILs. Upon addition of molecular solvents like water to AIL ([C_6DBU][OH]), hydrogen bonding and ion-dipole interactions induce strong association or self-assembly.The aggregation behavior of the AIL depends on the specific interactions in the binary systems with water to give variation in physicochemical properties.

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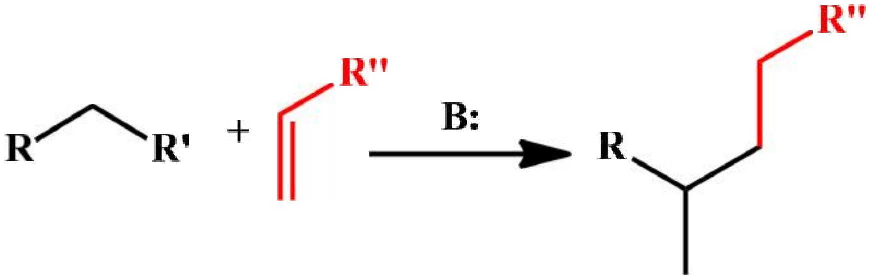
Abstract

Kinetics of Michael addition reaction between acetylacetone and 2-cyclohexene-1-onewas investigated using protic ionic liquids (PILs) ([DBU][OH] and [DBU][CH_3COO]),aprotic ionic liquid (AIL) ([C_6DBU][OH]) and the binary systems of ILswith molecular solvents, water, DBU, and acetic acidover a wide range of compositionas catalyst in absence of organic solvents. Thin layer chromatography (TLC) technique has been used to determine the reaction completion time using mixed solventas the mobile phase. The reaction was also investigated in presence of the bases, DBU and NaOH. The catalytic performances of the organic base and ILs have been compared and the role of bases and ILs in the mechanism of the reaction has been explained at the molecular level. To investigate the performance of catalytic activity of the ILs and their binary systems the reaction was carried out in presence of NaOH with different concentrations of ILs. The product of the reaction was characterized by spectral(FTIR, ^{1}H NMR, ^{13}C NMR) and chemical analyses. The role of the ILs and their binary mixtures as catalyst and reaction medium has been discussed.

4.1. Introduction

The Michael reaction or Michael addition is the nucleophilic addition of a carbanion or another nucleophile to an α,β-unsaturated carbonyl compound(Scheme 4.1). It belongs to the larger class of conjugate additions. This is one of the most useful methods for the formation of C-C bonds.



Scheme 4.1. General equation of Michael addition reaction.

In scheme 4.1, the R and Ŕsubstituents on the nucleophile (Michael donor) are electron-withdrawing groups such as acyl and cyano which make the methylene hydrogen acidic. This methylene, -CH_2-, forms the carbanion on reaction with base

B**:**. The substituent on the activated alkene, also called a Michael acceptor, is usually a ketone making it an enone.It can also be a nitro group. Classical examples of the Michael reactions are the reaction between diethyl malonate (Michael donor) and diethyl fumarate (Michael acceptor),mesityl oxide and diethyl malonate, diethyl malonate and methyl crotonate, 2-nitropropane and methyl acrylate, ethyl phenylcyanoacetate and acrylonitrile and nitropropane and methyl vinyl ketone.

The Michael addition reaction is generally catalyzed by bases and sometimes acids. The procedure requires large volume of organic solvents as reaction medium, high temperature and long reaction time. The product obtained is separated from the reaction mixture by solvent extraction which needs volatile organic solvent or mixture of solvents. The product separation is not easy as it contains some other undesired products. If the product appeared as solid then the isolation of product becomes easy. Solid organic compounds when isolated from organic reaction mixtures are seldom pure; they are usually contaminated with small amounts of other compounds that are produced along with the desired product. The purification of impure compounds is affected by crystallization from suitable solvents or mixture of solvents. The crystallization is based on their solubility in a given solvent or mixture of solvents. The crystallization process consists of:

(1) dissolving the impure substance in some suitable solvent at or near the boiling point;
(2) filtering the hot solution from particles of insoluble material and dust;
(3) allowing the hot solution to cool thus causing the dissolved substance to crystallize out; and
(4) separating the crystals from the supernatant solution (or mother liquor).

The resulting solid after drying is tested for purity.

The most desirable characteristics of a solvent for recrystallization are as follows:

(a) A high solvent power for the substance to be purified at elevated temperatures and a comparatively low solvent power at laboratory temperature or below,
(b)should dissolve the impurities readily or to only a very small extent,
(c) should yield well-formed crystals of the purified compound, and
(d) must be capable of easy removal from the crystals of the purified compound.

It is assumed that the solvent does not react chemically with the substance to be purified. If two or more solvents appear to be equally suitable for recrystallization, the final selection will depend upon such factors as ease of manipulation, toxicity, flammability, and cost. The solvent extraction and recrystallization, both are applied to separate and purify the product from reaction mixture. These two processes can also be applied for isolation of the product in pure state from the reaction mixture of the Michael addition reaction.

The Michael addition is one of the most importantand useful C-C bond-forming reactions inorganic synthesis [1-2]. This reaction is an important reaction inorganic chemistry especially for the synthesis of cyclic/heterocyclic compounds containing carbonyl, amino carbonyl unit. Amino carbonylcompounds are useful building blocks for the moleculeswith applications in pharmaceuticals and fine chemicals [3-9]. They are versatile intermediates for the synthesis ofbiologically important natural products and antibiotics.Normally, this reaction iscatalyzed by strong bases [10, 11] or Lewis acids [12,13], which usually lead to undesirable sideproducts.However, the reactionis associated with disadvantages like drastic reaction conditionsand longer reaction times [14].ILs have attracted extensive interest as excellentalternatives to organic solvents, due to their favorableproperties. Recently, there were reports of Michaelreactions conducted in ILs [15]. However, these reactionswere unsuccessful in water alone, without using acid orbase catalyst. Combining the useful characteristics of solidacids and mineral acids, Brønsted acidic task-specific ionic liquids (TSILs) are designed to replace traditional mineralliquid acid catalysts, such as sulfuric acid and hydrochloricacid in chemical processes.

As solvents, ILs have found applications ina number of reactions [16-26]. Dupont et al. extensivelyreviewed the application of ILs as catalytic phase invarious organometallic reactions [27]. Catalytic applicationsof metal nanoparticles have been explored in ILmedia by Migowski and Dupont [28,29].

A basic IL, 1-butyl-3-methylimidazoliumhydroxide, [BMIm][OH] was reported to efficiently catalyze Michael addition reaction of active methylene compoundsto conjugated ketones, carboxylic esters and nitriles without requiring any othercatalyst and solvent[30, 31]. Moreover, these [BMIm][OH]catalyzedreactions showed many remarkable advantages,such as operational simplicity, short reactiontime, high yields of products, andgreenness of procedure, avoiding hazardous organicsolvents and toxic catalysts. This indicatesthat the ILs can be the betterand practical substitutes to the traditional catalysts.

Research to date includes various attempts to study the kinetics of Michael addition reaction catalyzed by pure ILs which is expensive and hazardous to handle and storage. There have been no reports on the investigation of the kinetics of the Michael addition reaction catalyzed by binary systems of ILs with molecular solvents. Theaim of the work has been the development of a simple general model for the Michaeladdition reaction of active methylene compoundsto better understand the role of the ILand its binary systems with molecular solvents in the reaction at the atomic and molecularlevels.

4.2. Experimental

4.2.1. Materials and Methods

All chemicals were of analytical grades and were used as received without further purification. Acetylacetone was from Scharlau (Spain), 2-cyclohexen-1-one and 1,8-diazabicyclo[5.4.0]undec-7-ene werefrom Sigma-Aldrich.Sodium hydroxide pellet was from Merck Chemicals Ltd. Chloroform was supplied from Fisher Scientific; while *n*-hexane and acetic acid were provided by RCI Labscan Ltd. (Thailand) and absolute ethanol was obtained from Merck Chemicals Ltd. (Germany). Ultrapure water (specific conductivity is 0.055 μS cm^{-1}) was used for the preparation of the binary mixtures of the IL. For this purpose HPLC grade water purification system from BOECO (Germany) was used.

For weighing the reactants, catalyst and components for preparing binary mixtures digital microbalance UBT-110 from UNILAB, USA was used.

The mixture of reactants and catalyst were magnetically stirred by amagnetic stirrer (79-1 Magnetism Heating Mixer)for proper and homogeneous mixing.

Thermogravimetric measurements and differential thermal analysis of the neat ILs and their binary mixtures with water and DBU were conducted under N_2 atmosphere (100 mL/min) with a Seiko Instruments TG-DTAnalyzer (TG DTA 6200). The accuracy of measurements of temperature and mass, were ± 1^oC and 10^{-3} mg respectively.

FTIR spectra were recorded by a Fourier transform spectrophotometer *Frontier*^{TM} by PerkinElmer in transmittance mode with 20 scans for each sample in KBr in the range between 400 and 4000 cm^{-1} at 4.0 cm^{-1} resolution.

NMR measurements were carried out on a BRUKER Ascend 400 spectrometerusing a frequency of 400 MHz at 298K using deuterated chloroform ($CDCl_3$) as solvent and tetramethylsilan (TMS) as the standard.

4.2.1.1. Kinetic Measurement

The kinetic measurements were carried out using TLC technique where commercially available aluminum TLC plates coated with silica gel 60 F_{254}were used as the stationary phase. Samples were applied on the plate by capillary tube. The spotted plate was developed in ascending process and mixture of chloroform and *n*-hexane (1:1 by volume) was used as the eluent. The spots on developed plates were located under UV lamp. In the initial stage of the reaction the reaction mixture contains both the reactants (Figure 4.1.a) and at the time when the reaction mixture contains no reactants is taken as the reaction completion time (Figure 4.1.b).

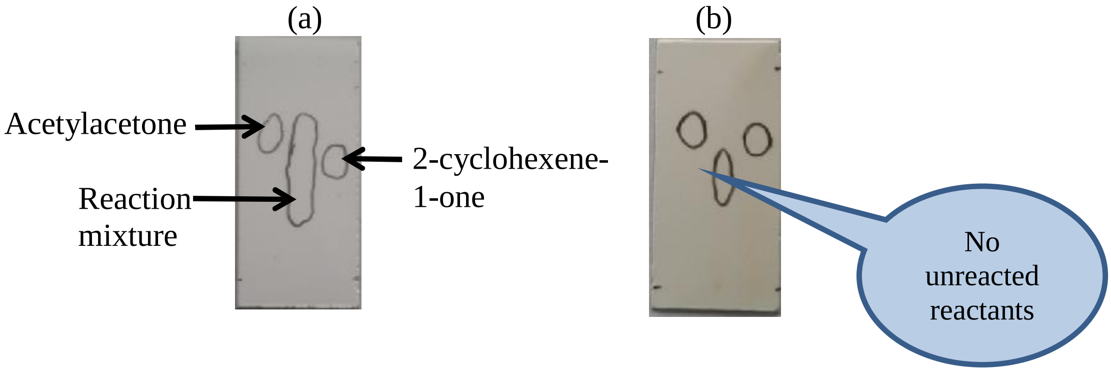
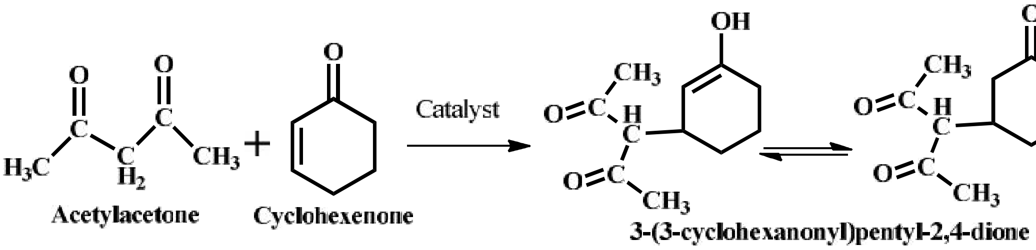


Figure 4.1. TLC plates (a) at initial stage and(b) after completion of the reaction.

4.2.1.2. Michael Addition Reaction of Acetylacetone and2-Cyclohexene-1-one

4.2.1.2.1. Reaction of Acetylacetone and 2-Cyclohexene-1-one in the Molar Ratio of 1:1 Catalyzed by Sodium Hydroxide in Absolute Ethanol at Room Temperature

A mixture of acetylacetone (5 mmol) and 2-cyclohexene-1-one (5 mmol) was taken in a test tube. A freshly prepared sodium hydroxide solution (0.5mmol, 0.2 g NaOH in 4 mL ethanol) was mixed in the test tube. The mixture was then stirred at room temperature (≈ 20 ^{o}C) with a magnetic stirrer. The progress of the reaction was followed by TLC on silica gel coated aluminum plates (eluting solvent- 1:1 by volume of chloroform and *n*-hexane). Crystalline product, 3-(3-cyclohexanonyl)pentyl-2,4-dione (Scheme 4.2), was obtained after solvent extraction where diethyl ether was used as the solvent. The product was characterized by chemical and FTIR, ^{1}H NMR, ^{13}C NMR spectral analyses.



Scheme 4.2. Michael addition reaction between acetylacetone and 2-cyclohexene-1-one.

4.2.1.2.2. Reaction of Acetylacetone and 2-Cyclohexene-1-one in the Molar Ratio of 1:1 Catalyzed by DBU, [DBUH][OH], [DBU][CH$_3$COO] and the Binary Systems of [DBU][OH] with Water and DBU and [DBU][CH$_3$COO] with Acetic Acid and DBUat Room Temperature

A mixture of acetylacetone (5 mmol) and 2-cyclohexene-1-one (5 mmol) was taken in a test tube. Pure DBU (0.5 mmol)/ [DBU][OH] (0.5 mmol)/binary systems of [DBU][OH] water and DBUand [DBU][CH$_3$COO] with acetic acid and DBUwas mixed in the test tube. The mixture was then stirred at room temperature (≈ 20 ^{o}C) with a magnetic stirrer. The progress of the reaction was followed by TLC on silica gel coated aluminum plates (eluting solvent- 1:1 by volume of chloroform and *n*-

hexane). Crystalline product was obtained after solvent extraction where diethyl ether was used as the solvent. The product was characterized by chemical and FTIR, ^{1}HNMR, ^{13}CNMR spectral analyses.

4.2.1.2.3. Enhancement of the Rate of the Reaction of Acetylacetone and 2-Cyclohexene-1-one in Presence of NaOH with Different Concentrations of PIL and AIL

A mixture of acetylacetone (5 mmol) and 2-cyclohexene-1-one (5 mmol) were taken in a test tube. Different concentrations (0.005, 0.05, and 0.5 mmol) of [DBU][OH]/[C_6DBU][OH] were added with a fixed concentration (0.005/0.05/0.5 mmol) of NaOH. The reaction was carried out at room temperature (≈20 ^oC) with a magnetic stirrer. The progress of the reaction was followed by TLC on silica gel coated aluminum plates (eluting solvent- 1:1 by volume of chloroform and *n*-hexane) and reaction completion time was recorded.

