IONIC LIQUIDS: MESURING THERMOSOLVATOCHROMISM AND HAMMETT ACIDITY FUNCTION AND UNDERSTANDING KINETICS OF ORGANIC REACTIONS

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FOR THE DEGREE OF
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IN CHEMISTRY

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CERTIFICATE

This is to certify that the work incorporated in this thesis entitled, "**Ionic liquids: Measuring thermosolvatochromism and Hammett acidity function and understanding kinetics of organic reactions**" submitted by **Mr. Shashi Kant Shukla**, for the degree of **Doctor of Philosophy** to **Savitribai Phule Pune University**, was carried out by the candidate under my supervision in the Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Pune 411008, India. Any material that has been obtained from other sources has been duly acknowledged in the thesis.

Date:

Place: Pune

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(Research Guide)

DECLARATION

I, Mr. Shashi Kant Shukla, hereby declare that the work incorporated in the thesis entitled "**Ionic liquids: Measuring thermosolvatochromism and Hammett acidity function and understanding kinetics of organic reactions**" submitted by me to **Savitribai Phule Pune University** for the degree of **Doctor of Philosophy** is original and has not been submitted to this or other University or Institution for the award of Degree or Diploma. Such material, as has been obtained from other sources has been duly acknowledged.

Date:

Place: Pune

Shashi Kant Shukla

Dedicated to my parents,

Parent-in-laws

my wife "Priya"

and

to my lovely daughter "Unnati"

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"Gratitude is the most exquisite form of courtesy." – Jacques Maritani

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Shashi Kant Shukla

Abstract

THERMOSOLVATOCHROMISM AND HAMMETT ACIDITY FUNCTION AND UNDERSTANDING KINETICS OF ORGANIC REACTION

Solvent and solute are ubiquitous in nature. The most interesting phenomena in living and non-living worlds are mediated by the solvent. The *solvent effects* on various processes are defined in terms of *solvent polarity* which includes all specific and non-specific interactions excluding those which leads definite chemical alterations. These include coulombic, hydrogen bonding, hydrogen bond donor, hydrogen bond acceptor, and dispersion forces. The efficacy of a solvent depends on the intensity of these forces. The hazards caused by the use of volatile organic compounds (VOCs), due to of their volatility and non-recyclability, contribute to disturb ecological balance. Several attempts have been made in this direction and the use of green solvents, which produces least damage to the environment have become very popular under the branch *Green Chemistry*. In these views, several alternatives to these VOCs such as water, ionic liquid, supercritical fluid, and eutectic solvents are being explored as solvents in various processes.

The present thesis is an attempt to understand the solvation behavior of protic ionic liquid, and their implications on the dissociation mechanism of carboxylic acids and on the rate and selectivity of Diels-Alder reaction. The observations and the conclusions derived from the experimental results depict an interesting dependence on the physicochemical properties of protic ionic liquid. The whole thesis is divided into the eight chapters.

Chapter 1 encompasses the critical literature survey made in the area of current studies and includes synthesis of ionic liquid, properties, and their applications in various fields. In order to enhance the applicability of ionic liquids to a variety of problems, an understanding of ionic liquids and their interactions with other solvents is necessary. The physical properties of ionic liquids like polarity, acidity, viscosity, density, melting and boiling points are essential before using them for several applications. In this dissertation, an effort has been to concentrate on thermosolvatochromism, Hammett acidity function and kinetics of Diels-Alder reactions. A critical review of the work carried out by different authors is presented.

The objectives undertaken in the thesis, based on the literature survey of the solvent effects, are discussed in **Chapter 2**. The principal approach employed to measure the influence of solvation are also discussed in short.

The various experimental techniques used for the measurement of polarity, viscosity, Hammett acidity and kinetic study of Diels-Alder reaction are enumerated in **Chapter 3**. This also includes synthesis of different ILs and their characterizations by ^{1}H NMR, Karl-Fisher coulometer and Volhard titration.

The solute/solvent interactions based on the thermosolvatochromic study in different PILs is discussed in **Chapter 3**. The PILs which are used for the thermosolvatochromism includes, 1-methylimidazolium ($[HmIm]^+$) and 1-butylimidazolium ($[HbIm]^+$) cations with bisulphate (HSO_4^-), formate ($HCOO^-$), acetate (CH_3COO^-), and propionate ($CH_3CH_2COO^-$) anions. Polarity (E_T^N) and different polarity parameters such as hydrogen bond donor acidity (α), hydrogen bond accepter basicity (β), and polarity index (π^*) values of PILs were measured by using solvatochromic probes- Reichardt's dye (30), Reichardt's dye (33), *N,N*-diethyl-4-nitroaniline, and 4-nitroaniline between 298 to 338 K. A constant polarity was observed for PILs within the experimental temperature range 298 to 338 K. Contrary to the protic solvents and aprotic ionic liquids, polarity of PILs depends on the basicity of anion. Highly basic anion binds strongly with counterpart cation and therefore controls polarity. The strong interaction between cation and anion leads polarization of anion and therefore develops covalent character in ionic liquids and thereby lowers polarity according to the Fazans' theory of polarization.

The Hammett acidity determination of different carboxylic acids in PILs, water, and their binary mixtures has been discussed in **Chapter 5** which involves two sections.

Section 5.1 is aimed towards the Hammett acidity (H_0) measurement of carboxylic acids ($HCOOH$, CH_3COOH, and CH_3CH_2COOH) in PILs, water, and their binary mixtures. The PILs which are used in the current work comprise of 1-methylimidazolium ($[HmIm]^+$), 1-butylimidazolium ($[HbIm]^+$), 1-methylpyrrolidinium ($[HPyrr]^+$), and 1-methylpiperidinium ($[HPyrd]^+$) cations and formate ($HCOO^-$), acetate (CH_3COO^-), and propionate ($CH_3CH_2COO^-$) anions. A reverse order of H_0 for carboxylic acids in PILs was observed than that of water. However, the higher strength of carboxylic acids in PILs was independent of different structural and electronic features. The unusually higher strength of weak acids in PILs was noted to affect by the more specific hard soft acid base (HSAB) interactions between conjugate base of carboxylic acid and conjugate acid of PIL cation.

Section 5.2 includes the H_0 of carboxylic acids (HCOOH, CH_3COOH, and CH_3CH_2COOH) in the binary mixtures of PILs and water. The H_0 was noted to vary with the composition of PIL and nature of carboxylic acid. Any change in the composition of the solvation shell of solute leads an abrupt change in the property. The interactions between solvents always result a new medium called a "pseudosolvent". The properties of the pseudosolvent depend the component which preferentially solvate the indicator. The H_0 values for HCOOH increase with the addition of PIL in water. This indicates the dominant role of PIL in governing the acidity. The H_0 values at binary compositions were noted higher than that of pure component. The higher H_0 values at binary compositions suggest the involvement of pseudosolvent having characteristic similar to that of PIL. The positive deviation in the H_0 becomes negative with the increase in concentration of CH_3COOH at fixed binary composition. For CH_3CH_2COOH, the H_0 values were noted to vary with the addition of PIL in water. The deviation in H_0 values depends on the difference in the H_0 values of pure components.

The effects of ionic strength and temperature on H_0 in PIL systems are discussed in **Chapter 6**. The chapter is divided into two sections.

In **Section 6.1** effect of inorganic salts on the Hammett acidity in binary mixture of PILs and water is discussed. The PILs which are used for investigating the effect of NaCl, Na_2SO_4, $MgCl_2$, and $MgSO_4$ includes [HmIm][HCOO], [HPyrr][HCOO], and [HPyrd][HCOO]. The behavior of salt in controlling the H_0 varies with the concentration of PIL in water. At lower concentration of PIL, all salts, except $MgSO_4$ was noted to decrease H_0, while, at higher concentration all salts acted as salting out agent and promote H_0. The Hofmeister ordering of different salt ions on the H_0 was disobeyed in binary mixtures of PIL and water. The Hofmeister series effects on the H_0 were noted with "free ion" concentration obtained from the ion speciation rather than that of total ion concentration.

The effect of mixed ions (common and uncommon ions) on the H_0 is observed to follow the Youngs' cross square rule (YCSR). The YCSR rule helps in predicting the H_0 in binary salt mixtures with uncommon ion by using the knowledge of the H_0 change in binary salt mixtures with a common ion.

Thermal effects on the H_0 of aliphatic carboxylic acids in different PILs are discussed in **Section 6.2**. An Arrhenius-type of equation, based on the linear relation between ln H_0 and $1/T$, is used to measure the activation energy of proton transfer, $E_{a,H+}$. The $E_{a,H+}$ denotes the solvation of proton by medium and is noted to decrease with the increasing concentration of carboxylic acid.

Thermodynamic parameters assist in understanding the solute-solvent interactions. In this connection, thermodynamic parameters (ΔH^0 and ΔS^0) for HCOOH, CH_3COOH, and CH_3CH_2COOH were determined in the [HmIm][HCOO], [HPyrr][HCOO], and [HPyrd][HCOO]. A novel method using indicator-overlapping technique is employed for the measurement of thermodynamic parameters. Contrary to the small standard enthalpy change (ΔS^0) for carboxylic acid in water, very large ΔS^0 is noted in PILs. An inverse polarity order of PILs was observed effective in the dissociation of carboxylic acid.

Chapter 7 deals with the kinetics of Diels-Alder reaction between cyclopentadiene and methylacrylate in [HmIm][HCOO], [HPyrr][HCOO], [HPyrd][HCOO], [HbIm][HCOO], [HmIm][HSO_4] and in the equimolar mixtures of [HPyrr][HCOO] + CH_3OH and [HmIm][HCOO] + CH_3OH. PILs are amphiphilic in nature and have hydrogen bonding tendency similar to water, therefore can be a promising solvent for executing the Diels-Alder reaction. However, the observed rate constant and endo/exo ratio suggest lower acceleration in PILs than that in water. In PILs rate constant (k_2) for the Diels-Alder reaction depends on the hydrogen bond donor acidity (α) and viscosity (η).