4.2.1.2.4. Reaction ofAcetylacetone and 2-Cyclohexene-1-one in the Molar Ratio of 1:1 Catalyzed by thePure andBinary Mixtures of [C_6DBU][OH] with H_2O at Room Temperature

A mixture of acetylacetone (5 mmol) and 2-cyclohexene-1-one (5 mmol) was taken in a test tube. Binary mixtures of [DBU][OH] with water were prepared at various molar ratio to have compositions varying from water-rich conditions to [C_6DBU][OH]-rich conditions. Michael addition reaction was carried out using these mixtures as catalyst. The reaction was carried out at room temperature (≈20 ^oC) with a magnetic stirrer. The progress of the reaction was followed by TLC on silica gel coated aluminum plates (eluting solvent- 1:1 by volume of chloroform and *n*-hexane) and reaction completion time was recorded.

4.2.1.2.5. Isolation of the Product of the Michael Addition Reaction

The product appeared as crystalline solid after solvent (diethyl ether) extraction from the reaction mixture. The isolated product with very high purity was achieved by washing the crystals with chloroform.

4.3. Results and Discussion

4.3.1. Michael Addition Reaction Catalyzed by NaOH, DBU, [DBU][OH] and the Binary Mixtures of [DBU][OH] with Water and DBU

The Michael addition reaction of acetylacetone and 2-cyclohexene-1-onewas carried out usingNaOH, DBU, [DBU][OH] and the binary mixtures of [DBU][OH] with water and DBU as catalysts at room temperature (≈ 20 °C). The reaction completion time was measured by using TLC technique. The average rate was calculated with respect to the initial concentration of the substrate, acetylacetone (3.791mol/L).

Table 4.1. Reaction completion time and average rate for different systems as catalyst and reaction medium in the Michael addition reaction

Chemical Systems (0.5 mmol)	**Reaction Completion Time (min)**	**Average Rate (v) (mol L^{-1} s^{-1})×10^4**	**Observations**
NaOH	250	2.53	Long time and large amount of solvent required
DBU	240	2.63	Long time
[DBU][OH]	180	3.51	Short time and without any solvent
[DBU][OH] with H_2O	120	5.27	Shorter time
[DBU][OH] with DBU	110	5.74	Shorter time

When NaOHwas used as catalyst it required large volume of ethanol to make a solution. If the base DBU was used as catalyst, it required longer time to complete the reaction and it was completely miscible with both reactants. But for the catalyst [DBU][OH], it took shorter time for completion of the reaction without the use of any solvent. It was very interesting that the binary systems of [DBU][OH] with water and

DBU took shorter reaction completion time (Table 4.1). The rate was also faster (3.51×10^{-3} $molL^{-1}s^{-1}$) for [DBU][OH] and its binary systems (5.74×10^{-3} $molL^{-1}s^{-1}$) compared to the organic bases, DBU and NaOH (Table 4.1).

4.3.2. Enhancement of the Rate of the Michael Addition Reaction in Presence of NaOH with Different Concentrations of [DBU][OH]

The reaction between acetylacetone and 2-cyclohexene-1-onewas carried out in presence of fixed amount of NaOH using different concentrations of [DBU][OH] as the catalyst. With addition of very small amount of [DBU][OH] the reaction completion time decreased (arrow in Figure 4.2) with the same concentration of NaOH. When the concentration of added NaOHwas 0.005 mmol, the reaction completion time decreased from 490 to 300 min with the addition of 0.005 mmol of [DBU][OH] into the reaction mixtures.Thereby, [DBU][OH] acted as a catalyst for the reaction.

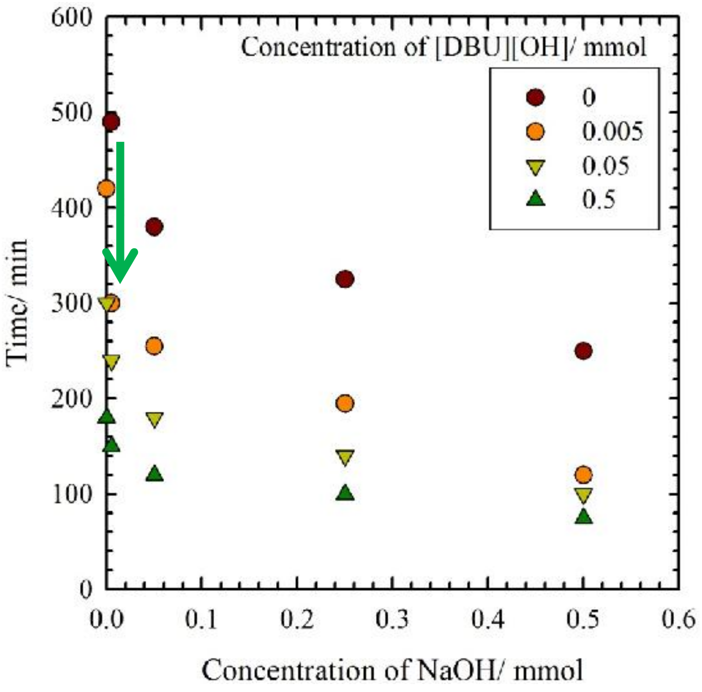


Figure 4.2. Michael addition reaction in presence of NaOH with different concentrations of [DBU][OH].

4.3.3. Reaction ofAcetylacetone and 2-Cyclohexen-1-one in the Molar Ratio of 1:1 Catalyzed by the Binary Mixtures of [DBU][OH] with DBU and H_2O at Room Temperature

Binary mixtures of DBU with water were prepared at various molar ratio to have compositions varying from water-rich conditions to DBU-rich conditions.Michael addition reaction was carried out using these mixtures as a catalyst. The progress of the reaction was followed by TLC and reaction completion time was recorded. The reaction completion time plotted against mole fraction of DBU is shown in Figure 4.3.

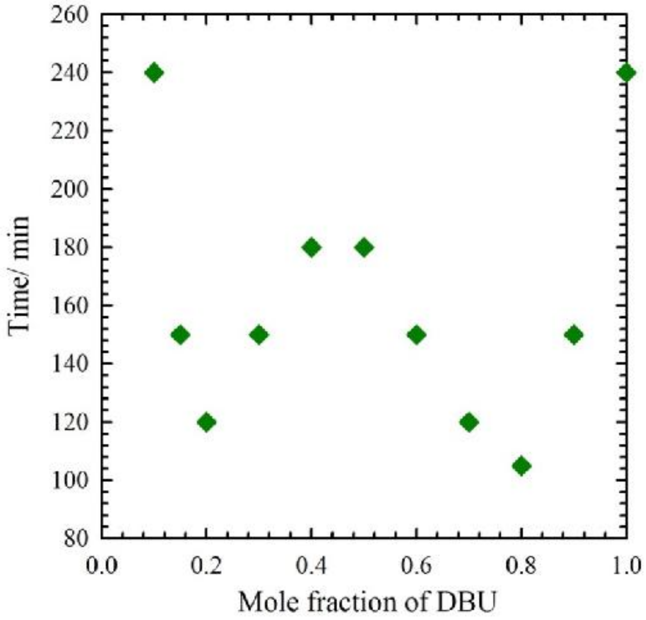
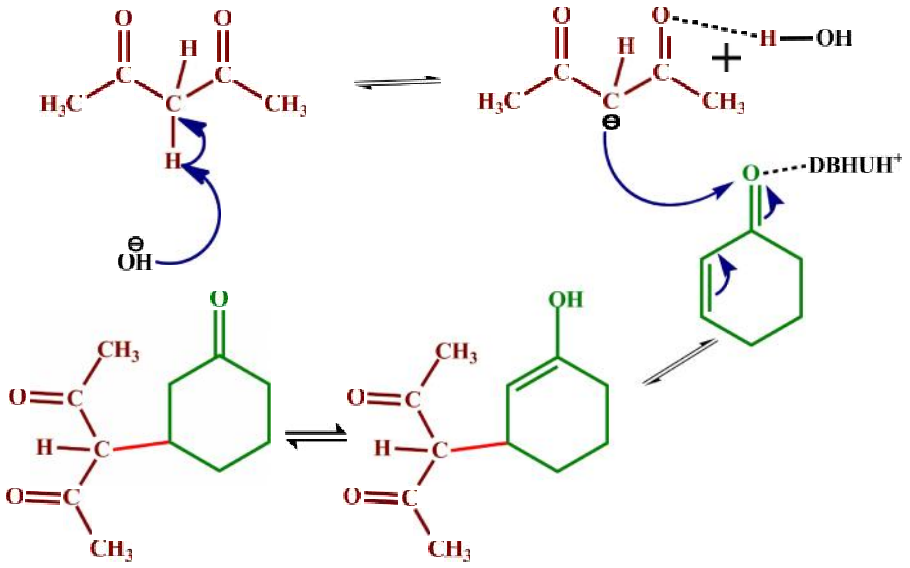


Figure 4.3. The variation of reaction completion time with mole fraction of DBU for Michael addition reaction in presence of [DBU][OH] and its binary systems with water and DBU.

As the amount of water increases ($x < 0.5$) the reaction completion time decreases i.e. the rate of the reaction increases. Water mainly breaks the three dimensional network of cations and anions into smaller ionic clusters [32] and accelerates the transfer of OH^- ions from ionic cluster to free water via the Grotthuss mechanism [33], which makes OH^- ions available for catalysis and reaction time decreases. On further addition of water all the available sites of cations and anions are bonded by water i.e. ions are completely solvated [34]. As OH^- ions get hydrated, the reaction completion time increases.

With increase in concentration of free DBU (x> 0.5), interchange of proton between DBUH$^+$ and molecular DBU may increase. This makes the OH$^-$ ions free for catalysis. As a result reaction completion time decreases. In excess DBU (x> 0.8), the number of cations and anions decreases i.e. the number of OH$^-$ ions are less for catalysis and the reaction completion time increases; thus rate of the reaction decreases.

It can be been that [DBU][OH] took shorter time to complete the reaction than that of pure base, DBU. This can be explained with the help of reaction mechanism using IL, [DBU][OH] (Scheme 4.3) . It may be noted here that the mechanism of the Michael addition reaction using base catalyst is shown in Figure 1.14 (Chapter 1).The reaction possibly follows the same mechanism as in base catalyzed Michael addition and the anion of the [DBU][OH] works as the base [30,31]. The main difference of using IL is the formation of hydrogen bonds between the reactants and ions (Figure 4.3). The formation of hydrogen bond with the carbanionenhances its nucleophilic ability and the hydrogen bond with the α,β-unsaturated carbonyl compound increases its electrophilic ability [35]. For this, the reaction becomes more favorable and requires lower time to complete for [DBU][OH].



Scheme4.3. Reaction mechanism of the Michael addition reaction using [DBU][OH] as catalyst.

4.3.4. Reaction of Acetylacetone and 2-Cyclohexene-1-onein the Molar Ratio of 1:1 Catalyzed by the Binary Mixtures of [DBU][CH_3COO] with DBU and CH_3COOH at Room Temperature

CH_3COOH/DBU binary systemswith compositions varying from acetic acid-rich conditions to DBU-rich conditions were prepared at various molar ratio by mixing appropriate amounts of DBU and acetic acid. Michael addition reaction was carried out by using each of these mixtures and the catalytic activity was checked. TLC technique was used to follow the progress of the reaction and the reaction completion time was recorded. The reaction completion time plotted against mole fraction of DBU is shown in Figure 4.4.

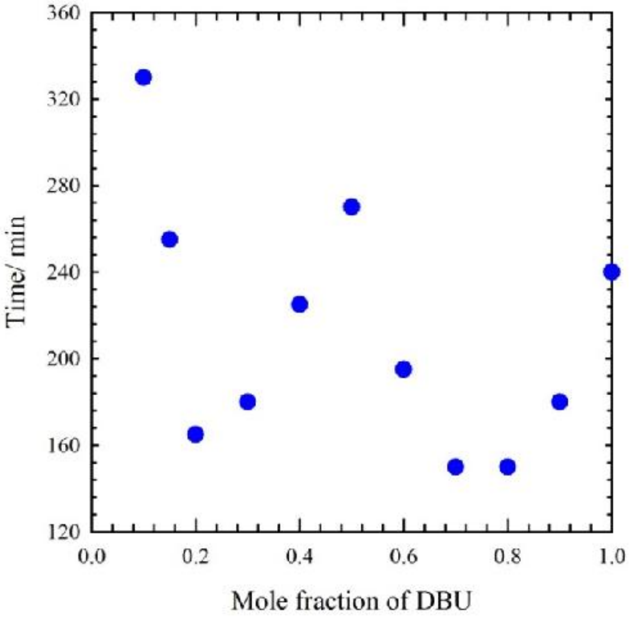


Figure 4.4. The change in reaction completion time with mole fraction of DBU in presence of [DBU][CH_3COO] and its binary systems with acetic acid and DBU.

As the amount of acetic acid increases ($x < 0.5$), the reaction completion time decreases i.e. rate of the reaction increases. There is also a possibility of hydrogen bonding between ions of [DBU][CH_3COO] and acetic acid.The three dimensional network of cations and anions breaks into smaller ionic clusters and accelerates the transfer of CH_3COO^- ions for catalysis and reaction time decreases. On further addition of acetic acid, all the available sites of cations and anions are bonded by free acetic acid i.e. ions are completely solvated. As CH_3COO^- ions get solvated, the reaction completion time increases i.e. reaction rate decreases.

With increase in concentration of free DBU ($x> 0.5$), the proton transfer between cations and molecular DBU increases. The proton transfer seems to follow the Grotthuss mechanism in excess DBU compositions that makes the CH_3COO^- ions free for catalysis. As a result reaction completion time decreases. In excess DBU ($x> 0.8$), the number of cations and anions decreases i.e. number of CH_3COO^- ions are less for catalysis and the reaction completion time increases thus rate of the reaction decreases.

4.3.5. Enhancement of the Rate of the Michael Addition Reaction in Presence of NaOH with Different Concentrations of [C_6DBU][OH]

The reaction between acetylacetone and 2-cyclohexene-1-onewas carried out in presence of fixed amount of NaOH using different concentrations of [C_6DBU][OH] as the catalyst. With addition of very small amount of [C_6DBU][OH], the reaction completion time decreases (arrow in figure 4.5) with the same concentration of NaOH. The reaction completion time decreases from 490 to 255 min with the addition of 0.005 mmol of [C_6DBU][OH] into the reaction mixtures. Therefore, [C_6DBU][OH] acted as a catalyst for the reaction.

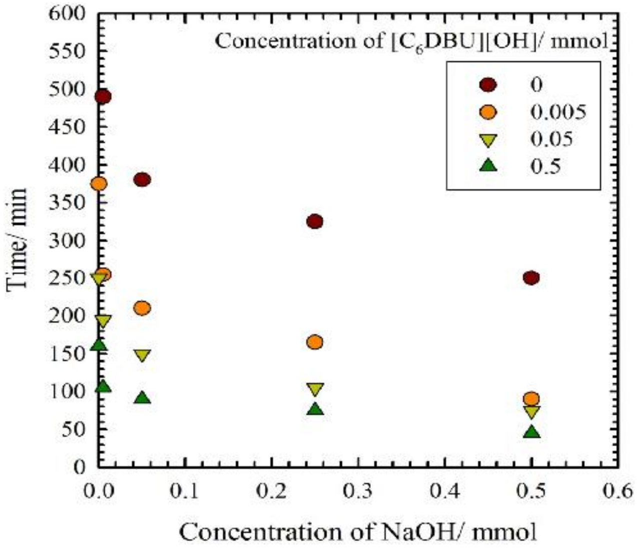


Figure 4.5. Reaction completion time for Michael addition reaction in presence of NaOH with different concentrations of [C_6DBU][OH].

4.3.6. Reaction of Acetylacetone and 2-Cyclohexene-1-one in the Molar Ratio of 1:1 Catalyzed by the Binary Mixtures of [C_6DBU][OH] with Water at Room Temperature

The reaction completion time plotted with mole fraction of [C_6DBU][OH] in the binary systems of [C_6DBU][OH] with water is shown in the figure 4.6. With increasing mole fraction of [C_6DBU][OH] (x = 0-0.5)the reaction completion time decreases (Figure 4.6), i.e. rate of the reaction increases. With increasing mole fraction of [C_6DBU][OH], the number of ions increases which made the catalysis favorable and the rate increases. The study of physicochemical properties of [C_6DBU][OH] and its binary systems with water (in chapter 3) shows that micelle like structure may be formed in water-rich region and reverse micelle like structure in [C_6DBU][OH]-rich region. In case of micelle like structure the nonpolar part of the cation is pointed to the center of the micelle and the polar part is directed to the outside of the micelle and the anion is in the bulk aqueous phase along with the polar part. Such arrangement makes the anion available for catalysis.

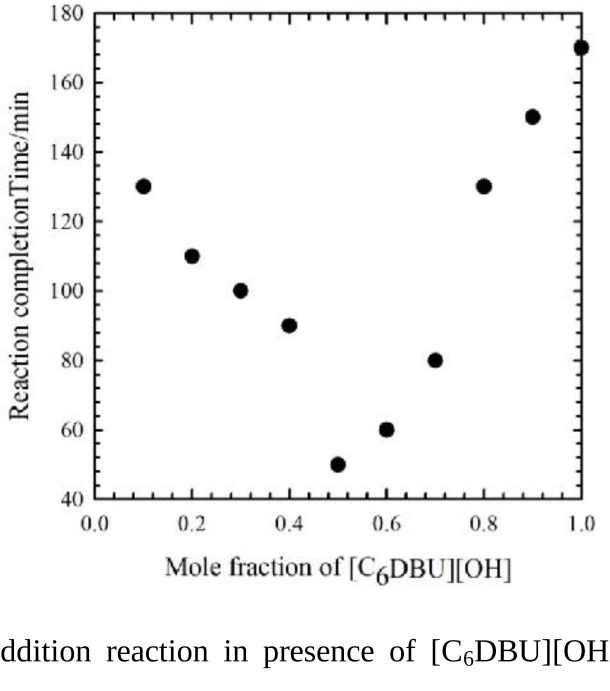


Figure 4.6. Michael addition reaction in presence of [C_6DBU][OH] and its binary systems with water.

Therefore, with addition of [C_6DBU][OH] in water-rich region the rate of reaction increases. In case of reverse micelle like structure, the polar part is pointed to the center of the reverse micelle and the nonpolar part is directed towards outside of the reverse micelle and the anion is in the core along with the polar part. Therefore, anions are not so available for catalysis and with the addition of $[C_6DBU][OH]$ (x = 0.5 - 1.0) rate has been found to decrease.

4.3.7. Characterization of the Obtained Product

4.3.7.1. Chemical Analysis of the Product

Test for carbonyl group

On addition of 2, 4-dinitrophenylhydrazine (2,4-DNPH) (8-10 drops) to the ethanolic solution of product, orange precipitate was formed indicating the presence of carbonyl group (Figure 4.7.a).

(a) **(b)**

Figure 4.7. Chemical analysis: (a) orange precipitate formed on addition of 2,4-DNPH (b) solution turns from colorless to violet on addition of $FeCl_3(aq)$.

Test for enol group

On addition of neutral ferric chloride ($FeCl_{3(aq)}$) solution (2-3 drops) to the ethanolic solution of the product, violet colour was observed, indicating the presence of enolic OH^- group (Figure 4.7.b).

4.3.7.2. Spectral Analysis of the Product

FTIR Spectra:

The IR spectra (Figure 4.8) of the compound showed a sharp band at 3354 $cm^{-1}$for OH^- group, sp^3(alicyclic) C-H absorption occurs at 2987 cm^{-1}, CH_2 bending at 1464 $cm^{-1}$and CH_3 bending at 1374 cm^{-1}, >C=O stretching occurs approximately at 1704 cm^{-1}.

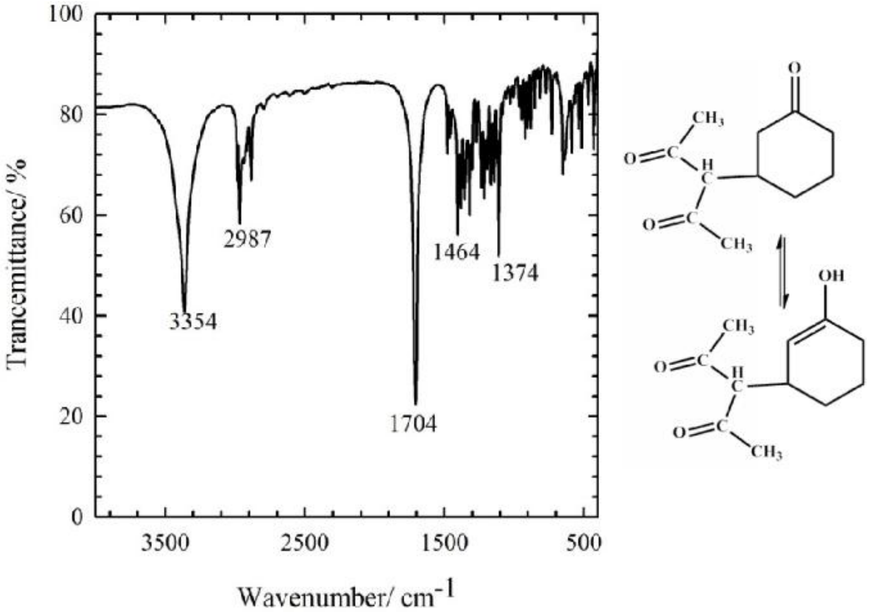


Figure4.8.(a) FTIR spectra of the product and (b) the expected structure of the product, pentane-3-cyclohexanonyl-2,4-dione (PCD).

^{1}H NMR spectra

The^{1}H NMR spectrum was measured in $CDCl_3$ (Figure 4.10). The proton of C-x appeared at 2.560 ppm as singlet. This proton appeared at low field as it is deshielded due to the presence of two >C=O, electron withdrawing groups adjacent to the C-x. Six proton of two methyl groups appeared at 2.322 ppm as singlet. The signals for other protons are summarized as follows –

^{1}HNMR (400 MHz, $CDCl_3$): δ 2.560 (s, 1H, COCHCO), 2.327 (s, 6H, $–CH_3$), 2.246-2.260 (t, 2H, $CH_{2(b)}$), 1.802-1.831 (m, 1H, CH_y), 1.625-1.709 (m, 4H, $CH_{2(c,d)}$), 1.566-1.579 (t, 2H, $CH_{2(a)}$).

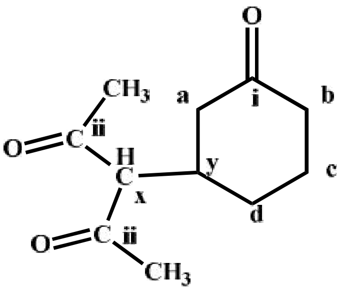


Figure 4.9. Expected structure (keto form)of the PCD.

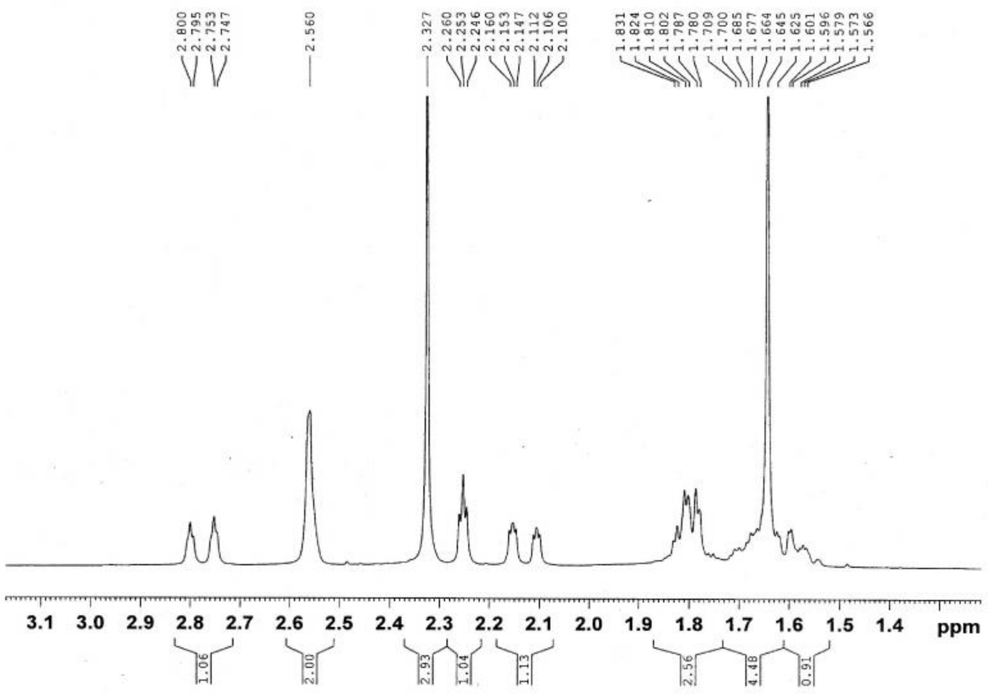


Figure 4.10.^{1}H NMR spectrum of the product PCD in $CDCl_3$ at 400 MHz.

^{13}C NMR spectra

The ^{13}C NMR spectrum for the product is shown in the figure 4.11. Two deshielded carbons due to the presence of more electronegative oxygen atoms appeared at 208.879 and 214.995 ppm. The two methyl carbons appeared at 28.202 ppm.

The ^{13}C NMR spectrum for eleven carbons is summarized as-

^{13}C NMR (400 MHz, $CDCl_3$): δ 208.879 (CO_i), 214.995 (CO_{ii}), 73.339 (CH_x), 56.888 ($CH_{2(a)}$), 40.431 ($CH_{2(b)}$), 31.356 ($CH_{2(d)}$), 28.202 (CH_3), 25.733 ($CH_{2(c)}$), 19.789 (CH_y).

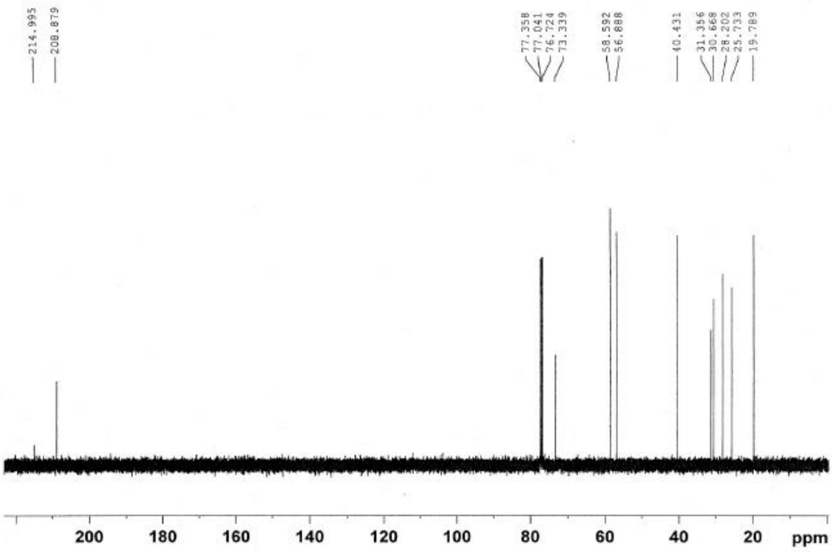


Figure 4.11.^{13}C NMR of the product(pentane-3-cyclohexanonyl-2,4-dione) in $CDCl_3$ at 400 MHz.

4.3.8. Yield of the Product of the Michael Addition Reaction

The isolated yield of the Michael addition reactioncatalyzed by DBU and DBU derived PILs and AIL and their binary systems was 74-80 % where all experiments were carried out under the same reaction conditions. But the reaction completion time was different for each experiment. When the same reaction was carried out in ethanol solution with base (NaOH), the product yield was poor (40%) and the reaction requiredmuch longer time. In this context, the IL mediated reaction has greater advantage for enhancing the reaction rates by reducing the reaction time and the product yield is enormously increased. In addition, the process is environmentally friendly. Another salient feature of ILmediatedreaction is that the reaction resulted in pure products without any side products and processing is very simple. When the reaction was carried in presence of ethanol and organic bases, the reaction resulted in gummy products, which were difficult to handle at the processing stage.

4.4. Conclusions

Organic synthesis by Michael addition reaction of acetylacetone and 2-cyclohexen-1-one is catalyzed by inorganic base, NaOH, organic base DBU, and ILs, [DBU][OH], [DBU][CH_3COO], [C_6DBU][OH] and their binary systems with water, DBU, and acetic acid.The use of solid base NaOH requires use of large volume of volatile organic solvent and makes the synthesis process environmentally hazardous. The organic base DBU catalyzes the reaction without using any solvents, but the base itself is expensive. The catalytic performance of the binary systems of ILs is better than that of by ILs themselves and the bases too. The binary systems of ILs do not require any external solvents and very small amount (0.005 mmol) of these systems can catalyzethe synthesis process efficiently. Therefore, the binary systems of ILs are better catalysts and they provide anenvironmentally benign and cost effective route for the reaction. The catalytic activity of [DBU][OH] is better than that of [DBU][CH_3COO] since the anion, OH^-, is more nucleophilic than the CH_3COO^- anion. Besides this, [C_6DBU][OH] acts as a better catalyst compared to [DBU][OH] for the synthesis.

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Abstract

Physicochemical properties, such as, conductivity, density, viscosity, thermal stability, particle size, and spectral characteristics of pure and binary systems of DBU basedprotic ionic liquids (PILs), ([DBU][OH] and [DBU][CH_3COO]) and aprotic ionic liquid (AIL), ([C_6DBU][OH]) with water, acetic acid, and DBU have been correlated with the structure of the ILs, composition in the binary systems, and the ionicity based on protic/aprotic nature. Attempts have also been made to correlate physicochemical properties with kinetic results of Michael addition reaction of acetylacetone and 2-cyclohexene-1-one. With increasing concentrationof PILs ($X_{[DBU][OH]/[DBU][CH_3COO]}$ = 0 to 0.5)in the binary systems with water, acetic acid, and DBU, the conductivity increases and degradation temperature decreases and reaction completion time also decreases. The rate of the reaction increases depending on the availability of the anion. In case of the binary systems of [C_6DBU][OH] with water, conductivity increases with increasing $X_{[C_6DBU][OH]}$ upto a value of 0.2 and after that the value of conductivity decreases.The degradation temperature, however, decreases and shows lower value at $X_{[C_6DBU][OH]}$ = 0.5 and after that it increases again. The aggregations of ions with water are different in two different regions (IL-rich and IL-deficient region).Such association of ions with wateris also supported by particle size analyses, spectral characteristics, density, and viscosity.The rate of the Michael addition reaction is faster when the conductivity of the binary system is higher, i.e. the mobility of anions is higher and the availability of anions is higher for catalysis. Rate is also higher where the degradation temperature of the binary systems of ILs is lower to indicate that anions are relatively free.