Chapter 8 summarizes the principal conclusions from the research work. The following are the significant contributions from the working chapters,

1. Polarity of protic ionic liquids depends on the basicity of anion,

2. Hammett acidity of carboxylic acids in protic ionic liquids depends on the specific interactions between the conjugate base of carboxylic acid and conjugate acid of protic ionic liquids,

3. In binary systems of protic ionic liquid and water, Hammett acidity varies according to the relative difference between the Hammett acidities of pure components,

4. The Hammett acidities of aromatic carboxylic acids vary with the nature of substituent,

5. Hammett acidity of carboxylic acids in salt solutions depends on the availability of "free ions" rather than their Hofmeister ordering,

6. Thermal effect affects solvation of indicator, thus change Hammett acidity and

7. The catalytic ability of protic ionic liquids in accelerating Diels-Alder reaction is masked by their viscosity.

List of Acronyms/Abbreviations*

[HmIm]	1-methylimidazolium
[HbIm]	1-butylimidazolium
[HPyrr]	1-methylpyrrolidinium
[HPyrd]	1-methylpiperidinium
[EMIm]	1-ethyl-3-methylimidazolium
[BMIm]	1-butyl-3-methylimidazolium
[HMIm]	1-hexyl-3-methylimidazolium
[OMIm]	1-octyl-3-methylimidazolium
[OP]	1-octylpyridinium
$[HSO_4]$	bisulphate
[HCOO]	formate
$[CH_3COO]$	acetate
$[CH_3CH_2COO]$	propionate
$[BF_4]$	tetrafluoroborate
$[PF_6]$	hexafluorophosphate
$[N(Tf)_2]$	bis(trifluoromethylsulphonyl)imide
$N(CN)_2$	dicyanamide
$[NO_3]$	nitrate
$[H_2PO_4]$	dihydrogenphosphate
HSAB	hard-soft acid-base principle
ICT	intramolecular charge transfer
YCSR	Youngs' cross square rule

(*common acronyms/abbreviations only)

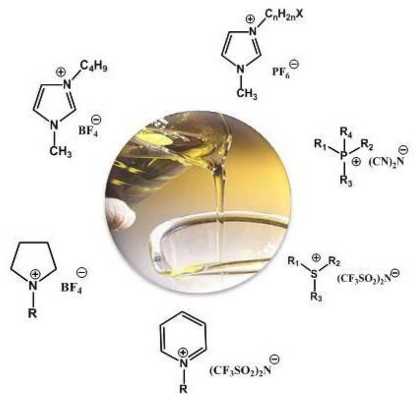
List of Symbols†

$E_T(30)$	Electronic transition energy of Reichradts'dye (30), kcal mol^{-1}
$E_T(33)$	Electronic transition energy of Reichradts'dye (33), kcal mol^{-1}
$E_T(\mathrm{NR})$	Electronic transition energy of Nile red dye, kcal mol^{-1}
E_T^N	Normalized E_T scale
α	Hydrogen bond donor acidity
β	Hydrogen bond acceptor basicity
π^*	Polarity index
ε	Relative permittivity
H_0	Hammett acidity
$H_{0,\mathrm{rel}}$	Relative Hammett acidity
$E_{a,H+}$	Activation energy of proton transfer, kcal mol^{-1}
η	Viscosity, cP/mPa s^{-1}
E_a	Activation energy, kcal mol^{-1}
$\Delta^{\#}H$	Enthalpy of activation, J mol^{-1}
$\Delta^{\#}S$	Entropy of activation, J mol^{-1}
ΔH^0	Standard enthalpy change, kJ mol^{-1} K^{-1}
ΔS^0	Standard entropy change, kJ mol^{-1}
$\Delta_{\mathrm{hyd}}G$	Gibbs' free energy of hydration, kJ mol^{-1}
$\Delta_{\mathrm{hyd}}S$	Molar entropy of hydration, J K^{-1} mol^{-1}
k_2	Second order rate constant, M^{-1} s^{-1}
λ	Wavelength, nm
K_a	Dissociation constant of weak acid
γ	Activity coefficient
Γ	Transfer activity coefficient
T	Temperature, K

(†common symbols only)

"If there's a book you really want to read but it hasn't been written yet, then you must write it."- Toni Morrison

1.1: Introduction



"Environment" is a polycentric and multifaceted problem influencing the human life. The literal meaning of environment is surrounding. Man is nature's the best promise and worst enemy. In order to make progress in society, the development of industry is essential and hence pollution is inevitable. It is seen that in both developed and developing countries, progress and pollution go hand in hand, and since it cannot be avoided, it is impossible to avoid pollution in our environment. The protection of environment is thus, a global issue.

Environmental pollution is "the contamination of the physical and biological components of the earth/atmosphere by pollutants at a rate higher than that required to assimilate them". This causes damage and adversely affects normal environmental processes. The environmental pollution can be borne either by air, water, or earth. The pollution is transboundary in nature *i.e.* it spreads in all directions and do not recognize boundaries.

Out of several pollutants which create pollution such as, fossil fuels, power generating plants, petroleum refineries, petrochemical plants, and so on; pollution by chemicals produces permanent damage to the environment. The devastating action of chemicals on ecosystem was outlined by Rachel Carson, a marine biologist and conservationist, in her book *Silent Spring* in 1962.[1] In 1970, U.S. Environmental Protection Agency (EPA) was established for protecting human health and environment. In 1990, Pollution Prevention Act (PPA) was established. The philosophy behind PPA was to avoid the creation of pollution whenever and wherever possible. The different approaches used to prevent the pollution, are:

- Pollution should be prevented at the source,
- if cannot be prevented at source should be reduced at the source,
- if cannot be prevented or reduced should be recycled in an environmentally safe manner,
- if cannot be recycled should be treated in an environmentally safe manner, and
- the disposal into the environment should be least preferred and should be conducted in an environmentally safe manner.

The pioneering contributions of Trost and Sheldon have laid the foundation of "Green Chemistry". Trost has developed the atom-economy principle, while Sheldon devised E Factor for the environmental acceptability of the chemical processes. The E Factor represents the actual amount of waste produced during a chemical change and includes solvent loss, reagents, all process aids and even fuel. The ideal E Factor is zero. The E Factors in various segments of chemical industries are shown in Table 1.1.

Table 1.1: E Factors in the Chemical Industry.

industry segment	**volume (tons/annum)**[a]	**E factor (kg waste/kg product)**
Oil	10^5 - 10^8	< 0.1
Bulk chemicals	10^4 – 10^6	< 1-5
Fine chemicals Industry	10^4 - 10^2	5 - > 50
Pharmaceutical Industry	10 - 10^3	25 - > 100

[a]Annual production of the product world-wide or at a single site

Unlike E Factors, atom efficiency or atom economy is a theoretical number *i.e.* it assumes 100 % conversion of the product and excludes those which do not appear in the stoichiometric ratio.

1.2: Quest for a "Green" Solvent

The term "Green Chemistry" coined by the EPA staff advocates a different way of thinking about how chemistry can be practiced in the safer way to cause minimum damage to the environment. In 1988, Paul Anastas and John C. Warner outlined 12 principles of Green chemistry in their book; *Green Chemistry: Theory and Practice*. Green Chemistry is defined as “the design, manufacture and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances”.[2] The “Twelve principles” of Green Chemistry are,

1. **Prevention**. It is better to prevent waste than to treat or clean up waste after it has been created. 2. **Atom Economy**. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product. 3. **Less hazardous chemical syntheses**. Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment. 4. **Designing safer chemicals**. Chemical products should be designed to affect their desired function while minimizing their toxicity.

5. **Safer solvents and auxiliaries**. The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used. 6. **Design for energy efficiency**. Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure. 7. **Use of renewable feedstock**. A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable. 8. **Reduce derivatives**. Unnecessary derivatisation (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste. 9. **Catalysis**. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents. 10. **Design for degradation**. Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment. 11. **Real-time analysis for pollution prevention**. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances. 12. **Inherently safer chemistry for accident prevention**. Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

The twelve principles of Green Chemistry recommended for chemical synthesis cannot be included in a single process. By employing safer solvents in chemical processes which is the 5th recommendation of Green Chemistry the pollution created by the volatile organic compounds (VOCs) can be avoided. The recommendation 5 also encompasses the regulations 4, 7, and 9.

There are two ways to replace the VOCs with environmentally-benign Green solvents:

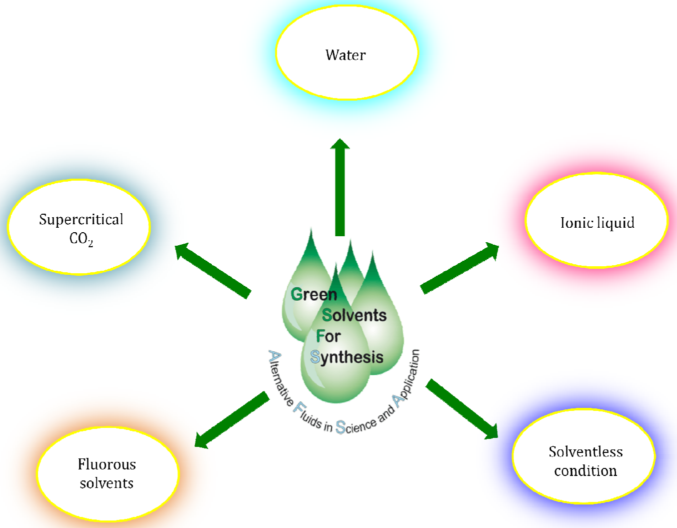
(**1**) the substitution of petrochemical solvents with the “bio-solvents” from natural sources, and

(**2**) substitution of the VOCs with better solvents in terms of environment, health, and safety (EHS).

The first route relies on the solvents derived from the biomass consumption, such as, ethanol which is obtained from the sugarcane and lignocellulosic materials. The second route depends on the innocuous organic solvents, such as alcohols and acetone, and neoteric solvents such as ionic liquids, supercritical fluids, fluorous solvents and deep-eutectic solvents (DESs). The choice of the alternative solvent should be based on workers safety, process safety, and environmental safety and safety for population.[3]

The various “Green” solvent systems are categorized into five groups (Scheme 1.1). These are: (1) solventless systems, (2) water, (3) ionic liquids, (4) supercritical fluids, and (5) fluorous solvents.

In solventless conditions, reactant combines with eachother and form product. However, the poor miscibility of reactants into eachother makes the solventless synthesis difficult. Water was thought as an unconventional solvent for organic reactions due to the poor miscibility of the reactants in it. However, the pathbreaking discovery of the Breslow and others have shown that water which acts as an anti-solvent for organic compounds can accelerate the rate of organic reactions due to the hydrophobicity of water.[4] Later, water promoted reactions are classified as; (1) in-water, and (2) on-water, depending on the solubility of reactant in water.[5] The potential of water is noteworthy in accelerating the pericyclic reactions such as Claisen rearrangement, 1,3-dipolarcycloaddition, and in particular, Diels-Alder reactions.



Scheme 1.1: Various Green solvents

A supercritical fluid (SCF) is a highly compressed gas that displays liquid-like properties. The term "supercritical" denotes any substance whose temperature, pressure and density are above the critical temperature (T_c), critical pressure (P_c), and critical density (d_c) of the substance, respectively. Supercritical fluids (supercritical carbon dioxide, $ScCO_2$) have wide applications in the chemical process and engineering and can be removed at the end of the process by lowering the pressure.

'Fluorous' solvents are analogous to the "aqueous" and high applicability of these solvents are owing to the higher chemical and thermal stability and inertness of the C-F bonds in reactions. Fluorous solvents show temperature dependent miscibility with organic solvents and are used as biphasic mixture for catalysis.

Ionic liquids are molten organic salts and consist of asymmetric organic cation and asymmetric organic/inorganic anion. They have been employed extensively in the chemical, biochemical and electrochemical applications. As compared to other "Green" solvents, ionic liquid is the most debatable environment friendly substitute because of their several advantageous properties. These are considered as future solvents for many potential applications particularly in catalysis, organic reactions, extraction and electrochemistry.

1.3: Ionic Liquids

Ionic liquids are the most explored source of alternative solvents in the past decade, as confirmed by the incredible amount of works in the literature on these materials. The increasing interest in these media is because of the several beneficial properties which render them highly applicable in various applications. The properties which make ionic liquids potential media are insignificant vapor pressure, high thermal and chemical stability, wide liquidus range, wide electrochemical window, low flammability, high ionic conductivity, and ability to act as catalyst.[6-9] Because of these remarkable properties ionic liquids are highly explored in organic synthesis, catalysis, electrochemical applications, solvent extraction, synthesis, and stabilization of nanostructure materials *etc*.

In contrast to the molecular solvents, ionic liquids are composed of oppositely charged ions and are liquid at ambient conditions. The physicochemical properties of ionic liquids, such as viscosity, density, polarity, surface tension, and hydrophobicity can be easily tuned by changing cation, anion or alkyl chain on cation. Because of the ability to tune properties by changing the chemical structure; ionic liquids are also named as “designer” solvents.[10] Thus, a suitable combination of cation and anion can be used to synthesize an efficient ionic liquid for a desired application.

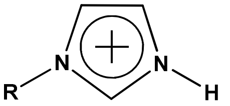
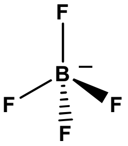
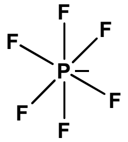
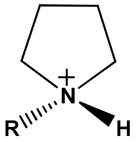
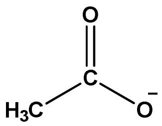
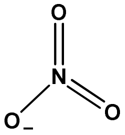
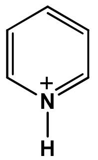
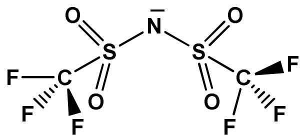
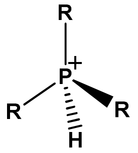
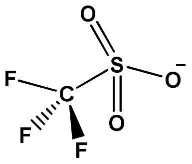
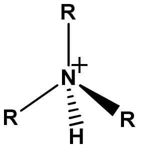
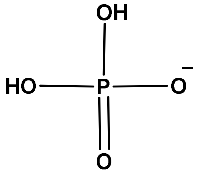
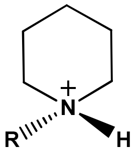
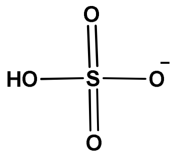
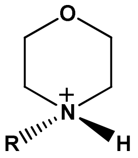
In view of the widespread commercial applicability of ionic liquids, the synthesis of ionic liquids has been a subject of further developments. In 1988, Gabriel synthesized first ionic liquid; ethanolammonium nitrate, which was solid (m. p. 52 – 55 ^{o}C) at room temperature.[11] In 1994, Paul Walden synthesized first ever room temperature ionic liquid (m. p. 12.5 ^{o}C) ethylammonium nitrate, $[Et_4N][NO_3]$.[12] Since then several ionic liquids are prepared which can be classified in order of their development and applications. The ancient ionic liquids (*first generation of ionic liquid*) were the eutectic mixture of aluminium chloride with ethylpyridinium halide and dialkylimidazolium chloroaluminate. These chloroaluminate ionic liquids were prone to hydrolysis producing corrosive acid HCl. The *second generations of ionic liquids* include more efficient non-chloroaluminate ionic liquids containing substituted imidazole, pyridine, pyrrolidine, and alkylamine cations along with weakly coordinating BF_4^-, PF_6^-, and NTf_2^- anions and are extensively applicable in various synthetic and catalytic processes. Unlike chloroaluminate ionic liquids, they are air and water stable for a longer period of time. The *third generation of ionic liquids* is "task specific" ionic liquid, which are prepared in order to achieve desired outcomes, *e. g.* chiral ionic liquids for stereochemical and stereospecific reactions. They contain substituted imidazole, pyridine, pyrrolidine, alkylammonium, alkylsulphonium and alkyphosphonium cations with halide free anions such as, CH_3COO^-, HSO_4-, SO_4^{2-}, PO_4^{3-}, BR_4^-, $C_6H_5SO_3^-$, and $(RO)_2PO_2^-$. They also have wide applications in biological systems.

1.4: Protic Ionic Liquids

1.4.1: Chemical Composition of Protic Ionic Liquids

Ionic liquids are the structural analogs of molten salts and possess molecular asymmetry in one of its ion. The asymmetry in structure normally opposes the Coulombic interactions and disturbs charge ordering between ions. The diffused charge and lower symmetry of cation and anion reduces their melting point. The directionality in the structure of ionic liquids arises because of the hydrogen bonding between the cation and anion.[13] Therefore, directionality in the structure of salts arises from the Coulombic interactions and in ionic liquids through the weak hydrogen bonding. Protic ionic liquids are composed of asymmetric organic cation and inorganic/organic anion formed during the irreversible proton transfer from Brønsted acid towards Brønsted base. The representative class of protic ionic liquids generally consists of imidazolium, pyridinium, pyrrolidinium, piperidinium, alkylphosphonium, alkylammonium, and morpholinium cations and tetrafluoroborate, hexaphlorophosphate, carboxylate, bistriflimide, triflate, bisulphate, nitrate, and halide anions. The strong hydrogen bonding between cation and anion transforms protic ionic liquid into solid form at room temperature. The alkylammonium-based protic ionic liquids were first synthesized as a substitute of high boiling liquids but later were also found useful as electrolyte in conducting cells. The conducting nature of protic ionic liquids makes them highly applicable in polymer membrane fuel cell. The structures of representative protic ionic liquids are shown in Table 1.2. There are approximately 10^{-18} different ionic liquids are possible based on the simple combinations of cations and anions.[14] However, in the last decade major emphasis is given to the protic ionic liquids containing imidazolium-, pyrrolidinium-, piperidinium-, and morpholinium-based protic ionic liquids with triflate, bistriflimide, and carboxylate anions as solvent and catalyst for various acid-catalyzed processes.

Table 1.2: Structures of Representative Protic Ionic Liquids.

structures of protic ionic liquid cations	**name of cations**	**structures of protic ionic liquid anions**
	1-alkylimidazolium	 
	1-alkylpyrrolidinium	 
	1-alkylpyridinium	
	1,1,1-trialkylphosphonium	
	1,1,1-trialkylammonium	
	1-alkylpiperidinium	
	1-alkylmorpholinium	**Cl^-, Br^-**
R = CH_3, C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$		

The most interesting properties of ionic liquids are governed by the nature and strength of interactions operating between the constituent ions.[15,16] Hydrogen bonding plays a significant role in the cation-anion interaction strength and affects physicochemical properties, such as melting point, viscosity *etc*.[17,18]

1.4.2: Critical Features of Protic Ionic Liquids

Ionic liquids can be divided into two broad categories depending on the quaternization process *i.e.* either by an alkyl group (-R) or by proton (H^+). Quaternization by alky group results aprotic ionic liquid, while quaternization by proton gives protic ionic liquid. Protic ionic liquids are synthesized by mixing equimolar amount of Brønsted acid with Brønsted base in a single step atom-economic reaction without creation of any byproduct. In comparison with aprotic ionic liquids, protic ionic liquids possess higher conductivity and fluidity. Protic ionic liquids form an extensive network of hydrogen bonding similar to water which lowers their “ionicity” in comparison with aprotic ionic liquids.[19,20] The presence of supramolecular assemblies in protic ionic liquids formed due to the hydrogen bonding can be detected by NMR, X-ray diffraction, and neutron scattering experiments.[21,22] There are no definite method for the ionicity measurement and various techniques such as NMR, Waldens’ fluidity–conductivity plot, $\Lambda_{imp}/\Lambda_{NMR}$, and IR spectroscopy are used in the qualitative assessment of the ionicity of ionic liquids.[23,24] The ionicity of ionic liquid is a measure of the ionic content of the medium and is expressed conveniently by using the “Walden plot”. A Walden plot represents a linear relation between the log Λ *vs.* log η^{-1} passing through the origin. The extent of proton transfer in protic ionic liquids depends on the difference in the aqueous pKa values of acid and base *i.e.* ΔpK_a.[25] A complete proton transfer takes place when $\Delta pK_a > 8$; giving nearly ideal Walden plot for protic ionic liquids.[26] However, the aqueous ΔpK_a values are not the reliable measure of ionicity in protic ionic liquids as observed in several studies. The equilibrium studies between acid and base signify that, at aqueous $\Delta pK_a = 4$, complete proton exchange occurs in water.[23] Similarly, the studies on the crystalline compounds formed by a combination of acids and base of varying ΔpK_a designate that substantial proton transfer takes place in the formation of crystal structure when $\Delta pK_a > 3$.[27] The crystal structure below $\Delta pK_a < 3$ was that of the co-crystals of acid or base. The structural features of amines also affect ionicity as noted in the case of the protic ionic liquids formed by primary, secondary, and tertiary amines with acetic acid for whom aqueous $\Delta pK_a \sim 6$.[28] The absence of hydrogen bonding in protic ionic liquids formed by tertiary amine produces lower ionicity than protic ionic liquids synthesized by primary amines. The hydrogen bonding network in protic ionic liquids helps in the stabilization of cation and anion and thereby reduces the probability of retro-transfer of proton from cation to anion.[29] The lower ionicity indicates materialization of neutral species due to the incomplete proton transfer. The formation of neutral species lowers the density and viscosity and increases the volatility of protic ionic liquids. From these observations it is clear that the proton transfer occurs through a quite different mechanism in protic ionic liquids than that in water and aqueous ΔpK_a is not a suitable indicator for predicting the extent of proton transfer in protic ionic liquids. However, the neutral species formed due to the retro-transfer of proton when present in small amount (1%) do not affect the characteristics of the protic ionic liquid.[30]