5.1. Introduction

ILshave been a key ally in helping run into the twin challenges ofefficient and environmentally benign chemical processing. They act much like good organic solvents, dissolving bothpolar and nonpolar species. In many cases, they have been foundto perform much better than commonly used solvents. Perhaps, themost intriguing feature of these compounds is that, while they areliquid in their pure state at room temperature, they have essentiallyno vapor pressure. They do not evaporateand thereforethey cannotlead to fugitive emissions. Many of these compounds are liquidsover incredibly large temperature ranges, from below ambient towell over 300 to 400°C, which suggests they could be used underunique processing conditions. ILsareorganic salts, whose cations, substituents, and anions can be variedto change their chemical and physical properties.

The studies of physicochemical properties, such as, conductivity, viscosity, density, thermal analysis, particle size analysis, spectral analysis etc. of ILs and their binary systems with molecular solvents provide information about the ionic nature and ionic structure of ILs, and possible interaction between ILs and solvents. The change in different physicochemical properties of ILs and their binary systems with different parameters can be correlated with each other.

There are numerous studies, both experimental [1-9] and theoretical [10-13], on physicochemical properties of ILs and correlation with the ionic structure. Quantitative information on the formation of ionic aggregates in several RTILs based on the ratios of molar conductivity values is also available in the literature[14-17]. The ratio of the molar conductivity has been correlated to the ionic structures, ionic concentrations, polarity, and other properties of RTILs [18]. Ionic structure has been reported to affect the ionic nature of the RTILs through their interionic and intermolecular interactions.

Although ideal ILs areconstituted by non-associated ions, inreality they form aggregates or clusters to some extent. Thereis experimental evidence of ionic association in ILs [19-24].Therefore it is important to evaluate the physicochemical properties of ILs and correlate with the aggregation behavior.

Investigation of the properties of ILs and the parameters that dominate the properties has therefore been an important task. In the present work, physicochemical properties of the ILs and their binary systems have been studied and discussed in detail and correlated with the structural features. A generalized concept has been established to understand the ion-ion interaction in pure ILs and ion-molecule interaction in binary systems of ILs with molecular solvents. Finally, different physicochemical properties of ILs and their binary systems have been correlated with the kinetic results of the Michael addition reaction using the ILs and their binary systems as catalyst and medium.

5.2. Experimental

5.2.1. Materials and Methods

DBU (Sigma), glacial acetic acid (RCI Labscan), 1-chlorohexane (Sigma), NaOH (Merck), DCM (Merck) were used as received without further purification. Double distilled de-ionized water (conductivity: 0.055 μScm^{-1} at 25.0 ^{o}C) from HPLC grade water purification system (BOECO, Germany) was used for neutralization reaction.

FTMIR spectra were recorded with a Perkin Elmer FTIR spectrometer (Frontier)in the spectral wavenumber range from 4000 to 400 cm^{-1}.KBr in the pellet form were used and microdrops of liquid samples were placed on the pellet by micropipette for recording FTIR spectra. The thermal degradation temperature of the ILs was measured using a thermogravimetric differential thermal analyzer (TG/DTA) (a Hitachi instrument, TG-DTA 7200). Samples were heated from 30 ^{o}C to 500 ^{o}C in an Al-pan under nitrogen atmosphere. The heating rate was 10 ^{o}C min^{-1}. Conductivity was measured by electrochemical impedance spectroscopic (EIS) measurements using Autolab PGSTAT302N – a high performance impedance analyzer with the FRA32M module over a wide frequency range of 10 μHz to 32 MHz.Density of the ILs and their binary systems were measured with an Anton Paar vibrating tube density meter (Model no. DMA 4500). The accuracy was 0.000005 gcm^{-3} and repeatability was 0.00001 gcm^{-3} of density measurement. Viscosity of pure ILs and their binary systems with molecular systems were measured with an Anton-Paar falling ball automated viscometer (Lovis-2000M/ME) with an accuracy of ±10^{-6}mPa.s. Refractive index (RI) was measured by using an Anton-Paar automated refractometer(Abbemat-300)with high resolution optical sensor. Diameters of the aggregates of ILs in the binary systems were measured using a particle size analyzer, Zetasizer Nano ZS90 (ZEN3690, Malvern Instruments Ltd, UK) by DLS measurements at different temperatures.

5.3. Results and Discussion

5.3.1. Correlation of Different Physicochemical Properties of [DBU][OH] and its Binary Mixtures

5.3.1.1. Conductivity and Thermal Stability

In binary systems of the [DBU][OH] with water and DBU the conductivity is determined by the arrangement of ions and the interactions of ions themselves and interactionswith solvent molecules. The thermal stability evaluated by the degradation temperature is controlled by the association of ions and solvent molecules. From Figure 5.1, it is apparent that the conductivity and the degradation temperature have an inverse relationship, i.e. where conductivity is high the degradation temperature is low. The reason of high conductivity of the system may be the loose arrangement of ions which makes the ions more mobile. The low degradation temperature may be due to the weak interaction of ions and solvent molecules.

Upon addition of water to [DBU][OH] ($X_{\mathrm{DBU}}< 0.5$) conductivity increases due to the increased mobility of ions. The formation of hydrogen bonds between water and the ions of [DBU][OH]distorted the three dimensional (3-D) network structure of the cations and anions and made the ions mobile. In presence of excess water ($X_{\mathrm{DBU}}<0.2$) the conductivity decreases because of decreased number of ions. Similarly, with addition of DBU ($X_{\mathrm{DBU}}> 0.5$) in [DBU][OH] the conductivity increases due to increased mobility of ions again. This is due to the formation of hydrogen bonding between the N-atom of DBU molecule and ions of [DBU][OH] which disturbed the interaction of ions themselves and made the ions mobile. Moreover there may H^+-exchange between molecular DBU and the cation. $DBUH^+$ which also made the anions mobile. With excess DBU ($X_{\mathrm{DBU}}>0.8$) the number of ions decreases to cause a decrease in conductivity.

On the other hand, the degradation temperature of pure [DBU][OH] is higher than that of its binary systems. Upon addition of water to [DBU][OH] ($X_{\mathrm{DBU}}<0.5$) the degradation temperature of the system decreases. Water forms hydrogen bonding with ions of [DBU][OH] and weakens the strong interaction between cations and anions.Thisbrings about a decrease in the degradation temperature with water added to [DBU][OH]. In presence of excess water the ions get fully hydrated in all possible sites of the ion which makes the ions strongly attracted to water and increases the degradation temperature. With further addition of DBU ($X_{\text{DBU}} > 0.5$) the degradation temperature decreases again due to the formation of hydrogen bonding between the N-atomof DBU and the ions of [DBU][OH]. The H^+ transfer between the cation and DBU may also be responsible for the distortion of 3-D network structure of [DBU][OH]. In presence of excess DBU, the ions are not highly solvated as is the case for excess water [25] and degradation temperature decreases again.

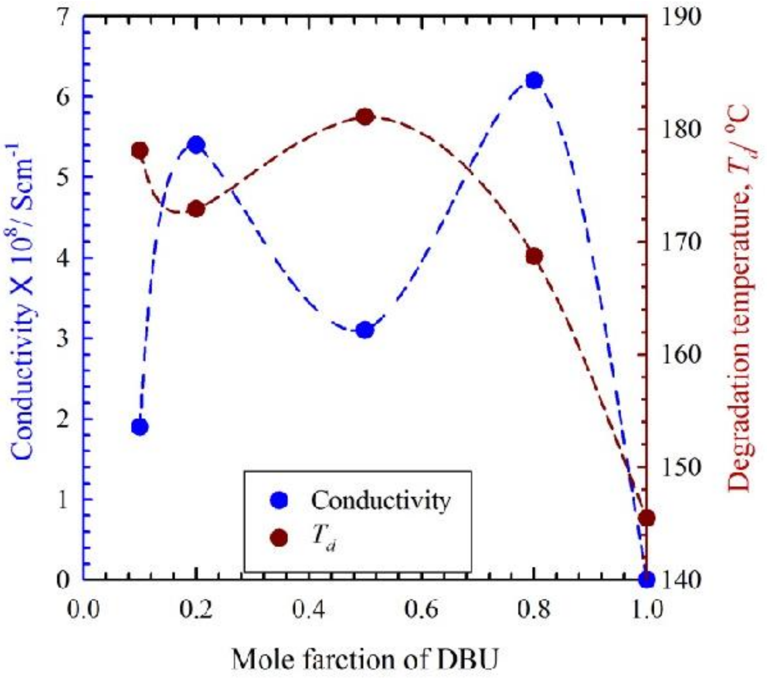

Figure 5.1. The change in conductivity and degradation temperature with mole fraction of DBU for binary systems of [DBU][OH] with DBU and water.

5.3.1.2. Conductivity andKinetic Results of Michael Addition Reaction

Figure 5.2 represents the change in reaction completion time and conductivity with mole fraction of DBU. It is clear that at $X_{\text{DBU}} = 0.2$ and 0.8 the rate of reaction is high, i.e. the required time for completion of the reaction is shorter.Inboth systems the conductivity was also high as compared to pure [DBU][OH]. Thus, the conductivity and the reaction completion time have an inverse relationship. The conductivity is high, due to high mobility of ions,which makes the ions easily available for catalysis of the reaction. This consequently increases the reaction rate and the reaction is completed within a short period. On the other hand for pure [DBU][OH], water and DBU the conductivity values are lower and the ions are less mobile and less available for catalysis of the reaction. The result is slower reactionrate.In other words, times for completion of reaction are longer.

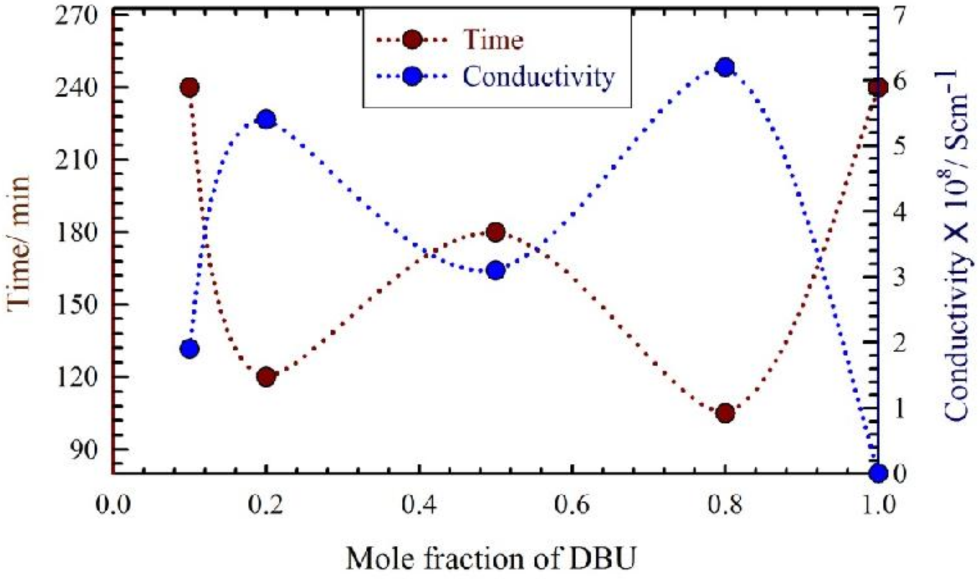

Figure 5.2. The variation of reaction completion time and conductivity with mole fraction of DBU for binary systems of [DBU][OH] with DBU and water.

5.3.1.3. Thermal Stability andKinetic Results of Michael Addition Reaction

The thermal stability and the rate of the reaction have inverse relationship. When the value of degradation temperature is high, the rate of the reaction has been observed to beslow. The value of degradation temperature is higher for pure [DBU][OH]. Upon the addition of solvents (water and DBU), the degradation temperature of [DBU][OH] decreases as the 3-D network structure of ions becomes distorted by the formation of hydrogen bonding between ions and solvent molecules [25]. This made the ions more available for catalysis of the reaction and rate of reaction increased (reaction completion time decreased). In presence of excess solvents (water and DBU), the degradation temperature decreased, but the rate of the reaction decreases too due to the decreased number of ions.

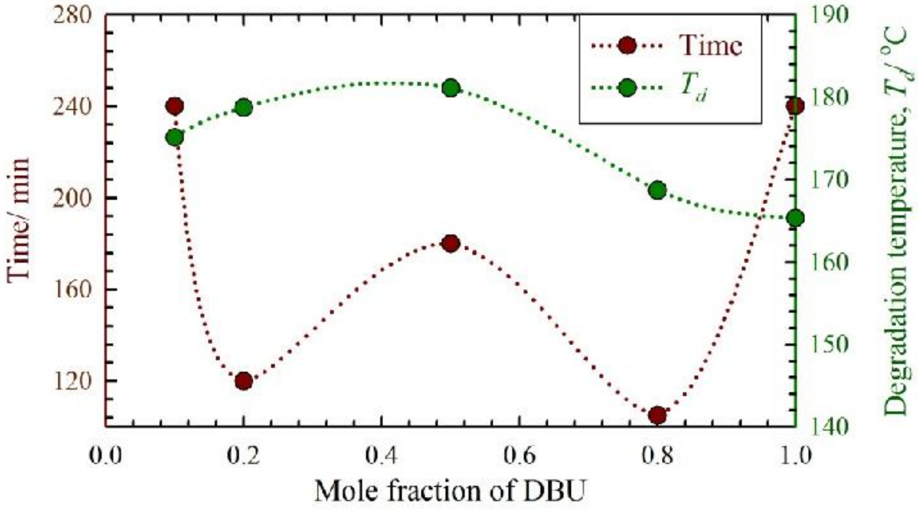

Figure 5.3. The change in reaction completion time and degradation temperature with mole fraction of DBU for binary systems of [DBU][OH] with DBU and water.

5.3.2. Correlation of Physicochemical Properties of [DBU][CH_3COO] and its Binary Mixtures

5.3.2.1. Conductivity and Thermal Stability

Figure 5.4 shows the variation of conductivity and degradation temperature with mole fraction of DBU. From Figure 5.4 it is apparent that, the conductivity and the degradation temperature have an inverse correlation, i.e. where conductivity is high,degradation temperature is low. The reason of high conductivity of the system may be the loose arrangement of ions which makes the ions more mobile. The low degradation temperature may be due to the weak interaction of ions and solvent molecules.

As water is added to [DBU][CH_3COO] (X_{DBU}< 0.5),the conductivity increases due to the increased mobility of ions. The formation of hydrogen bonds between CH_3COOH and the ions of [DBU][CH_3COO] distorts the 3-D network structure of the cations and anions and makes the ions mobile. In presence of excess CH_3COOH (X_{DBU}<0.2), the conductivity decreases because of the decreased number of ions. Similarly, with addition of DBU (X_{DBU}> 0.5) in [DBU][CH_3COO], the conductivity increases due to the increased mobility of ions again. This is because of the formation of hydrogen bond between the N-atom of DBU molecule and ions of [DBU][CH_3COO] which disturbs the interaction of ions themselves and makes the ions mobile. Moreover possible H^+-exchange between molecular DBU and the cationDBUH$^+$mayalso make the anions mobile. With excess DBU (X_{DBU}>0.8), the conductivity decreases due to the decreased number of ions.