Similar to the protic ionic liquids are the Brønsted acidic ionic liquids, in which proton occupies either on the alkyl chain of cation or anion, but not on the cationic core as in case of protic ionic liquids.[31] These Brønsted acidic ionic liquids thus can be classified as protic ionic liquids/aprotic ionic liquids. The Brønsted acidic ionic liquids have wide utilities because of the solvent-catalyst duality in product selectivity and homogeneous and heterogeneous acid catalysis. A higher yield during the esterification and trans-esterification was achieved using Brønsted acidic ionic liquids containing aliphatic cations and acidic anion, in particular HSO_4^- anion.[32] A quite good correlation between the conversion rate and Hammett acidity, H_0, signifies the involvement of acidic characteristics present in Brønsted acidic ionic liquids in the esterification and trans-esterification.

PILs have wide applications in chemical and biological systems chromatography.[33,34] In addition, protic ionic liquids have been widely explored as a proton conducting polymer electrolyte in fuel cells because of the high proton conductivity and defined proton activity, allowing the fuel cell to operate in a non-humidified conditions even at higher temperatures.[35-38] Protic ionic liquids have also been explored in various acid-base catalyzed reactions, such as Knoevenagel condensation, Aldol condensation, Diels-Alder reaction, Fischer esterification and

Pinacol-pinacolone rearrangement reactions because of their non-corrosive, non-volatile, and recyclable nature than that of the mineral acid/base.[39-42] Protic ionic liquids are excellent media/catalyst for microwave assisted reactions because of their good microwave absorbent abilities. A complete Pinacole-pinacolone conversion of hydrobenzoin was achieved in the optimized conditions using alkylammonium-based PILs after the microwave irradiation.[42] The Fischer esterification reactions of benzoic acid with alcohol and benzyl alcohol with carboxylic acids give good to excellent yield (77 – 98.5%) in pyridinium- and imidazolium-based protic ionic liquids without adding any catalyst under the microwave-irradiated conditions.[43] The microwave assisted esterification using protic ionic liquids has advantage over the conventional esterification methods in terms of the shorter reaction time, easy separation by decantation and high yield, and high reusability of the product.[44] The solvent free dehydration of D-glucose and fructose into more useful 5-hydroxymethylfurfural which is a versatile and key ingredient in the petroleum industry and biofuel chemistry can be conveniently performed in the mild solutions of protic ionic liquids as compared to that in the corrosive mineral acids.[45]

The use of protic ionic liquids in many applications is associated with the benefit that most of the protic ionic liquids can be purified by distillation at moderately temperatures under atmospheric pressure without decomposition.[46] The distillation begins with the retro-transfer of proton from the cation toward anion. The vapor phase consist only neutral molecular species *i.e.* acid and base, which forms protic ionic liquid upon condensation. The necessary criterion for the distillable protic ionic liquid is that they should possess weakly basic anion, such as CH_3COO^-, $N(Tf)_2^-$ *etc.* in order to avoid their decomposition before boiling.[47] Recently, the boiling point of several protic ionic liquids before decomposition is reported by for fuel cell applications.[48] Unlike protic ionic liquids, aprotic ionic liquids which contain strongly basic anion undergo distillation at very high temperature and reduced pressure. At atmospheric pressure aprotic ionic liquids undergo transalkylation forming a mixture of aprotic ionic liquids. For example, [EMIm]Cl decomposes at 190 ^{o}C under vacuum to form a ternary mixture of [MMIm]Cl-[EMIm]Cl-[EEIm]Cl due to the transalkylation.[46] However, the protic ionic liquids containing carboxylate anion along with the alkylammonium-based cations form amide during distillation.[49]

Compared to other ionic liquids, protic ionic liquids generally do not lead to the side reactions and therefore is greatly employed as a medium in several targeted reactions. However, protic ionic liquids are primarily employed in the energy industry and not as a medium. The potential of protic ionic liquids in several applications require the knowledge of physicochemical properties which varies with the structure of cation and anion.

1.5: Physicochemical Properties of Protic Ionic Liquids

The most significant characteristics of protic ionic liquids are thermal stability and thermal-phase behavior. Generally, stable protic ionic liquids possess high thermal stability which is necessary for their use in energy purposes without undergoing the phase transition. The magnitude of different physicochemical properties depends on the intermolecular and intramolecular interactions between cation and anion. However, the presence of trace of impurities, such as water and residual halide, has larger impacts on the physicochemical properties.[50,51]

1.5.1: Thermal Stability

High thermal stability and low melting temperature determine the liquidus range of ionic liquids. The thermal decomposition temperature (T_d) for protic ionic liquids ranges from 120 – 360 ^{o}C which is well below the T_d of analogous inorganic compounds (400 – 800 ^{O}C).[33] The thermal stability depends upon on the strength of cation-anion interactions. Generally, alkylammonium-, amino acid-, and pyrrolidinium cation-based PILs with $H_2PO_4^-$, $H_2PO_3^-$, HNO_3^- and BF_4^- possess lower decomposition temperature, while those with alkylimidazolium, alkylpyrrazolium, pyridinium, morpholinium, and piperazinium cations paired with TfO^-, $N(Tf)_2^-$, and HSO_4^- anions high thermal stability. The protic ionic liquids which require lower proton-transfer energy maintain their stability at elevated temperature and do not undergo decomposition.[52] The decomposition temperature (T_d) is defined as the temperature at which 10% mass loss occur using Thermogravimetric analysis (TGA).[53] The thermal stability of protic ionic liquids is dominated by the nature of anion. The anion which offers little interaction towards the cation exhibit lower T_d.[54]

The fluorous anions impart lower interaction strength and yields most thermally stable PILs.[55,56] The order of thermal stability increases in the order,

$$N(Tf)_2^- > PF_6^- > BF_4^- >> Cl^-$$

However, carboxylate anion-based PILs, particularly formate undergo condensation reaction to form amide.[57,58]

1.5.2: Thermal Phase Behavior

Almost all protic ionic liquids are fragile in nature which is indicated by the glass transition temperature, T_g. The glass transition temperature (T_g) denotes the transition point in the temperature vs. heat representation which is the characteristic of semicrystalline and amorphous materials including protic ionic liquids. The glass transition behavior is indicative of the cohesive energy of the salt and it decreases due to the repulsive Pauli forces which sets up due to the overlap of closed electron cloud and increases because of the attractive Coulomb and van der Waals forces.[59] Therefore, it is feasible to modify T_g by making suitable choice of cationic and anionic component of the salt. The deviation in the logarithm of viscosity with inverse of temperature *i.e.* log η vs. T_g/T is used to show the fragility of the materials (Figure 1.1).

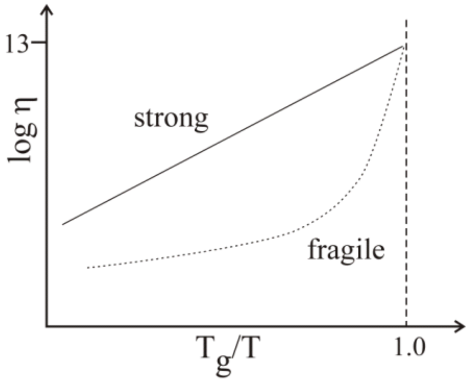


Figure 1.1: A schematic of the liquid log viscosity (η) vs. T_g/T for crystalline and noncrystalline materials.

The higher deviation from the linearity indicates more fragility, which represent that viscosity of the material decreases more with temperature than that expected from the Arrhenius equation. Almost all protic ionic liquids exhibit fragile behavior from intermediate to very high.[26]

The T_g can be lowered by decreasing the cation size or by increasing the asymmetry of cation which decreases the packing efficiency and cohesive energy of the salts.[60] The larger anion (NTf_2^-, OTf^-) decreases the T_g due to the lesser cation-anion interaction strength. For fluorinated anions Coulombic interaction decrease more than the small gain in van der Waal interactions which results net decrease in the cohesive energy and hence T_g.[61]

1.5.3: Melting Point

Protic ionic liquids generally exhibit wide range of melting temperature varying from -82 to 212 °C. The melting point depends on the packing efficiency of cation and anion and the extent of hydrogen bonding. The asymmetry in the structure of ions decreases the melting point due to the reduction of hydrogen bonding strength.[62] The PILs formed by the alkylammonium cations with the NO_3^-, PO_4^{3-}, Br^- and Cl^- anions have higher melting point, while imidazolium, pyrrolidinium, piperidinium, and morpholinium cations with BF_4^-, $N(Tf)_2^-$, OTf^-, $RCOO^-$ form room temperature protic ionic liquids. Initially, it was assumed that the larger radius of fluorinated anions leads to lower melting point due to the decreased electrostatic interactions in protic ionic liquids; however, several reports have shown the importance of ΔpK_a in regulating the melting point of protic ionic liquids. For example, very strong acid; $HN(Tf)_2$ than HNO_3 when paired with alkylammonium cations form protic ionic liquids with melting point 3.5 and 113 °C, respectively in spite of the larger size of $N(Tf)_2^-$ than NO_3^- . The higher ΔpK_a results complete transfer of proton from acid to base which increases the ionicity and thus melting point. Similarly, melting point of amino acid-based protic ionic liquids with carboxylate anions decrease as the number of hydrogen bonding site diminishes.

1.5.4: Viscosity

Protic ionic liquids are less viscous than their aprotic counterparts. The viscosity of protic ionic liquids generally ranges from 30 – 100 cP at room temperature, but in some cases, viscosity as high as 500 – 600 cP are observed.[23] The viscosity of protic ionic liquids follows the non-Arrhenius behavior *i.e.* a non-linear dependency between the log η and $1/T$.[63] The lower viscosity is attributed to the formation of neutral acidic and basic species formed by the retro-transfer of proton from cation to anion. However, protic ionic liquids having oxy-anions, such as HSO_4^- and NO_3^- are highly viscous in nature due to the formation of multiple hydrogen bonds.[64] The viscosity of protic ionic liquids is more susceptible to the change of anion rather than that of cation, though increasing the alkyl chain lengths on cation also increases the viscosity due to the increasing van der Waal interaction.[65] The viscosity of [EMIm][PF_6] (~ 1000 cP) is higher than that of [EMIm][N(Tf)$_2$] (69 cP) owing to the delocalization of negative charge on anion.[66] Alkanolammonium-based ionic liquids with carboxylate anions show higher viscosity than their non-hydroxyl counterparts. The increase in viscosity is due to the enhanced hydrogen bonding between the hydroxyl group on cation and anion.[67] The increased viscosity due to the stronger interactions between cation and anion is also supported by the higher viscosity of [DAA][HCOO] (Diallylammonium formate) than that of [DAA][CH_3COO] (Diallylammonium acetate).[68]

1.5.5: Ionic Conductivity

One of the many potential applications of protic ionic liquids is their use as proton conductor in the polymer membrane fuel cells (PEMs).[69-70] The ability of protic ionic liquids as proton conductor is governed by the degree of dissociation of ions, mobility, viscosity, and ionic charge. These factors are controlled by the effective ion size and shape. The ionic conductivity of protic ionic liquids depends on the viscosity of the medium. Walden plot (Figure 1.2), which relates the logarithm of ionic conductivity with logarithm of fluidity, gives an indication about the effective ionicity of protic ionic liquids. The variety of interactions renders the dissociation of ions very poor and therefore most of the protic ionic liquids have "poor" ionicity.[71] Generally, protic ionic liquids having delocalized charge and lower inter-ionic interactions possess higher ionicity. Alkylammonium-based protic ionic liquids containing $HCOO^-$ and CH_3COO^- anions exhibit higher conductivity. The maximum ionic conductivity 43.8 mS cm^{-1} at 25^{o}C is reported for the methylammonium formate (MAF). The conductance for the alkylammonium- and alkylimidazolium-based protic ionic liquids is obtained highly susceptible for the alkyl chain length, with the maximum change for the shorter alkyl chain (C_1 - C_4) and little or no change for the higher alkyl chains (C_4 – C_{12}). For heterocyclic systems, conductivity increases with the molecular mass or asymmetricity in the structure of ions.

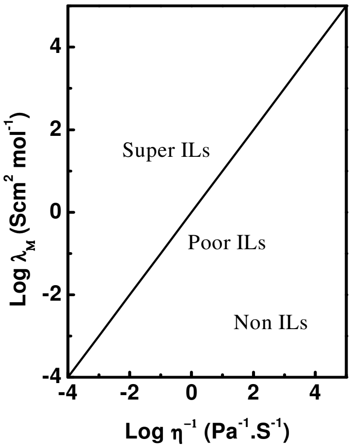


Figure 1.2: A typical Walden plot.

Recently, it has been reported that the ionicity of protic ionic liquids can be bettered by employing molecular solvents.[72] The molar conductivity (λ_M) of alkylimidazolium-based protic ionic liquids with $HCOO^-$, CH_3COO^- and $CH_3CH_2COO^-$ anions was observed higher in the polar protic solvents and lower in the polar aprotic solvents because of the hydrogen bonding ability of the former. The % ionicity of [HmIm][HCOO], [HmIm][CH_3COO], and [HmIm][CH_3CH_2COO] was obtained 58, 49, and 46 %, respectively.[72]

1.5.6: Structural Properties of Protic Ionic Liquids

An understanding of the solvent structure assists in predicting the solvation structure and various physical properties, such as, viscosity, conductivity, surface tension *etc.*, leading to the creation of new materials.[73] Until recently, protic ionic liquids were thought to be structurally homogenous, but several studies suggest that protic ionic liquids also form nanostructured polar and non-polar domains due to their amphiphilic nature. The atomic force measurements on the nano-confined protic ionic liquid; ethylammonium nitrate (EAN) in mica had shown the oscillatory motion due to the definite solvation layers of protic ionic liquids which is guided by the surface charge, surface roughness and orientation of cation in the interfacial layers.[74] The flexibility of solvation layers on highly charged and atomically smooth mica was more for the propylammonium nitrate than ethylammonium nitrate owing to the longer alkyl group on former. The structure peak, *q*, (Figure 1.3) for the deuterated ethylammonium nitrate and propylammonium nitrate by using small-angle neutron scattering (SANS) is obtained at 0.54 A^{o-1} and 0.66 A^{o-1}, respectively, corresponding to the Bragg spacings of 11.6 and 9.7 A^{o}.[75]

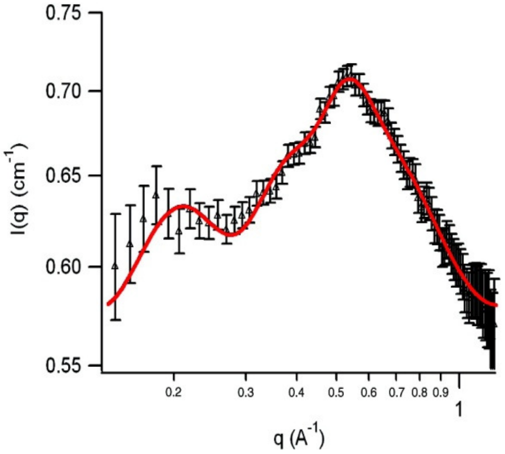


Figure 1.3: SANS spectrum for pure D-propylammonium nitrate at 45 °C.

These spacings are nearly double the ion-pair distance and implies that even the smallest protic ionic liquids; ethylammonium nitrate and propylammonium nitrate are structured, with the alkyl groups associated separately from the hydrogen bonded polar moieties $–ND_3^+$ and NO_3^-. The nanosegregation depends on the 1) electrostatic attractions between the cation and anion creating polar domain, 2) hydrogen bonding which promotes the polar assembles, and 3) solvophobic interactions between alkyl groups forming the nonpolar domains.[76-78]

The neutron diffraction studies on the two oldest protic ionic liquid, ethylammonium nitrate (EAN) and ethanolammonium nitrate (EtAN), have also corroborated the microheterogenity in these media.[79] The structure peak for ethanolammonium nitrate (EtAN) appears at 0.76 A^{o-1} and corresponds to the Braggs' spacing of 8.21 A^{o}. This distance is slightly less than the twice of the ion-pair dimension (2 x 5.4 A^{o}), but large enough to be attributed to a single ion-pair or constituent ion. Therefore, as compared to the ethylammonium nitrate a closer association between the constituent ions prevails in ethanolammonium nitrate because of the stronger hydrogen bond facilitated by the hydroxyl group present on cation.[84]

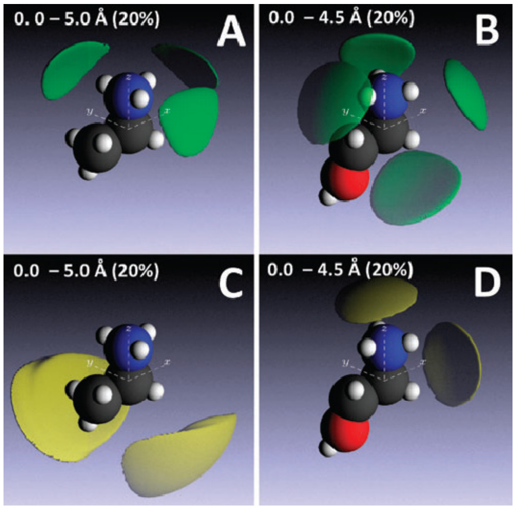


Figure 1.4: EPSR spatial density distributions of ions as a function of angular position and distance relative to a central (A) & (C) Ethylammonium (EA^+) or (B) & (D) Ethanolammonium (EtA^+) cation. Nitrate NO_3^- anion distribution is colored green and defined as the most probable regions the NO nitrogen occupies in 3-D space. Cation distribution is colored yellow and defined as the most probable regions the C_1 carbon occupies in 3-D space. The scale of the viewpoint windows is ± 5.5 A°. Atom colorings for the central cations are: H (white), C (grey), N (blue), O (red). (*Reproduced by permission from Royal Chemical Society*)

The neutron diffraction spectra modeled using empirical potential structure refinement (EPSR) and the different arrangements of cation, anion, and alkyl chains are shown by spatial density functions (SDF) (Figure 1.4 and 1.5).

As shown in Figure 1.4 nitrate anion is symmetrically distributed around the central ethylammonium (EA^+) (1.4A) or ethanolammonium (EtA^+) cation, respectively and three anions solvate each cation headgroup. For ethanolammonium nitrate an additional lobe is seen on the underside of ethanolammonium cation because of the hydrogen bonding between the nitrate oxygen and the hydroxyl group on cation.

The local arrangements of neighboring cations are shown in the Figure 1.4. There are two symmetric lobes around the alkyl cation segment for ethylammonium cation revealing that each cation interacts with two cations away from the polar head *i.e.* towards the hydrophobic tail (Figure 1.4C). In ethanolammonium nitrate, each cation is surrounded by two cations (Figure 1.4D). The neighboring cation locates around the charged amine rather than the alkyl tail. Thus the inclusion of –OH disrupts solvophobic interactions between alkyl group.