On the other hand, the degradation temperature of pure [DBU][CH_3COO] is higher than that of its binary systems. As$CH_3COOH$is added to [DBU][CH_3COO] (X_{DBU}<0.5), the degradation temperature of the system decreases. CH_3COOH forms hydrogen bond with ions of [DBU][CH_3COO] and weakens the strong interaction between cations and anions and lowers the degradation temperature. In presence of excess CH_3COOH, the ions get fully solvated in all possible sites of the ion which makes the ions strongly bounded to CH_3COOH and increases degradation temperature. With addition of DBU (X_{DBU}> 0.5), the degradation temperature decreases again due to the formation of hydrogen bonding between the N-atom of DBU and the ions of [DBU][CH_3COO]. The H^+ transfer between cation and DBU may also be responsible for the distortion of 3-D network structure of cations and anions in[DBU][CH_3COO] [25]. In presence of excess DBU the ions are not highly solvated as in excess acetic acidanddegradation temperature decreases again.

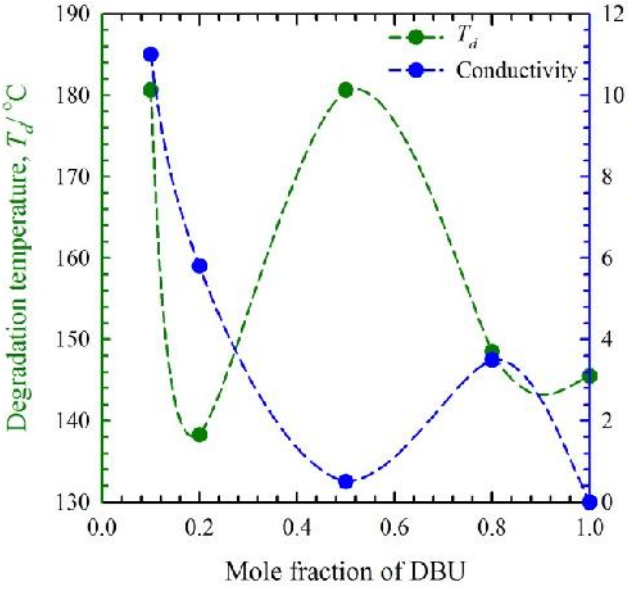

Figure 5.4. The change in degradation temperature and conductivity with mole fraction of DBU for binary systems of [DBU][CH_3COO] with DBU and acetic acid.

5.3.2.2. Conductivity andKinetic Results of Michael Addition Reaction

The variation of reaction completion time and conductivity with the mole fraction of DBU is shown in Figure 5.5. It is clear that at X_{DBU} = 0.2 and 0.8, the rate of the reaction is high, i.e. the required time to complete the reaction is slower and inboth systems the conductivity was also high as compared to the pure [DBU][CH_3COO]. Thus, the conductivity and the reaction completion time have an inverse relationship. The conductivity is high, i.e. the mobility of ions is high which makes the ions more available for catalysis of the reaction and increases the rate and in other words, decreases the reaction completion time. On the other hand, for pure [DBU][CH_3COO], CH_3COOH, and DBU the conductivity values are lower and the ions are less mobile and less available for catalysis. The result is slower reaction i.e. high reaction completion time.

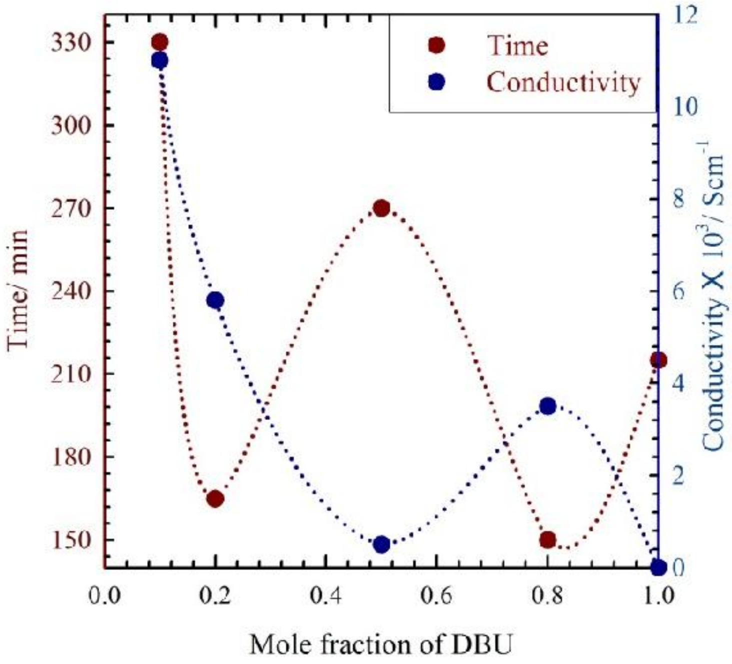

Figure 5.5. The variation of reaction completion time and conductivity with mole fraction of DBU for binary systems of [DBU][CH_3COO] with DBU and acetic acid.

5.3.2.3. Thermal Stability andKinetic Results of Michael Addition Reaction

The thermal stability and the rate of the reaction have inverse correlation. Where the degradation temperature is high, the rate of reaction is slower. The degradationtemperature is higher for pure [DBU][CH_3COO]. With the addition of solvents (CH_3COOH and DBU) the degradation temperature decreases as the 3-D network structure of ions becomes distorted by the formation of hydrogen bonding between ions and solvent molecules. This makes the ions more available for catalysis and the rate of reaction increases (reaction completion time decreases). In presence of excess solvents (CH_3COOH and DBU) the degradation temperature decreases and the rate of reaction decreases due to the decreased number of ions.

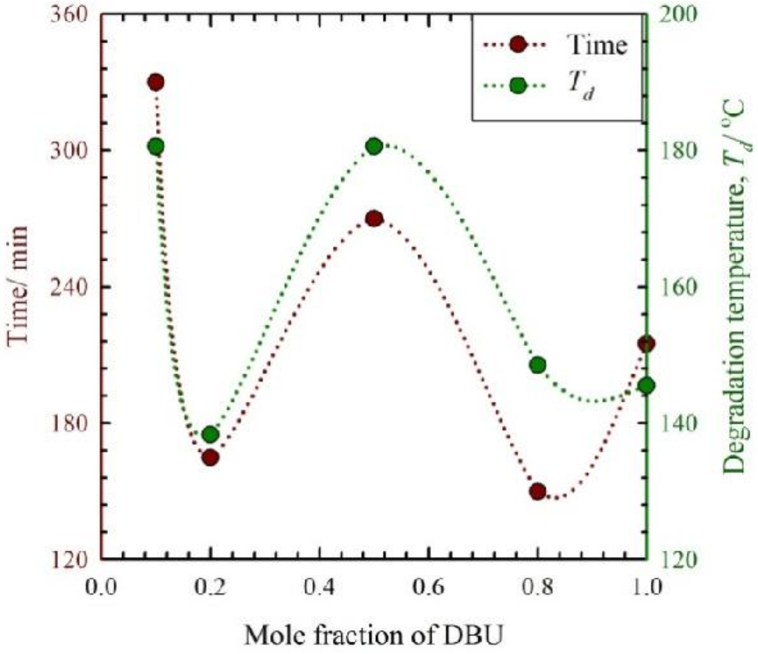

Figure 5.6. The variation of reaction completion time and degradation temperature with mole fraction of DBU for binary systems of [DBU][CH_3COO] with DBU and acetic acid.

5.3.3. Correlation of Physicochemical Properties of [C_6DBU][OH] and its Binary Systems with Water

5.3.3.1. FTMIR and FTNIR

Figure 5.7 represents the FTIR (MIR and NIR) spectra for [C_6DBU][OH] and its binary systems with water. From FTMIR (Figure 5.7a) it has been found that band corresponding to trapped water appeared at 3660-3680 cm^{-1}.The binary systems of $X_{[C_6\text{DBU}][\text{OH}]} > 0.4$ showed the existence of the trapped water. The FTNIR (Figure 5.7b)spectra also support the presence of trapped water at $X_{[C_6\text{DBU}][\text{OH}]} > 0.4$ and it has been observed at 5270 cm^{-1}.

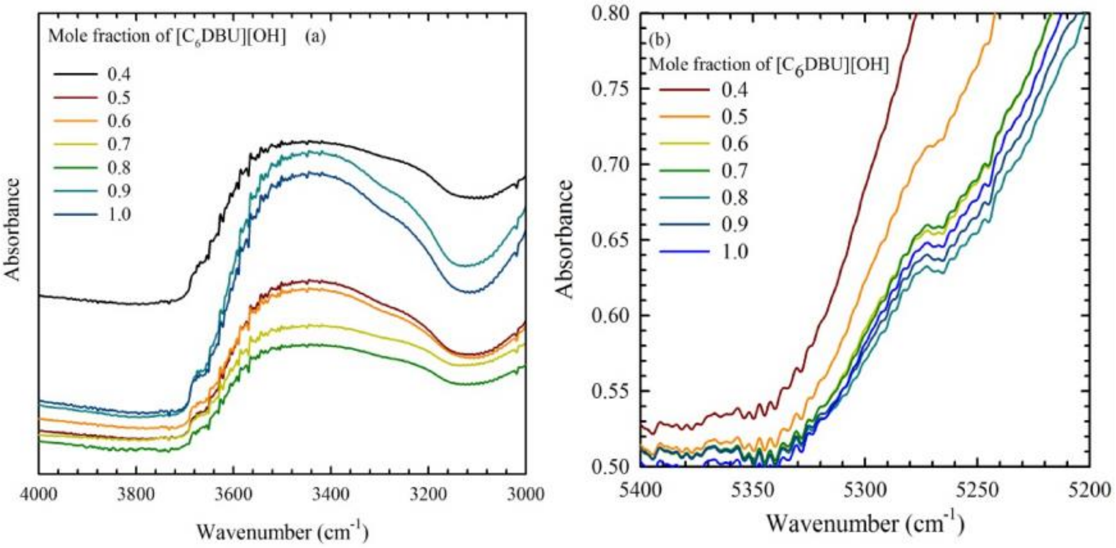

Figure 5.7.FTIR spectra (a) FTMIR and (b) FTNIR for [C_6DBU][OH] and its binary systems with water.

5.3.3.2. Particle Size from DLSMeasurements and Thermal Behavior from TG-DTA

Figure 5.8 shows comparison between the particle size and the degradation temperature for [C_6DBU][OH] and its binary systems with water. The degradation temperature of the system at $X_{[C_6\mathrm{DBU}][\mathrm{OH}]}$ = 0.5 is lowest and the size of the particle around this system ($X_{[C_6\mathrm{DBU}][\mathrm{OH}]}$ = 0.6) was smaller. As the IL [C_6DBU][OH] is hydrophobic and lipophilic in nature,it may act as a surfactant as well as hydrophobic phase and form microemulsion like microstructure even in the absence of externally added surfactant. Self-association of [C_6DBU][OH] may take place with water in water-rich region (it might resemble micelles). While self-association in [C_6DBU][OH]-rich region may give reverse micelles. Therefore, at $X_{[C_6\mathrm{DBU}][\mathrm{OH}]}$ = 0.5/0.6 the system shows the transition between the micelle and reverse micelle like arrangement of [C_6DBU][OH] with water and shows lowest degradation temperature and smaller particle size.

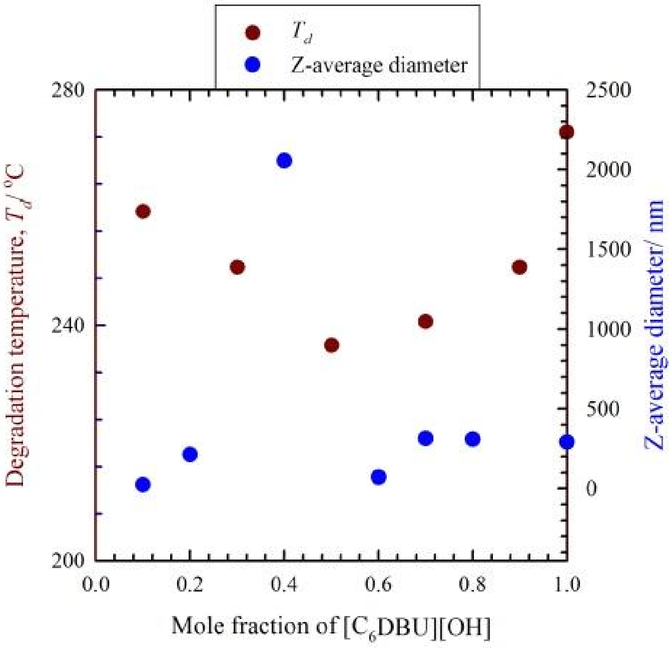

Figure 5.8. The change in degradation temperature and Z-average diameter of the particle size in the [C_6DBU][OH]-water systemswith mole fraction of [C_6DBU][OH].

5.3.3.3. Viscosity and Conductivity

In general, conductivity and viscosity are decided by the microstructures of microemulsion. This is due to the fact that the viscosity reflects the magnitude of inter-droplet interactions [26] and conductivity depends on the local viscosity experienced by the charge carriers [27]. The change of excess viscosity with the mole fraction of [C_6DBU][OH] divided the profile into two parts. One in water-rich region ($X_{[C_6\mathrm{DBU}][\mathrm{OH}]} < 0.5$), where the excess viscosity shows negative value to indicate that van der Waals forces dominated the system [28].In [C_6DBU][OH]-rich region ($X_{[C_6\mathrm{DBU}][\mathrm{OH}]} > 0.5$), on the other hand, the excess viscosity shows positive value. Thisindicates that ion-dipole interaction dominates and number and strength of H-bonds in the systemincreased. The conductivity is higher in water-rich region due to lower viscosity of the region and conductivity is lower in [C_6DBU][OH]-rich region where the viscosity is large.

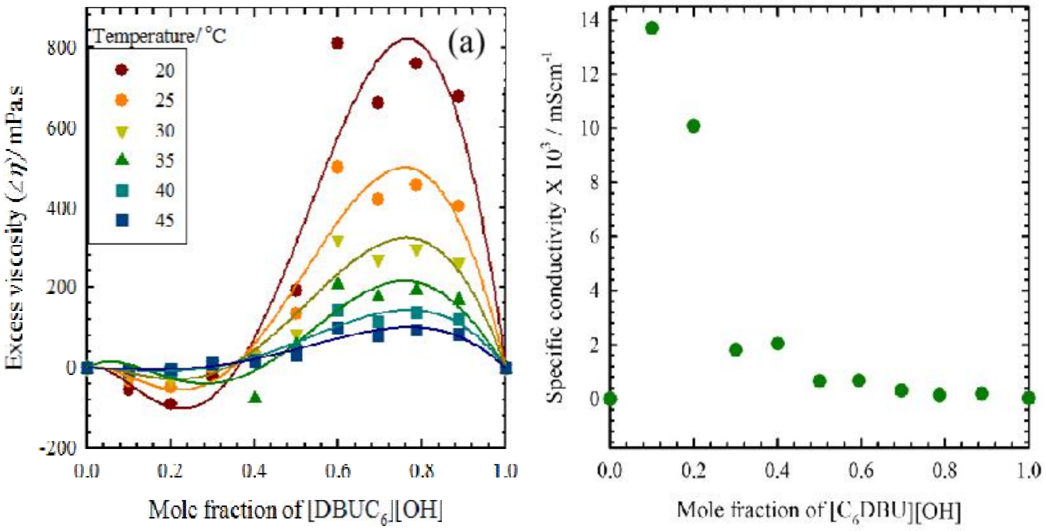

Figure 5.9. Change in (a) excess viscosityand (b) conductivitywith mole fraction of [C_6DBU][OH] for binary systems of [C_6DBU][OH] with water.