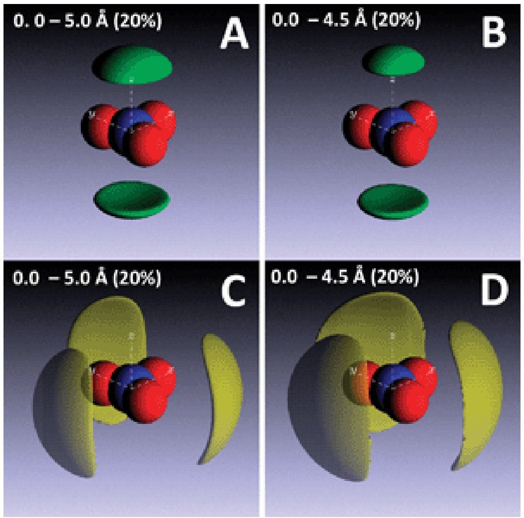


Figure 1.5: EPSR spatial density distributions of ions as a function of angular position and distance relative to: (A) & (C) EAN's Nitrate anion or (B) & (D) EtAN's Nitrate anion. Anion density is coloured green and defined as the most probable regions the NO nitrogen occupies in 3-D space. Cation density is coloured yellow and defined as the most probable regions the C_1 carbon occupies in 3-D space. The scale of the viewpoint windows is ± 5.5 A°. Atom colorings for the central anions are: N (blue), O (red). (*Reproduced by permission from Royal Chemical Society*)

Each anion is surrounded by two anions above and below the plane both for ethylammonium nitrate and ethanolammonium nitrate (Figure 1.5A and B). Similarly, the distribution of cation around the central anion is also similar for both ethylammonium nitrate and ethanolammonium nitrate and each anion is surrounded by three cations (Figure 1.5C and D).

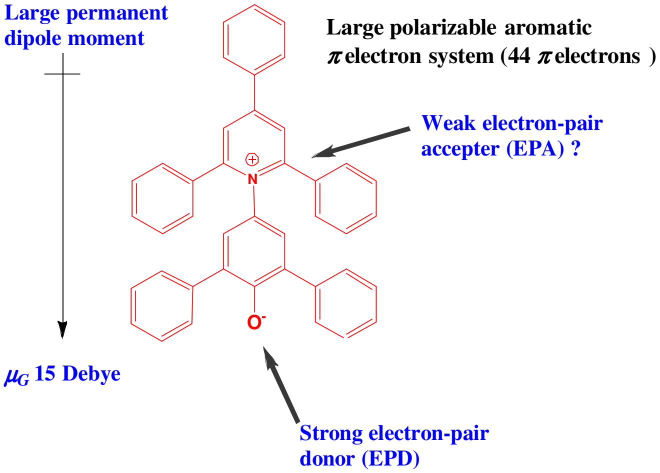
1.6: Polarity of Protic Ionic Liquids

Solvent influences the rate and equilibrium of a chemical reaction as well as the position and intensity of the absorption bands.[80-82] The appropriate choice of solvent is necessary for the process development and its fine tuning. The solvent effects on chemical reactions can only be understood in terms of the solvent polarity. The solvent polarity is too complicated and cannot be comprehended by using a single physical parameter. Chemists have developed empirical equations of polarity measurements using model processes. The model processes depend on the susceptibility of the spectroscopic changes, kinetic measurements or chemical equilibrium on the nature of solvent.[83] Polarity for a solute in nonstructured solvent, where only solute-solvent interactions are possible, can be estimated in terms of the physical parameters such as, relative dielectric permittivity (ε_s), dipole moment (μ), and refractive index (n).[84] However, the same scale of solvent polarity cannot be extended for the structured solvents, such as ILs, due to the existence of solvent-solvent interactions in addition to the solute-solvent interactions. Solvent polarity is thus defined as the "overall solvation capability of solvent which includes all possible intermolecular, specific and nonspecific, interactions between solute and solvent".[85] This led to the developments of the *empirical parameters* of solvent polarity.[86,87]

Though protic ionic liquids form hydrogen bonding network and help in the dissociation of carboxylic acids similar to water, their polarity values are quite different from eachother.[20,88] The polarity of protic ionic liquids is measured by using dielectric relaxation spectroscopy and solvatochromic method. The electrical conductivity of ionic liquids poses difficulty in the ε_s measurements, but microwave dielectric permittivity allows the separation of dielectric and conductive responses and therefore allows the measurement of ε_s.[89-91] Protic ionic liquids form strong hydrogen bonds and hence large ε_s is expected for them similar to hydrogen bonded molecular solvents where strong orientational correlations between dipoles promotes dielectric polarization.[92,93] For alkylammonium-based protic ionic liquids $\varepsilon_s \approx 40$ is observed which was independent of the choice of anions as incorporation of nitrate and formate anions with alkylammonium cation resulted nearly similar ε_s values.[94] The tethering of hydroxyl group on cation has significantly improved the ε_s 57.3

which is lower than that of water (ε_S = 78.3) due to very high molar volume (89.4 cm^3 mol^{-1}). This reduces the dipole densities five-times lower than that of water.[94]

Solvatochromic method is very popular in the determination of the polarity of ionic liquids and depends on the change in electronic transition due to the change in polarity of solvent. This method measures overall polarity, E_T30 (electronic transition energy in kcal mol^{-1}), because of the various possible specific and nonspecific interactions and Kamlet-Taft parameters such as, hydrogen bond donor acidity (α), hydrogen bond acceptor basicity (β), and dipolarity/polarizability (π^*). The E_T30 value of ionic liquids is calculated from the long-wavelength intramolecular charge-transfer absorption band of Reichardt's dye 30 (2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate) shown in Scheme 1.2.



Scheme 1.2: Structure of Reichardt's dye 30.

Reichardt's dye 30 shows large negative solvatochromism and undergoes largest solvatochromic shifts (375 nm between diethyl ether and water) depending on the nature of solvent. This dye assists in sensing the various possible solute-solvent interactions due to its large dipole moment, hydrogen bond donor and accepter sites and large polarizable π-electron systems.

The longest wavelength charge transfer absorption band of Reichardt's dye 30 (pK_a = 8.6) disappears in protic ionic liquids due to the complete protonation of dye.[95] Therefore, a less basic Reichardt's dye 33 (pK_a = 4.78) is used for the determination of polarity. For strongly acidic protic ionic liquids, least basic Nile red dye is used for the determination of polarity.

Solvatochromic method also reveals the *hyperpolar* nature of the protic ionic liquids. Generally, primary and secondary alkylammonium-based protic ionic liquids possess high polarity similar to that of water which is greater than that of organic solvents and aprotic ionic liquids.[96] In alkylimidazolium class of protic ionic liquids higher polarity was observed for protic ionic liquids which were formed between the strong acid and alkylimidazole base.[95]

Chromatographic method yields polarity comparable to the solvatochromic method. The polarity of alkylammonium formates (ethylammonium formate (EAF), propylammonium formate (PAF), and butylammonium formate (BAF)), obtained by using chromatographic method, was similar to those of the methanol and acetonitrile.[97]

1.7: Applications of Protic Ionic Liquids

Protic ionic liquids have been widely employed as solvent in organic synthesis, catalysis, and in separation of mixtures. Besides these they are also used as electrolyte in fuel cells and batteries, as a stabilizer in biological systems, in explosive formulations, and in lubricant industries. The potential of these protic media in governing the rate and endoselectivity of the Diels-Alder reaction is of current interest and is discussed in detail here.

1.7.1: Hammett Acidity

Acid-base properties and protonation-deprotonation phenomena are the most studied and readily understood chemical phenomena. The dependence of the acid-base equilibria on the molecular structure has been pivotal in the development of modern organic chemistry. The popular acidity scales for the measurement of acid-base properties are pK_a and pH, but later several acidity functions are employed to measure the acidity/basicity of the “superacid/superbase” and weak acid/base using appropriate indicator. The pH scale of acidity measurements is generally extended at either end using the pK_a’s of compounds/indicators which ionizes outside the pH range.[98] Acidity function denotes the ability of a solvent/solute to donate/accept proton to a solute.[99] The acidity function described by Hammett and Deyrup using neutral bases has been extensively applied in the acidity measurements. The development of the Hammett acidity function was due to its possible bearing on the acid catalysis. The bases which follow the Hammett function (H_0) are called Hammett bases.[100] Apart from the H_0, other acidity functions such as H_+ and H_- are also used for acidity measurements. The subscript $o, +,$ and $-$ denotes charge on the Hammett base. The H_- scale was used for the highly basic solutions; while H_+ scale is employed for superacidic solutions, such as sulphur dioxide in sulphuric acid. A parallel relation exists between H_- and H_0 and H_+ and H_0, but the magnitudes differs depending on the sensitivity of indicator. The typical absorbance spectra of 4-nitroaniline is shown in Figure 1.6.

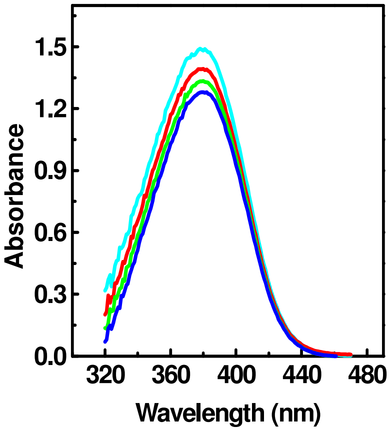


Figure 1.6: A typical absorbance spectra of 4-nitroaniline at various concentrations of an acid in protic ionic liquid.

The H_0 scale is constructed using the protonation equilibria of neutral bases:

$$\mathrm{I} + \mathrm{H}^+ = \mathrm{HI}^+$$

H_0 is defined by the equation:

$$H_0 = \mathrm{p}K(\mathrm{I})_{\mathrm{aq}} + \log\frac{[\mathrm{I}]}{[\mathrm{HI}]^+} \quad (1)$$

where, $\frac{[\mathrm{I}]}{[\mathrm{HI}]^+}$ is the ratio of unprotonated and protonated forms of indicator; also called as *indicator ratio*, and $\mathrm{p}K(\mathrm{I})_{\mathrm{aq.}}$ is the protonation constant of indicator in water. Equation 1 can also be written as

$$H_0 = -\log \mathrm{a}_{(\mathrm{H}+)\mathrm{aq}} - \log \gamma(\mathrm{I})/\gamma(\mathrm{HI})^+ - \log \tau(\mathrm{I})/\tau(\mathrm{HI})^+ \quad (2)$$

where, $\gamma(\mathrm{I})/\gamma(\mathrm{HI})^{+}$ is the ratio of activity coefficients and $\tau(\mathrm{I})/\tau(\mathrm{HI})^{+}$ is the ratio of transfer activity coefficients of unprotonated and protonated forms of indicator.