5.3.3.4. Degradation Temperature andKineticResults of Michael Addition Reaction

The degradation temperature of [C_6DBU][OH]decreasesas the mole fraction of [C_6DBU][OH] increases in the binary systems of [C_6DBU][OH] with water. This is due to the weakening of the strong electrostatic interaction betweenthe cation and the anion as the ions form H-bonds with water molecules. The ions become free for catalysis and the rate increases i.e. reaction completion time decreases. With further increase in the mole fraction of [C_6DBU][OH] ($X_{[C_6DBU][OH]} > 0.5$), the rate of the reaction decreases. This is due to the fact that in this region the hydrophilic part of the cation is pointed to the center of the self-associative arrangement (reverse micelle) of the [C_6DBU][OH] with water. Anion is also in the hydrophilic core of the reverse micelle.Moreover, with decrease of water, the interaction between cation and anion becomes stronger which is also supported by the higher value of degradation temperature. Therefore, the anion is not available for catalysis and the rate decrease.

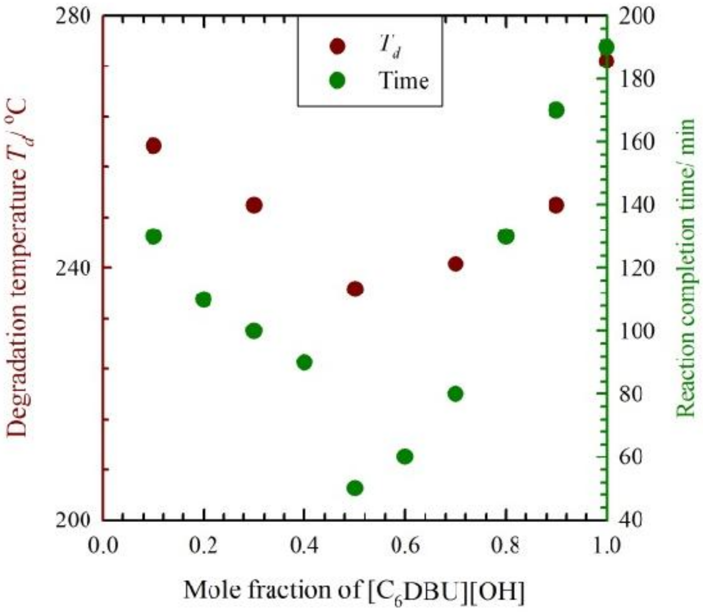

Figure 5.10. The change in degradation temperature and reaction completion time with mole fraction of [C_6DBU][OH] for binary systems of [C_6DBU][OH] with water.

5.4. Conclusions

Different physicochemical properties of protic ILs ([DBU][OH] and [DBU][CH_3COO]) and their binary systemswith water, acetic acid, and DBUare interrelated with each other. The properties correlate well with the rate of the Michael addition reaction catalyzed by these ILs and their binary systems. The change in physicochemical properties shows significantly different patterns in two regions: IL-rich and IL-deficientregion. The change in conductivity and thermal stability of the binary systems of the protic ILexplains the change in rate of reaction successfully. Similarly physicochemical properties such as spectral characteristics, particle size, thermal stability, density, viscosity, and conductivity of AIL and its binary systems with water are correlated well with each other. The change in physicochemical properties displaysdifferent self-associative structures with a transition from micelle like structure in water-rich (IL-deficient) region and reverse micelle like structure in IL-rich region. These self-associative microstructures of the binary systems of AIL in two different regions also correlate well with the rate of the Michael addition reaction. Thus, physicochemical properties of binary systems of PILs and AIL have excellent correlation with each other and with kinetic results of Michael addition reaction catalyzed by the PILs and AIL and their binary systems with water, acetic acid, and DBU.

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Abstract

Michael addition reaction of acetylacetone and 2-cyclohexene-1-one was investigated using bases (NaOH and DBU), PILs ([DBU][OH] and [DBU][CH_3COO]), the AIL ([C_6DBU][OH]), and binary systems of ILs with water, DBU, and acetic acid at room temperature and the kinetic profiles were compared. The reaction completion time was shorter for binary systems of ILs compared to that for pure ILs and bases. ILs, on the other hand, took shorter time to complete the reaction compared to bases without using any solvent. Moreover, a small amount (0.005 mmol) of IL was able to lower the reaction completion time in presence of NaOH. Thus, ILs acted as reaction medium as well as catalyst where the binary systems of ILs acted as better catalysts. The [DBU][OH] showed better catalytic behavior compared to the other PIL, [DBU][CH_3COO] and [C_6DBU][OH] exhibited the best catalytic behavior among all ILs in this study for the same Michael addition reaction.

6.1. Introduction

Michael addition reaction as described in chapter 4 (section 4.1) is an organic reaction used to convert an activated methylene and a conjugated olefin to the corresponding addition product generally using a base catalyst.ILs are low melting salts (< 100 °C) thathave attracted considerable attention as alternatives to organicsolvents in synthesis and catalysis [1-2]. Theoriginal motive for the interest in ILs as solventsfor synthesis and catalysis has been the intrinsic lack of vapor pressure. Some of the most notable results describeenhancements in chemical reactivity or catalytic performancethat result from the solvent characteristics of the IL [3-5]. The rate of Michael addition reaction is known to be changed by the basic/nucleophilic ability of the catalyst used. In case of ILs the basic nature of the anions plays the important role as catalysts for Michael addition reaction [6]. It may be worth mentioning that the effects of cations on the rate of Michael addition reaction have also been investigated [7]. As the Michael addition reaction is a nucleophilic addition reaction, it is important to produce a nucleophile by proton grabbing from active methylene compound (Michael donor) for initiating the reaction. Therefore, the catalysis process of the Michael addition reaction greatly depends on the basic or nucleophilic ability of anion.

A nucleophile is a chemical species that donates an electron pair to an electrophile to form a chemical bond in relation to reaction. All molecules or ions with a free pair of electrons or at least one π bond can act as nucleophiles. Since nucleophiles donate electrons, they are by definition Lewis bases. Nucleophilic describes the affinity of a nucleophile to the nuclei. Nucleophilicity, sometimes referred to as nucleophile strength, refers to nucleophilic character of a substance and is often used to compare the affinity of atoms. There are at least four key factors contributing to nucleophilicity. They are charge,electronegativity,solvent, andsteric hindrance.

Since a nucleophile is a species that donates a pair of electrons, it is reasonable to expect that its ability to donate electrons will increase as it becomes more electron-rich, and decrease as it becomes more electron-deficient. Nucleophilicity therefore, increases with increasing electron density on an atom.

Assuming an atom has a pair of electrons to donate, the ability of a species to donate that pair should be inversely proportional to how “tightly held” it is. The key factor for determining how “tightly held” an electron pair is bound is the familiar concept of electronegativity. As electronegativity increases, nucleophilicity decreases.

Nucleophilicity is not a property inherent to a given species; it can be affected by the medium it is in. A polar protic solvent can participate in hydrogen bonding with a nucleophile, creating a “shell” of solvent molecules around it. The lone pair of electrons of solvent is interacting with the electron-poor hydrogen atoms of the solvent. A polar aprotic solvent does not hydrogen bond to nucleophiles to a significant extent meaning that the nucleophiles have greater freedom in solution.

The bulkier the nucleophile is, the slower the rate of its reactions, i.e. the lower its nucleophilicity. So comparing several deprotonated alcohols, in the sequence methanol >ethanol>isopropanol>*t*-butanol, deprotonated methanol is the strongest nucleophile, and deprotonated *t*-butanol is the poorest nucleophile.

Michael addition is one of the most useful C–Cbond-forming reactions and has wide synthetic applicationsin organic synthesis [8-11]. Thereaction is usually catalyzedby strong bases such as alkali hydroxides or tertiary aminesthat can often result in undesirable side reactions, particularlywhen functionalized substrates are used. Transitionmetal catalysis under neutral and mild conditions can solvethese issues, and the iron(III)-catalyzed Michael addition ofketo esters to enones is one of the most prominent examplesfor iron catalysis [12, 13]. The imidazolium-based ILshave been used as solvents for transitionmetal catalyzed Michael addition [14]. Thebasic IL, 1-butyl-3-methylimidazolium hydroxide([C_4MIm][OH]) has been reported as catalyst for conjugateadditions [6].It has been found that L-proline in IL is a very good catalyticsystem for the Michael addition of aliphatic aldehydes andketones to β-nitrostyrenes [15].Michael addition of thiols to α,β-unsaturatedketones has also been catalyzed by 2:1 mixtures of [BMIm][BF_4]-H_2O and [BMIm][PF_6]-H_2Omixtures [16]. Similarly,theMichael addition ofthiols and thiophosphate to α,β-unsaturated carbonyl compounds has been catalyzed by [PMIm][Br][17].

The elucidation of mechanism necessitates the understanding of the difference between the interactions of PILs and those of AILs and thereby, it is crucial to understand the unique properties of the ILs. Quite reasonably, so far there are several reports in the literature focusing on ecotoxicity of PILs and AILs [18], thermal properties [19], physical chemistry and applications [20], physicochemical studies [21], and ionicity of ILs [22].

In spite of numerous studies, there have been no reports on the comparative study of the kinetics of the Michael addition reaction catalyzed by ILs and their binary systems with molecular solvents. To understand the mechanism of this reaction under different reaction environments, kinetic studies need to be systematically and intensively conducted in presence of PILs and AILs and their binary systems. In this work, the kinetic results of Michael addition reactionof acetylacetone and 2-cyclohexene-1-one using bases have been compared with those using pure ILs, PILs ([DBU][OH] and [DBU][CH_3COO]) and an AIL ([C_6DBU][OH]) and their binary systems with water, acetic acid, and DBU. Moreover, the kinetic results of the Michael addition reaction using PIL and its binary systems as catalysts have been compared with those using theAIL and its binary systems.

6.2. Experimental

6.2.1 Materials and Methods

All chemicals were of analytical grade and were used as received without further purification. Ultrapure water (specific conductivity is 0.055 µS cm^{-1}) was used for the preparation of the binary mixtures of the IL.

For weighing the reactants, catalyst and components for preparing binary mixtures digital microbalance UBT-110 from UNILAB, USA was used.For mixing the mixture of reactants and catalyst properly, magnetic stirrer (79-1 Magnetism Heating Mixer) was used.The reaction completion time was recorded using TLC technique.
Binary systems of ILs ([DBU][OH], [DBU][CH_3COO], and [C_6DBU][OH]) and molecular solvents (water, acetic acid, and DBU) with compositions varying from IL-rich condition to IL-deficient condition were prepared at various molar ratio by mixing appropriate amounts of ILs and molecular solvents. The mixtures required sonication to ensure homogeneous mixing.

The binary systems of the ILs with the molecular solvents were used as catalysts for the Michael addition reaction of acetylacetone and 2-cyclohexene-1-one and reaction completion time were measured by using TLC technique. Aluminum TLC plates coated with silica gel 60 F_{254} were used as the stationary phase and mixture of chloroform and *n*-hexane (1:1 by volume) was used as eluent to develop the TLC plates. UV lamp was used to locate the spots on the developed plates.

Materials used and methods followed have been described in detail in section 4.2.1.

6.3. Results and Discussion

6.3.1. Comparative Study of Michael Addition Reaction

6.3.1.1. Michael Addition Reaction using Bases and IL Systems as Catalyst

Michael addition reaction of acetylacetone and 2-cyclohexene-1-one was carried out using bases (NaOH, DBU), PILs ([DBU][OH] and [DBU][CH_3COO]) and theirbinary systems with water, acetic acid, and DBU, and AIL ([C_6DBU][OH])and its binary systems with water at room temperature (≈ 20 ^{o}C) and the catalytic performance was compared. The reaction completion time was measured by using TLC technique. In case of base, NaOH, it required large amount of ethanol to make a solution and longer time to complete the reaction. When DBU was used as the base, it required longer time to complete the reaction and it was completely miscible with both reactants. But for ILs, ([DBU][OH], [DBU][CH_3COO], and [C_6DBU][OH]), they took shorter time for completion the reaction without the use of any solvent. It is very interesting that the binary systems of the ILs took shorter reaction completion time (Table 6.1). For ILs, the rate of the reaction was approximately 1.4 times faster than that of the bases, DBU and NaOH and for binary systems of the ILs the rate of the reaction was 1.6 – 4.8 times faster than that of the organic bases.

Table 6.1. Reaction completion time and average rate for different systems as catalyst and reaction medium in the Michael addition reaction

Chemical Systems (0.5 mmol)	**Reaction Completion Time (min)**	**Average Rate (*v*) (mol L^{-1} s^{-1})×10^4**	**Observations**
NaOH	250	2.53	Long time and large amount of solvent required
DBU	240	2.63	Long time
[DBU][OH]	180	3.51	Short time and without any solvent
[C_6DBU][OH]	170	3.72	
[DBU][OH] with H_2O and DBU	110 - 120	5.27-5.94	Shorter time
[DBU][CH_3COO] with acetic acid and DBU	160-152	3.95-4.16	
[C_6DBU][OH] with H_2O	50	12.64	

Thus, pure ILs serve both as reaction medium and catalyst and the binary systems of the ILs showed better catalytic performance.

6.3.1.2.Rate of the Michael Addition Reaction in Presence of NaOH with Different Concentrations of ILs, PIL ([DBU][OH]) and AIL ([C_6DBU][OH])

Rate of the reaction between acetylacetone and 2-cyclohexene-1-one was investigated in presence of the same amount of NaOH using different concentrations of PIL and [DBU][OH] at room temperature. With addition of very small amount of [DBU][OH] the reaction completion time decreased (arrow in Figure 6.1) with the same concentration of NaOH. When the concentration of added NaOH was 0.005 mmol, the reaction completion time decreased from 390 to 300 min with the addition of 0.005 mmol of [DBU][OH] into the reaction mixtures. Thereby, the PIL, [DBU][OH] acted as a catalyst for the reaction.

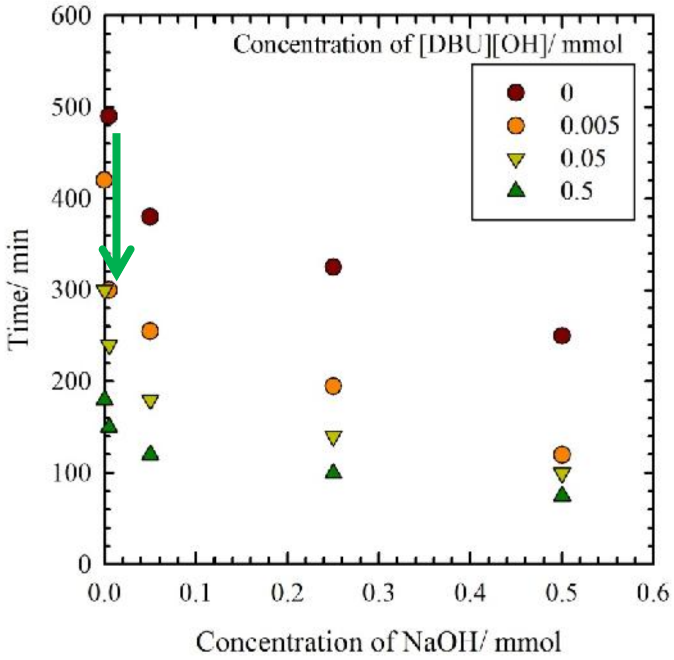

Figure 6.1. Reaction completion time for the Michael addition reaction in presence of NaOH with different concentrations of [DBU][OH].

The Michael addition reaction with the same reactants was carried out in presence of fixed amount of NaOH using different concentrations of [C_6DBU][OH] as the catalyst. With the addition of 0.005 mmol of [C_6DBU][OH], the reaction completion time decreases from 390 to 255 min (Figure 6.2). Therefore, [C_6DBU][OH] acted as better catalyst than PILs ([DBU][OH] and [DBU][CH_3COO]) for the same reaction.

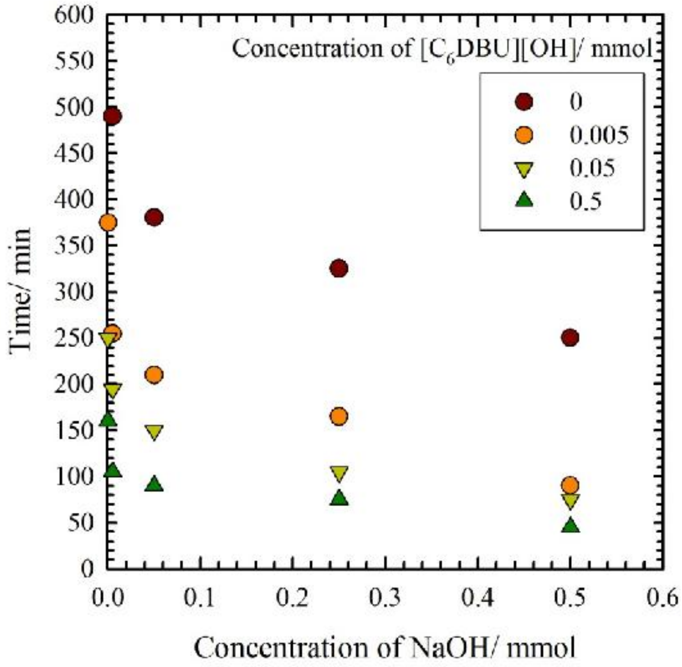

Figure 6.2. Reaction completion time for the Michael addition reaction in presence of NaOH with different concentrations of [C$_6$DBU][OH].

In case of AIL, [C$_6$DBU][OH], the study on the rate of the same Michael addition reaction using different concentrations of [C$_6$DBU][OH] with same amount of NaOH showed similar trends (decreasing reaction completion time) but the catalytic performancewas much better (detail explanation is given in the section 6.3.1.5).

6.3.1.3. Rate of the Michael Addition Reaction in Presence of [DBU][OH] and [DBU][CH$_3$COO] and their Binary Systems with Water, Acetic Acid, and DBU as Catalysts and Reaction Medium

Figure 6.3 shows the comparison of the reaction completion time with mole fraction of DBU for PILs, [DBU][OH] and [DBU][CH$_3$COO] and their binary systems with water, acetic acid and DBU. [DBU][OH] and its binary systems with water and DBU took shorter time to complete the reaction than [DBU][CH$_3$COO] and its binary systems with acetic acid and DBU. It should be noted here that both ILs, [DBU][OH] and [DBU][CH$_3$COO] are protic in nature. Here the cations (DBUH$^+$) are same in both the ILs, but the anions are different. In [DBU][OH] the anion is hydroxyl ion (OH$^-$) and in [DBU][CH$_3$COO] the anion is acetate ion (CH$_3$COO$^-$). Both the anions are Lewis base and responsible for catalysis. But the hydroxyl ion is more basic than acetate ion. The electron density on acetate ion is less as it is delocalized over the two oxygen atoms andthe bigger size of the acetate ions is also responsible to decrease the nucleophilic ability of the ion. Thus, hydroxyl anion takes H^+ more efficientlythan acetate ion. That is why the reaction completion time becomes shorter for [DBU][OH] and its binary systems than that of [DBU][CH_3COO] and its binary systems.

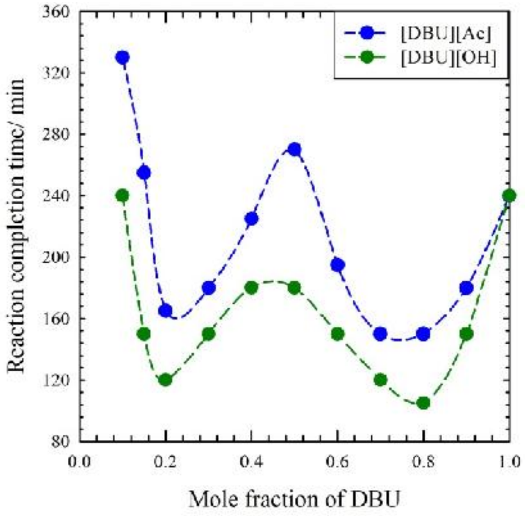

Figure 6.3. Reaction completion time as a function of mole fraction of DBU for the Michael addition reaction catalyzed by [DBU][OH] and [DBU][CH_3COO] and their binary systems with water, acetic acid, and DBU.

6.3.1.4. Kinetic Study of the Michael Addition Reaction in Presence of [DBU][OH] and [C_6DBU][OH] and their Binary Systems with Water as Catalysts and Reaction Medium

The the reaction completion time with mole fraction of ILs ([DBU][OH] and [C_6DBU][OH]) for PIL, [DBU][OH] and AIL, [C_6DBU][OH] and their binary systems with water has been compared in Figure 6.4. [C_6DBU][OH] and its binary systems showed faster rate of the reaction(shorter time to complete the reaction) than [DBU][OH] and its binary systems. It should be noted here that [C_6DBU][OH] is aprotic and hydrophobic in nature whereas [DBU][OH] is protic and hydrophilic. Here the anions (OH^-) are same in both the ILs but the cations are different. In [C_6DBU][OH] the cation is alkylated DBU, (C_6DBU^+) and in [DBU][OH] the cation is protonated DBU ($HDBU^+$). Both the anions are same and are responsible for catalysis. But cations must play a role for completion the reaction as the kinetic profiles are different for the two ILs. The interactive forces of ILs change with change in alkyl chain length and the cumulative effect of the electrostatic interaction between the ionic species and the induction interactions between the ions, aggregates, and clusters determine the properties of ILs [23]. In the present case, the carbon number in the substituent group of the cation of [DBU][OH] is 0 and [C_6DBU][OH] is 6. The packing of cations and anions in [C_6DBU][OH] is probably loose due to large size of the cation having hexyl group. Moreover the hexyl group is nonpolar and hydrophobic in nature which also disturbed the tight packing of ions. Therefore, the anion is more mobile in [C_6DBU][OH] and available for catalysis the reaction. That is why the reaction completion time becomes shorter for [C_6DBU][OH] and its binary systems than that of [DBU][OH] and its binary systems.

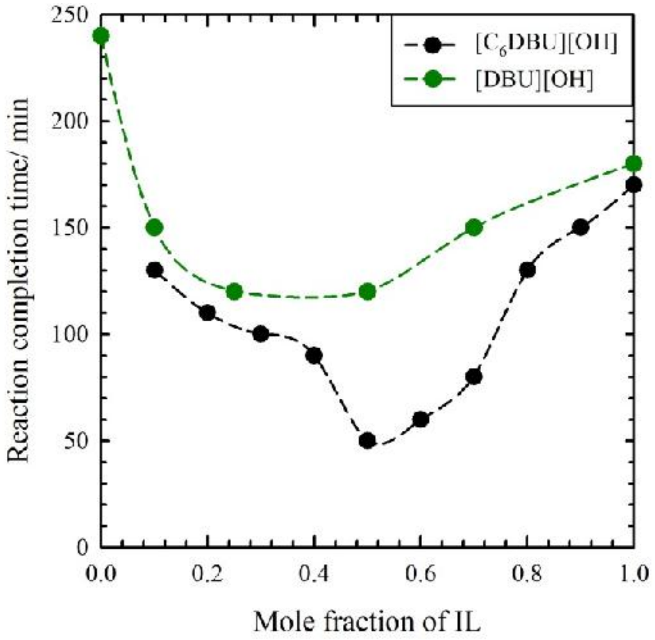

Figure 6.4. Reaction completion time with mole fraction of IL ([DBU][OH] and [C_6DBU][OH]) for the Michael addition reaction catalyzed by [DBU][OH] and [C_6DBU][OH] and their binary systems with water.

6.3.1.5. Kinetic Study of Michael Addition Reaction in Presence of[DBU][CH_3COO] and [C_6DBU][OH] and their Binary Systems with Water and Acetic Acid as Catalysts and Reaction Medium

Figure 6.5 shows the comparison of the reaction completion time with mole fraction of ILs, [DBU][CH_3COO] and [C_6DBU][OH] and their binary systems with water and acetic acid. [C_6DBU][OH] and its binary systems showed faster rate of the reactionthan [DBU][CH_3COO] and its binary systems.

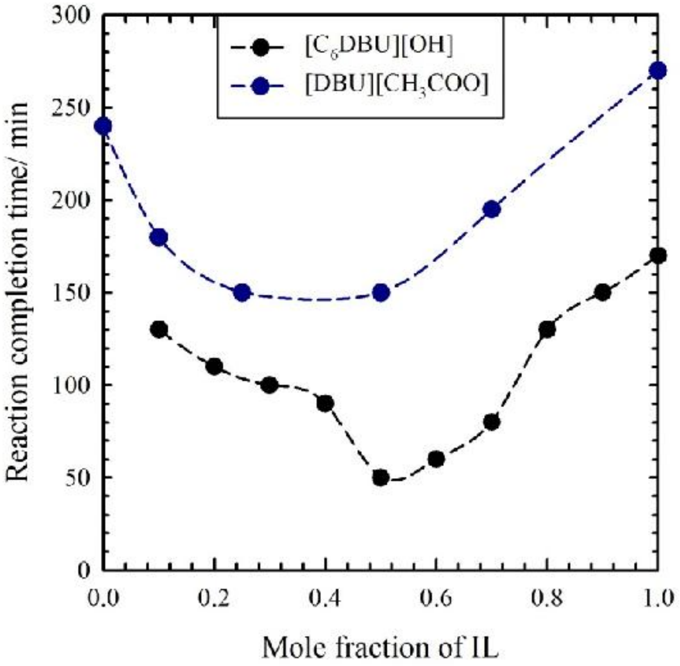

Figure 6.5. Reaction completion time with mole fraction of ILs ([C_6DBU][OH] and [DBU][CH_3COO]) for the Michael addition reaction catalyzed by [C_6DBU][OH] and [DBU][CH_3COO] and their binary systems with water and acetic acid.

It would be worth mentioning that [C_6DBU][OH] is aprotic and hydrophobic in nature whereas [DBU][CH_3COO] is protic and hydrophilic. In this case both the anions are different and the cations are also different. The OH^- ion is more basic and takes proton more easily than CH_3COO^-. Therefore, [DBU][CH_3COO] takes longer time to complete the reaction as compared to [C_6DBU][OH]. Moreover, in both the cations, the substituent groups are different. Therefore, the interactive forces between ions of the two ILs are different and effect of electrostatic interaction between the ionic species is not identical [23]. The anion in [C_6DBU][OH] may be more mobile and available for catalysis due to large size of the cation and nonpolar substituent in the cation. Thus, [C_6DBU][OH] and its binary systems showed better catalytic performance for Michael addition reaction than [DBU][CH_3COO] and its binary systems.

6.4. Conclusions

Pure ILs ([DBU][OH], [DBU][CH_3COO], and [C_6DBU][OH]) exhibit better catalytic performance than bases (NaOH and DBU) for Michael addition reaction without using any organic solvent. Pure ILs are also good reaction medium for the reaction. It is interesting that the binary systems of the ILs with water, acetic acid, and DBU show better catalytic perfomance than pure ILs. Among the PILs, [DBU][OH] shows faster rate of the reaction has been shown by [DBU][OH] and its binary systems as compared to [DBU][CH_3COO] and its corresponding binary systems.The rate of the Michael addition reaction is the fastest for the AIL, [C_6DBU][OH] among all the ILs used in this study.

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7.1 General Conclusions

The neutralization reaction between an organic base, 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) with water and acetic acid gives (1,8-diazabicyclo[5.4.0]-undec-7-ene-8-ium hydroxide, [DBU][OH] and 1,8-diazabicyclo[5.4.0]-undec-7-ene-8-ium acetate, [DBU][CH_3COO]) which are protic in nature and are liquid at room temperature and possess unique characteristics of ILs like good thermal stability, good ionic conductivity, outstanding dissolving ability etc. Alkylation of DBU followed by anion metathesis also gives a novel IL which is aprotic in nature. Thus, an AIL based on DBU can also be successfully synthesized which shows exclusive features of ILs. The computational study based on DFT best describes the structure and spectral results of the AIL.The physicochemical properties of the pure ILs and their binary systems with molecular solvents varywith the nature of the ILand composition. A range of attractive interactions for instances, van der Waals, dispersion, Coulombic, hydrogen bonding etc. are dominant to determine the properties of theILs. In presence of molecular solvents hydrogen bonding and ion-dipole interactions dominate which induce strong association or self-assemblyto make them primarily responsible for differences in physicochemical properties.

The protic ILs, [DBU][OH] and [DBU][CH_3COO], and aprotic IL, [C_6DBU][OH] in their pure form and their binary systemswith water, acetic acid, and DBUcatalyze a model organic reaction. Michael addition reaction occurs with high yield(74-80%)without using any hazardous organic solvent.The catalytic performance of the binary systems of ILswith water, acetic acid, and DBU is better than that of pure ILs. It requires very small amount of the ILs and thereby serves as a catalyst and no volatile solvent is requiredfor the synthesis for high yield of the product. Therefore,the binary systems of ILs with molecular solvents makethe synthesis environmentally benign and less expensive.