For a dilute solution of indicator, the ratio $\gamma(\mathrm{I})/\gamma(\mathrm{HI})^{+}$ remains constant. The ratio $\tau(\mathrm{I})/\tau(\mathrm{HI})^{+}$ arises due to the different solvation of indicator during the transfer from one medium to other medium. The solvation of protonated and unprotonated forms differ from eachother therefore it is difficult to maintain the ratio $\tau(\mathrm{I})/\tau(\mathrm{HI})^{+}$ constant. However, for structurally similar indicators this ratio is assumed independent of the solvent. In a medium of low relative permittivity, it is reported that the H_0 measurements are affected due to the ion-pair formation between the protons and conjugate anion of acid.[101]

For all Hammett bases/spectroscopic indicators a point comes at which the absorbance of protonated and nonprotonated forms becomes equal. This point is called as "isosbestic point".[102] The presence of isosbestic point indicates the equilibrium between the non-protonated and protonated forms of indicator. The Hammett acidity observes the variation of spectral changes due to the protonation/deprotonation.

The development of H_0 by Paul and Deyrup was because of its possible bearing on the kinetics of acid-catalyzed recations.[99] For a large number of acid-catalyzed reactions, a linear dependency of rate constant on the H_0 was revealed. A linear relation is obtained between the hydrolysis rate of sucrose and H_0 by Hammett and Paul.[103] The Zucker-Hammett hypothesis was followed in various acid-catalyzed reactions. According to this hypothesis "in an acid-catalyzed reaction if a linear relation exists between $\log k_1$ and H_0, water does not participate in the transition state of the rate-determining step, and if $\log K_1$ is linear with log [H^+] water involve in the rate-controlling step".

1.7.1.1: Hammett Acidity in Ionic Liquids

The Hammett scale of acidity determination is not much developed in ionic liquids. The first report on the H_0 in ionic liquids is reported by Gilbert *et al.* almost a decade ago.[104] They have measured the H_0 of triflic acid (HOTf) and bistriflimide acid ($HNTf_2$) in imidazolium-based ionic liquids having [$N(Tf)_2$] and [BF_4] anions using 2,4-dinitroaniline base. It is observed that as compared to water, much lower acidity level can be achieved using ionic liquids because of the poor solvation of proton. The presence of acidic hydrogen has little effect on the Hammett acidity as similar H_0 values were obtained for both acids in alkylated and non-alkylated ionic liquids. Recently a detailed account of the H_0 of carboxylic acids in imidazolium-, pyrrolidinium-, and piperidinium-based protic ionic liquids with carboxylate anions and water is reported.[105] The dissociation of weak acids in protic ionic liquids follows a different mechanism of dissociation than that of water. A reversal in the order and magnitude of H_0 was noted in protic ionic liquids than those in water. The higher acidic strength of carboxylic acids in protic ionic liquids in comparison to water was independent of the large structural and electronic differences.[88] A linear relation is obtained between the H_0 of all carboxylic acids in protic ionic liquids and water suggesting analogous nature of these media. The higher H_0 for the longer carboxylic acids in protic ionic liquids is facilitated by the hard-soft acid base (HSAB) interactions between conjugate anion of acid and protic ionic liquid cation.

1.7.1.2: Effect of Neutral Salts on Hammett Acidity Function

Unlike systematic studies on the Hammett acidity in molecular solvents, very few reports are available on the salting phenomena on Hammett acidity function. Salt induced effects operate through the change in hydrogen bonding network of water and are ubiquitous in chemistry and biology.[106] The salt-effects are pertinent to the protein and enzyme activity and to the bacterial growth but the fundamental mechanism behind these effects are not yet established.[107-111] The hydration theory suggests that the precipitation of nonpolar solute is due to the change in the structure of water, while the dissolution of solute in water is due to the location of solute at interstitial spaces between the solvent layers. Several studies suggest that the salting-out effect operate through the ion-water interaction, whereas salting-in effects is due to the interaction of salt ions with hydrophobic moieties which interacts the solubility in water.[112,113] These assumptions were discarded by several workers and it was reported that salting effect originated from more specific ion-solute interactions.[114,115]

Setschenow has first measured the activity coefficients of non-polar solutes and observed that activity coefficient varies with the nature of salt.[116] The pioneering work of Franz Hofmeister on the protein precipitation has begun the new era on the salt induced effects.[117] Later Gurney classified salts as “salting-in” and “salting-out” based on the influence of different salts on the structure of water.[118] Collins and Washabaugh have proposed “Law of matching Water Affinity” to interpret the molecular mechanism behind salt induced effects.[119] This law states that a perfect match between the hydration enthalpy of salt ions inhibit them to interact with water. A kosmotrope (order-maker) stabilizes the structure of protein and membrane, while chaotrope (disorder-maker) destabilize them.[120] Omta *et al.* have strongly contradicted with the Collins generalizations and put forwarded that salt induced effects in water remain effective only up to the first hydration layer.[121] However, within the dilute range, validity of the Hofmeister effect is undisputed.[122-125]

For the first time, Harbottle studied the H_0 for perchloric acid-sodium perchlorate solutions and obtained the higher acidic strength with the increasing concentration of salt.[126] The increased ionic strength affects the activity coefficients and hence the indicator ratio which in turn promotes the H_0. A linear relationship between the activity coefficients (log γ_I) and solubility ratios corroborated the decreasing solubility of indicator for protonation.[127] Paul has examined the influence of salts on the availability of *p*-nitroaniline at different concentrations of acid. Each salt has a conspicuous effect over H_0 and salts having the larger anions cause salt-in of the indicator and decreases the activity coefficient of indicator.[128] Based on the linear dependence between the log γ_I and C_s and between the $-H_0$ and C_s; two equations are proposed relating the dependency of salt concentrations on log γ_I and $-H_0$.

$$-\Delta H_0 = \alpha C_s \tag{3}$$

$$\log \gamma_I = k_B C_s \tag{4}$$

where, $\Delta H_0 = H_{0,\text{salt+acid}} - H_{0,\text{acid}}$ and k_B and α are the salting-out coefficients. Salt effect on H_0 depends on the nature of indicator. A larger slope in the $-\Delta H_0$ versus C_s is obtained for the diphenylamine than that of 4-nitroaniline. The conjugate basicity of strong acids has observed to influence the H_0. For example, Cl^- forms HCl_2^- in the solution and increases the proportion of unprotonated form of indicator.[129] The homoconjugation is more evident for 1:2/2:1 and 2:2 salts, where triple ions and quadrupole appears in solution.[130] The stability of these ions in the solution affects the protonation equilibria and therefore H_0.

$$\text{Ind-}H^+ + \text{M}^+ \leftrightarrow \text{Ind} - \text{M}^+ + \text{H}^+ \qquad (5)$$

$$\text{Ind} - \text{H}^+ + 2\text{X}^- \leftrightarrow \text{Ind} + \text{HX}_2^- \qquad (6)$$

where, $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{or I}^-$

However, such rigorous studies on the salting effect in ionic liquids could not be made owing to the lower solubility of the salts. The presence of nonpolar domains in ionic liquids inhibits the ion-solvent interaction and reduces the solubility of salt. The maximum solubility of a salt reported in ionic liquids is 0.4 mol kg^{-1}.

1.7.1.3: Thermal Effect on Hammett Acidity

The medium effect on the dissociation of acid can be affected by the thermal change. With the rise in temperature thermal energy of both solvent and solute increases which lowers the solvation of indicator and proton. The lower solvation of indicator and proton at the higher temperature facilitates the protonation of indicator and increases the Hammett acidity. On the H_R scale (Hammett acidity function for alcohols) it was found that the acidity at lower concentration does not depend on the temperature and the large dependency of the H_R scale on the temperature was observed for the acid concentration above 65%.[131]

The intermolecular interaction operates between the solute and solvent is calculated by the temperature-dependent acidity parameter, such as the pK_a or H_0. The thermodynamic parameters obtained from the temperature-dependent acidity parameters are used to interpret the nature and strength of the intermolecular interaction. The efficacy of an indicator in sensing the solute-solvent interaction depends on the solvation of indicator by medium. The large temperature-dependency of acidity functions for the carbonium-based indicator than that of the ammonium-based indicator was owing to the solvation of former by the medium.[132] The different degrees of solvation of these indicators bring different H_R and H_0 values. The temperature-dependent H_0 for the different proportion of H_2SO_4 is extensively studied by Shapiro *et al.* as aqueous solution of H_2SO_4 is employed as an efficient catalyst for various acid-catalyzed reactions.[133] The Hammett acidity was found to vary linearly with the reciprocal of temperature according to the equation,[134]

$$H_0(T) = \mathrm{K}/T + \mathrm{L} \tag{7}$$

where, K and L are the constants.

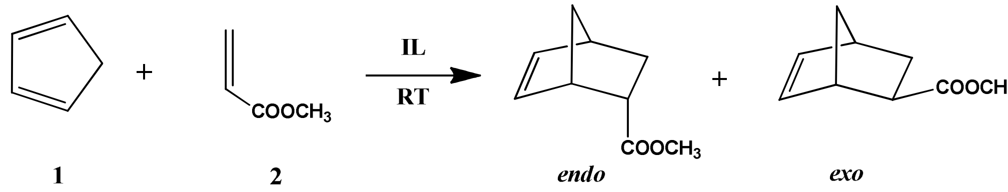
A parallelism between the temperature-dependent H_0 and H_R scales was observed for the aqueous H_2SO_4 solutions.[133]

1.7.2: Diels-Alder Reaction in Protic Ionic Liquids

The bimolecular Diels-Alder reaction is of great synthetic value and offers an easy route to synthesize the six-membered ring between the preshaped diene and an electron deficient dienophile via the concerted step. Initially, the Diels-Alder reactions were considered as independent of the solvent and catalyst due to the nonpolar transition state until the work of Berson *et al.*[135] The pioneering work of the Rideout and Breslow has inspired a number of studies on the cycloaddition and rearrangement reactions in water and other polar medium.[4] The promoting role of water on the kinetics of the Diels-Alder reaction is because of the hydrophobicity of water molecules which unites nonpolar molecules together as oily phase and pushes them into close proximity.[136,137] The asymmetry in dienophile generates polarity in the transition state of the Diels-Alder reaction and makes them sensitive towards the presence of solvent and catalyst.[138]