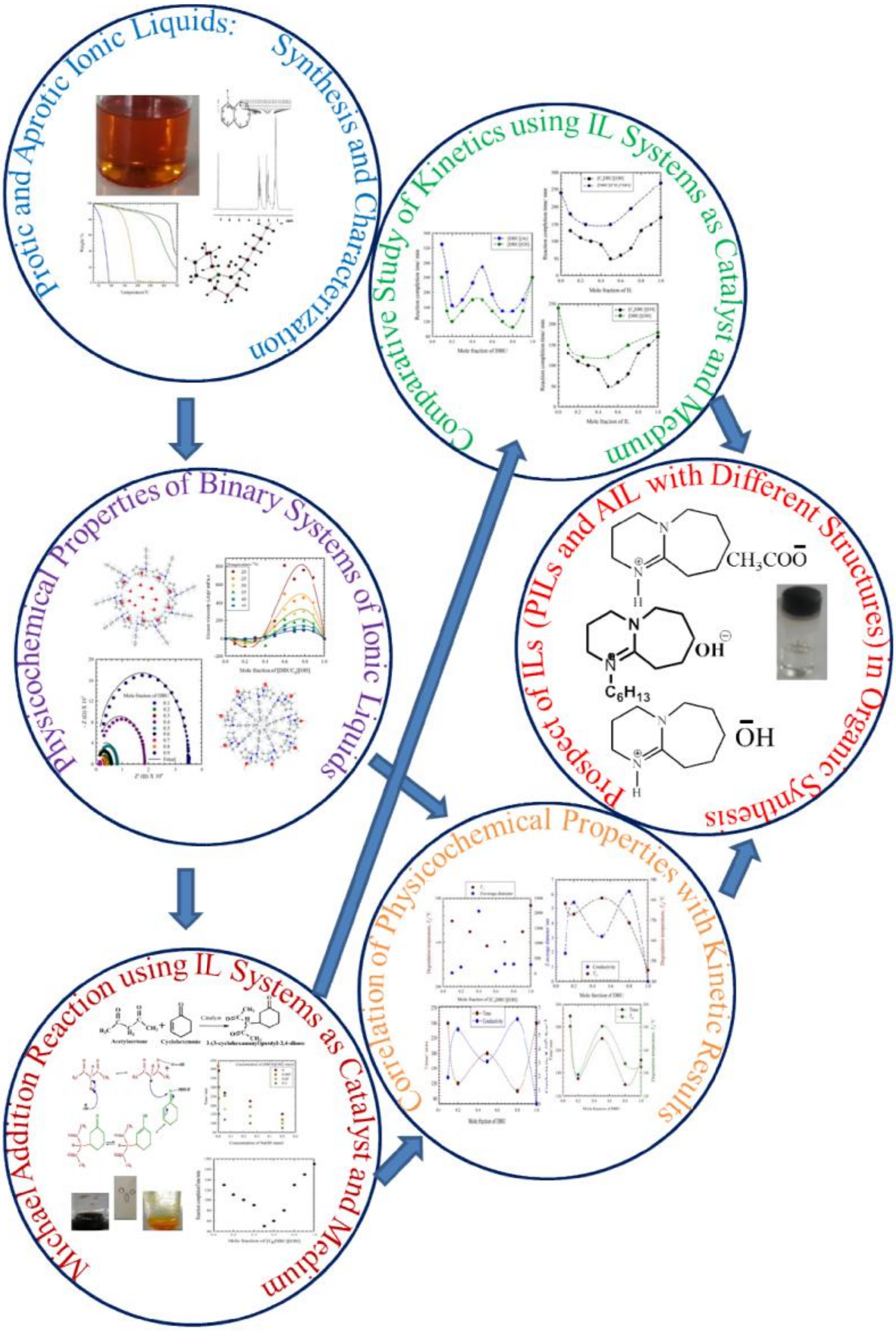
The physicochemical properties of the ILs and their binary systems show excellent correlation with each other and also with the kinetic results of the Michael addition reaction catalyzed by these ILs and their binary systems. Thus the variation of the physicochemical properties determines the role to be played by the ILs and their binary systems with molecular solvents in the mechanism of the catalysis of the Michael addition reaction at molecular level. The comparative study of the kinetics of

Michael addition reaction shows that AIL has better catalytic performance than PILs and in the PILs, [DBU][OH] plays better role as a catalyst as compared to [DBU][CH_3COO].Therefore, we can design ILs and their binary systems for task-specific applications, especially, in organic synthesis.

7.2 Outlook

The DBU serves as an excellent organic base for preparation of both protic and aprotic ILs. The structure of the anion may be widely varied and the DBU may be derivatized with variation of alkyl chain length to prepare a series of ILs both protic and aprotic ILs. The ILs can be solubilized in both polar and nonpolar solvents and therefore binary systems with tunable properties may be prepared from the ILs.The problems associated with pure ILs in few instances like high viscosity, lower conductivity, storage difficulty, high cost etc may be overcome by the use of such binary systems. Moreover, long chain alkyl substituted ILs can form self-associated microstructures as they show surfactant like behavior and can form microemulsion without using conventional surfactants. As they are miscible with both the polar and nonpolar substrate, they have therefore a bright prospect in the field of organic synthetic chemistry as reaction media and catalyst and they can be a suitable candidate for versatile applications in environmentally friendly organic synthetic process, pharmaceutical industry, pollution control and new kind ofnovel reaction media.

The synthesis of the PILs and the AIL based on DBU, their characterization and correlation of the physicochemical properties for exploitation of the potential for organic synthesis using a model Michael addition reaction is schematically presented in Scheme 7.1. The properties of task-specific ionic liquids may thus be tuned by designing novel ionic liquids and their binary systems with molecular solvents for use as catalysts and media in organic synthesis.



Scheme 7.1 Prospect of novel IL-based systems as catalysts and media for organic synthesis.

Table A1

Experimental density (ρ), viscosity(η), refractive index (n), excess molar volume (V^E), excess viscosity ($\Delta\eta$), and excess refractive index(Δn) of[C_6DBU][OH]-H_2O binary mixturesat several temperatures.

$X_{[C6DBU][OH]}$	ρ/ gcm^{-3}	η/ mPa.s	n	V^Ex10^6/m^{3}mol^{-1}	$\Delta\eta$/ mPa.s	Δn
20 °C						
0.0000	0.9987	1.0080	1.3331	0.0000	0.0000	0.0000
0.1003	1.0129	27.619	1.4312	-0.2810	-54.606	0.0895
0.1996	1.0157	73.234	1.4563	-0.4825	-89.399	0.0916
0.3004	1.0453	252.26	1.4795	-2.9873	-18.995	0.0989
0.4005	1.0386	352.90	1.4847	-3.0359	27.590	0.0882
0.5006	1.0218	598.38	1.4881	-1.5267	192.02	0.0758
0.5981	1.0474	1293.2	1.4958	-5.4482	870.89	0.0680
0.6961	1.0303	1223.9	1.4953	-3.4042	659.23	0.0520
0.7868	1.0320	1509.8	1.4956	-4.0916	758.09	0.0379
0. 8875	1.0222	1396.2	1.4949	-2.4932	676.55	0.0240
1.0000	1.0107	810.75	1.4915	0.0000	0.0000	0.0000
25 °C						
0.0000	0.9976	0.8954	1.3326	0.0000	0.0000	0.0000
0.1003	1.0097	21.845	1.4298	-0.2515	-31.191	0.0883
0.1996	1.0121	55.441	1.4546	-0.4350	-49.215	0.0907
0.3004	1.0418	156.95	1.4779	-2.9621	-0.1067	0.0981
0.4005	1.0352	240.29	1.4831	-3.0273	31.197	0.0875
0. 5006	1.0184	397.33	1.4864	-1.5072	136.20	0.0752
0.5981	1.0440	811.49	1.4941	-5.4507	499.68	0.0675
0.6961	1.0269	780.33	1.4934	-3.4061	417.571	0.0514
0. 7868	1.0287	959.90	1.4939	-4.1080	455.34	0.0377
0. 8875	1.0189	865.25	1.4934	-2.5030	402.99	0.0239
1.0000	1.0074	520.74	1.4898	0.0000	0.0000	0.0000
30 °C						
0.0000	0.9962	0.8027	1.3320	0.0000	0.0000	0.0000
0.1003	1.0064	17.499	1.4287	-0.2215	-18.052	0.0870
0.1996	1.0088	43.139	1.4533	-0.4060	-26.815	0.0901
0.3004	1.0383	112.77	1.4763	-2.9395	7.8945	0.0974
0.4005	1.0318	171.19	1.4815	-3.0139	31.635	0.0869
0. 5006	1.0149	259.47	1.4848	-1.4845	85.236	0.0747
0.5981	1.0406	528.92	1.4924	-5.4548	320.91	0.0671
0.6961	1.0236	513.37	1.4920	-3.3992	271.41	0.0514
0. 7868	1.0254	627.55	1.4923	-4.1103	297.61	0.0375
0. 8875	1.0156	571.00	1.4917	-2.5005	262.73	0.0238
1.0000	1.0041	347.25	1.4881	0.0000	0.0000	0.0000

			35 ^{o}C			
0.0000	0.9946	0.7252	1.3314	0.0000	0.0000	0.0000
0.1003	1.0031	14.042	1.4344	-0.1939	-11.252	0.0859
0.1996	1.0053	34.350	1.4524	-0.3718	-15.268	0.0901
0.3004	1.0347	83.534	1.4747	-2.9085	9.2244	0.0967
0.4005	1.0284	123.89	1.4798	-2.9938	-74.939	0.0863
0. 5006	1.0116	181.89	1.4833	-1.4535	58.540	0.0743
0.5981	1.0371	355.84	1.4908	-5.4404	208.61	0.0667
0.6961	1.0203	347.45	1.4904	-3.3951	176.212	0.0511
0. 7868	1.0221	423.39	1.4907	-4.1172	193.38	0.0374
0. 8875	1.0123	386.84	1.4901	-2.4983	168.72	0.0238
1.0000	1.0009	245.68	1.4864	0.0000	0.0000	0.0000
			40 ^{o}C			
0.0000	0.9927	0.6599	1.3307	0.0000	0.0000	0.0000
0.1003	0.9997	11.306	1.4395	-0.1675	-6.768	0.0840
0.1996	1.0017	27.731	1.4556	-0.3340	-7.584	0.0941
0.3004	1.0312	63.371	1.4731	-2.8922	10.556	0.0961
0.4005	1.0249	91.969	1.4782	-2.9770	21.774	0.0858
0. 5006	1.0081	130.78	1.4818	-1.4267	43.206	0.0740
0.5981	1.0338	249.23	1.4891	-5.4639	144.73	0.0662
0.6961	1.0169	236.15	1.4888	-3.4026	114.63	0.0508
0. 7868	1.0187	294.55	1.4891	-4.1348	137.48	0.0372
0.8875	1.0089	274.74	1.4885	-2.5119	119.99	0.0237
1.0000	0.9976	174.28	1.4847	0.0000	0.0000	0.0000
			45 ^{o}C			
0.0000	0.9907	0.6045	1.3299	0.0000	0.0000	0.0000
0.1003	0.9964	9.1548	1.4345	-0.1469	-4.1733	0.0818
0.1996	0.9982	22.329	1.4579	-0.3036	-3.5959	0.0974
0.3004	1.0276	49.294	1.4716	-2.8686	10.582	0.0957
0.4005	1.0214	70.084	1.4766	-2.9595	18.674	0.0854
0. 5006	1.0046	96.303	1.4804	-1.3983	32.195	0.0738
0.5981	1.0303	177.77	1.4874	-5.4580	101.29	0.0659
0.6961	1.0136	169.27	1.4872	-3.4024	80.361	0.0506
0.7868	1.0154	211.61	1.4874	-4.1531	96.366	0.0370
0.8875	1.0057	196.78	1.4868	-2.5193	83.593	0.0236
1.0000	0.9943	127.46	1.4831	0.0000	0.0000	0.0026

List of Publications

1. Kumkum Ahmed, AnikaAuni, **GulshanAra**, M. MuhiburRahman, M. Yousuf A. Mollah, Md. Abu BinHasan Susan; "Solvatochromic and fluorescence spectroscopic studies on polarity of ionic liquid and ionic liquid-based binary systems"; *Journal of Bangladesh Chemical Society,* 2012, 25, 146-158.

2. LailaArzuman, SadiaNazninKarobi, M. Jahirul Islam, **GulshanAra**, M. MuhiburRahman, M. Yousuf A. Mollah, Md. Abu BinHasan Susan; "Effect of urea on the kinetics of the alkaline hydrolysis of crystal violet catalyzed by aqueous micellar solutions of cetyltrimethylammonium bromide"; *Taylor & Francis*, 2013, 45, 764-769.

3. **GulshanAra**, Md. Mominul Islam, Md.Yousuf Ali Mollah and Md. Abu Bin Hasan Susan, "Synthesis of Aprotic Ionic Liquids Derived from 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) and Characterization", in preparation.

List of Attended Workshops and Seminars

1. Workshop on "Preparation and Characterization *ofNovel Functional Materials with Emphasis on Electrochemistry"*, organized by the sub-project: Development of Novel Functional and Smart Materials for Technological Applications(CP 231) under the Higher Education Quality Enhancement Project (HEQEP) of the University Grants Commission (UGC) Bangladesh, 16 February, 2012.

2. Workshop on *Characterization and Application ofNovel Functional Materials*, organized by the sub-project: Development of Novel Functional and Smart Materials for Technological Applications(CP 231) under the Higher Education Quality Enhancement Project (HEQEP) of the University Grants Commission (UGC) Bangladesh, 31 August and 01 September, 2013.

3. Seminar on *Air Quality and Its Consequence: Bangladesh Perspective,* organized by Establishing Air Quality Monitoring Centre (CP-2196), Dhaka, Bangladesh, 28 December, 2013.

4. Seminar on *3D Gel Printer and Future Life Innovation*, organized by the Material Chemistry Research Laboratory, Department of Chemistry, University of Dhaka, Dhaka, 30 August, 2015.

Abstracts Published as Contribution in the Scientific Meetings

1.GulshanAra, Md. Mominul Islam, Md. Yousuf A. Mollah, and Md. Abu Bin Hasan Susan, *"Michael Addition Reaction of Acetylacetoe and Cyclohexene Catalysed by Organic Bases and Ionic Liquid"* International Conference on Materials Chemistry (ICMC-2014), Shahjalal University of Science and Technology,Sylhet, Bangladesh, December 06, 2014 (Poster presentation).

2. GulshanAra, Md. Mominul Islam, Md. Yousuf A. Mollah, and Md. Abu Bin Hasan Susan, *Michael Addition Reaction of Acetylacetone and CyclohexenoneCatalysed by an Ionic Liquid and Its Binary Mixtures with Strong Base and Watert*, 37th Annual Conference of Bangladesh Chemical Society (ACBCS), 37th Annual Conference of Bangladesh Chemical Society (ACBCS), 11 April, 2015, Comilla University, Comilla, Bangladesh (Oral presentation).

3.GulshanAra, Md. Mominul Islam, Md. Yousuf A. Mollah, and Md. Abu Bin Hasan Susan, *Michael Addition Reaction of Acetylacetone and CyclohexenoneCatalysed by Ionic Liquids and Their Binary Systems*, 16thAssian Chemical Congress (16 ACC), held on 16-19 March, 2016, Dhaka, Bangladesh (Oral presentation).

4. GulshanAra, Md. Mominul Islam, Md.Yousuf Ali Mollah and Md. Abu Bin Hasan Susan, *Protic Ionic Liquids and Their Binary Systems as Catalyst and Reaction Medium for Michael Addition Reaction of Acetylacetone and Cyclohexenone*, 1st Symposium on Chemistry for Global Solidarity 2016, held on 02 September, 2016 in the Department of Chemistry, Jagannath University, Dhaka, Bangladesh (Oral presentation).

5. GulshanAra, Md. Mominul Islam, Md.Yousuf Ali Mollah and Md. Abu Bin Hasan Susan, *Protic Ionic Liquids and Their Binary Systems for Michael Addition Reaction of Acetylacetone and Cyclohexenone,* 3rd International Conference of Kathmandu

Symposia on Advanced Materials (KaSAM 2016), held on 17-20 October, 2016, Pokhara, Nepal (Poster presentation).

6. **GulshanAra**, Md. Mominul Islam, Md.Yousuf Ali Mollah and Md. Abu Bin Hasan Susan, *Synthesis of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) Based Aprotic Ionic Liquid and Study of Physicochemical Properties of its Binary Mixtures with Water,* Conference on Material Science and Nano-electrochemistry (CMSN-2017), held on 8-9 April, 2017, Rajshahi University, Rajshahi, Bangladesh (Oral Presentation).

7. **GulshanAra**, *Ionic Liquids and their Binary Systems with Water in Organic Synthesis*, Commonwealth Science Conference (CSC-2017), held on 13-16 June 2017 in Singapore (Poster Presentation).