Apart from the hydrophobicity, other factor which affects the rate and selectivity of the Diels-Alder reaction is hydrogen bonding.[139] The strong hydrogen bonding between the Lewis acid catalyst and dienophile lowers the energy of the highest occupied molecular orbitals (HOMO) on dienophile and improves the endoselectivity of the Diels-Alder reaction. The regio- and stereoselectivity of Diels-Alder reaction largely depends on the solvophobicity (S_p) and hydrogen bond donor (HBD) ability (α) of the solvent.[140] The solvophobicity of the solvent controls the stereoselectivity, while the HBD ability the regioselectivity. The high polarity of solvent also favors the hydrophobicity and therefore promotes the kinetics of the Diels-Alder reaction. The computational study on the Diels-Alder reactions corroborates the role of hydrogen bonding on the activation and acceleration of the reaction.[141]

Jeager and Tucker, for the first time, have studied the kinetics of Diels-Alder reaction in room temperature ionic liquid; ethylammonium nitrate, $[E_tNH_3][NO_3]$.[142] Later, Welton *et al.* have used imidazolium-based ionic liquids containing $[BF_4]$, $[PF_6]$, $[ClO_4]$ and $[NO_3]$ anions for carrying out the Diels-Alder reaction and concluded that the hydrogen bond donor tendency (α) of ionic liquid directs the endo/exo ratio in ionic liquids.[143] The Lewis acidity of the chloroaluminate-based ionic liquids transforms an exo-selective Diels-Alder reaction to endo-selective.[144] The acidity of ionic liquids causes asymmetry in the structure of dienophile and makes transition state more susceptible towards the polarity and hydrogen bonding effects. Similarly, the improved endoselectivity were noted during the execution of Diels-Alder reaction in molecular solvents containing $LiClO_4$ despite the lower solvophobicity of the solution.[145] A detailed account of different factors on the rate and selectivity of Diels-Alder reaction in water, salt solution, and in ionic liquids is studied by Kumar.[146]



Scheme 1.3: Diels-Alder reaction between cyclopentadiene (**1**) and methylacrylate (**2**).

The Diels-Alder reactions are primarily assumed to be affected largely by the hydrophobicity of solvent.[147] *Per contra*, the lower rate for Diels-Alder reaction is observed with increasing hydrophobicity of aprotic ionic liquids (Scheme 1.3).[148] Though the alkylation on parent cation increases the hydrophobicity, it also enhances the viscosity of aprotic ionic liquids, which retards the translational and rotational motion for inter- and intramolecular Diels-Alder reactions, respectively.[149,150] A 10-times higher rate was shown in water than that in 1-butyl-3-methylimidazolium iodide, [BMIM]I.

The behavior of different salts *i.e.* salting-in and salting-out, on the rate and selectivity of Diels-Alder reaction is also studied. Diels-Alder reaction between anthracene-9-carbinol and *N*-ethylmalemide in different salt solution has shown a large dependency of the rate and selectivity depending on the presence of prohydrophobic/antihydrophobic salt in the solution.[151]

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"*What the mind can conceive and believe, and the heart desire, you can achieve*." – *Norman Vincent Peale*

2. Aims and Objectives

Room temperature ionic liquids are the structural analogs of molten salts. They have emerged as a substitute for volatile organic compounds (VOCs) because of their vaporless nature. Protic ionic liquid constitutes a subclass of room temperature ionic liquids and contain dissociable proton in their continuum. Because of the acidic nature protic ionic liquids have find applications in various processes *e.g.* as electrolyte in fuel cells, solvent and catalyst in acid-catalyzed reactions, chromatography etc. The use of protic ionic liquids in various purposes requires the knowledge of different physicochemical properties and their correlation with structure. The structure-property relationships have been vital in predicting the molecular level solute-solvent interactions in protic ionic liquids.

Protic ionic liquid offers both specific and non-specific interactions toward polar and non-polar molecules, therefore serves as an excellent media for various applications. Though protic ionic liquids are highly explored as reaction media, their solvation dynamics are not well established. The relative permittivity (ε) of few protic ionic liquids suggests them as a "hyperpolar" medium. The knowledge of solvation characteristic of protic ionic liquids can be beneficial in optimizing various processes. The dissociation mechanism for acids in ionic liquids is not much explored. The lower strengths for acids in aprotic ionic liquids than that in water are reported. In a different study it is reported that the higher dissociation of the indicator acid can be achieved by using the highly basic anion. Therefore, it is possible to tune the dissociation of weak acids in by using ionic liquids having highly basic anions. The carboxylate anion-based protic ionic liquids display large basicity and can be employed in attaining the maximum strength of weak acids and also in unraveling the dissociation mechanism of acids in ionic liquids. The salting phenomena *i.e.* salting-in and salting-out of a non-polar solute from water is well established, but very few reports are available on the salting behavior in protic ionic liquids probably due to the amphiphilic nature of these coulombic media. Protic ionic liquids have been utilized in several organic transformations because of their solvent-catalyst duality. The acidic nature of protic ionic liquids promotes endoselectivity in Diels-Alder reaction. However, several studies have observed lower rate for bimolecular reactions in ionic liquids than that in water due to the detrimental effect caused by the higher viscosity of ionic liquids which makes diffusion of reactants difficult. Hence, use of less viscous protic ionic liquids can be productive in accelerating the rate and endoselectivity of bimolecular reactions.

In view of the remarkable effects of protic ionic liquids in controlling physical and organic processes, there might well be a large impact of these media on the dissociation of weak acids, salting phenomena and achieving high rate and endoselectivity for sluggish reactions such as Diels-Alder reaction. Acidity functions are very useful in measuring the acidity/basicity of superacidic/superbasic compounds. The selection of suitable indicator is however necessary for the Hammett acidity measurement. In summary, following questions will be addressed in this thesis:

1. to select the representative class of protic ionic liquids after a detailed literature survey,

2. to investigate the thermosolvatochromism (temperature-dependent polarity) of protic ionic liquids and their relation with the structural components,

3. to probe the mechanism of carboxylic acid dissociation in protic ionic liquids, water and their binary mixture,

4. to examine the significance of solute-solvent interactions in the dissociation of carboxylic acids using thermodynamic parameters,

5. to probe the salt effects on the Hammett acidity in the binary mixture of protic ionic liquids and water, and

6. to investigate the role of protic ionic liquids on the rate and stereoselectivities of bimolecular organic reactions.

"*An experiment is a question which science poses to Nature, and a measurement is the recording of Nature's answer.*" *– Max Planck*

3. Instrumentation Techniques

3.1: Introduction

The present chapter outlines the basic principles and theories of different techniques employed for achieving the experimental data reported in this thesis. To understand the polarity of protic ionic liquids and Hammett acidity of different carboxylic acids in ionic liquid systems UV-visible absorption spectroscopy was used. The kinetics of Diels-Alder reactions in protic ionic liquids and their binary mixtures was investigated by the gas chromatographic technique. The viscosity of protic ionic liquid systems is measured by the Brookfield viscometer. The important components of different instruments used in the present work are also briefly described in the current chapter. The thermodynamic parameters for the dissociation of carboxylic acids in protic ionic liquids are derived by using the "indicator-overlapping" technique.

3.2: UV-visible Absorption spectroscopy

In UV-visible spectroscopy material absorbs ultraviolet and visible lights from the electromagnetic spectrum. The absorption of light corresponds to the excitation of outer electrons to the next level in the molecule. When a molecule absorbs energy electrons having lower energy gets excited from the Highest Occupied Molecular Orbital (HOMO) to Lowest Unoccupied Molecule Orbital (LUMO). The occupied molecular orbitals are divided as bonding (σ, π), non-bonding (n), and anti-bonding (π^* and σ^*). The energy of these orbitals increases in the order, $\sigma^* > \pi^* > n > \pi > \sigma$. Figure 3.1 shows the electronic energy levels and transitions.

The absorption can be measured using monochromatic light or polychromatic light. The UV-visible light is enough energetic to excite outer electrons to high energy level and hence is also known as *Electronic Spectroscopy*. The UV-visible spectroscopy is based on the Beer–Lambert Law and is used to determine the concentration of analyte by measuring the absorbance at various wavelengths.

The Beer–Lambert Law governs the relationship between absorbance and concentration. It can be written as.

$$A = \varepsilon c l \qquad (1)$$

where, A is the absorbance, ε is the molar absorptivity and has unit L mol^{-1} cm^{-1}, c is the concentration in mol L^{-1}, and l is the path length of the cell in cm.

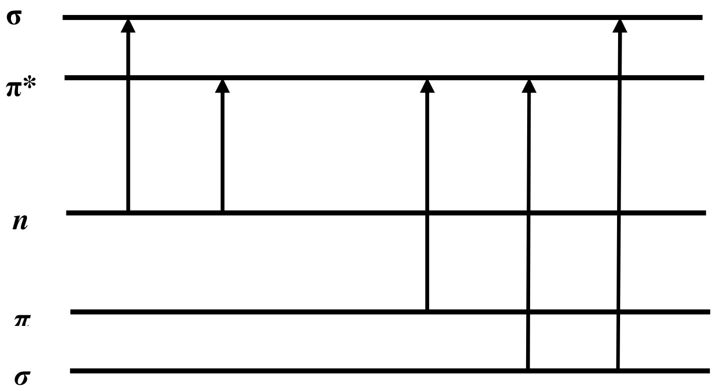


Figure 3.1: A schematic representation of different transition in UV-visible spectroscopy.

The light generated from a Xenon flash lamp of a decent intensity passes through the dispersion device which that causes dispersion different wavelength of light to be dispersed at different angles. The dispersion devices used in UV-visible spectrophotometer are prism or holographic grating. After passing through the dispersion device and sample light reaches to the detector. The detector in UV-visible spectroscopy is photomultiplier tube and provides good sensitivity throughout the whole range and is highly sensitive at low light levels. The entrance slit, dispersion device, and exit slit are referred to as monochromator.

In a conventional spectrophotometer, polychromatic light from a monochromator is transmitted through the sample. The intensity 'I_0' measured by the fraction of beam redirected using beam splitter. The transmitted intensity 'I' of the light beam is measured at photodetector and the absorbance is calculated by the following formula.

$$A = \log\frac{I_0}{I} \qquad (2)$$

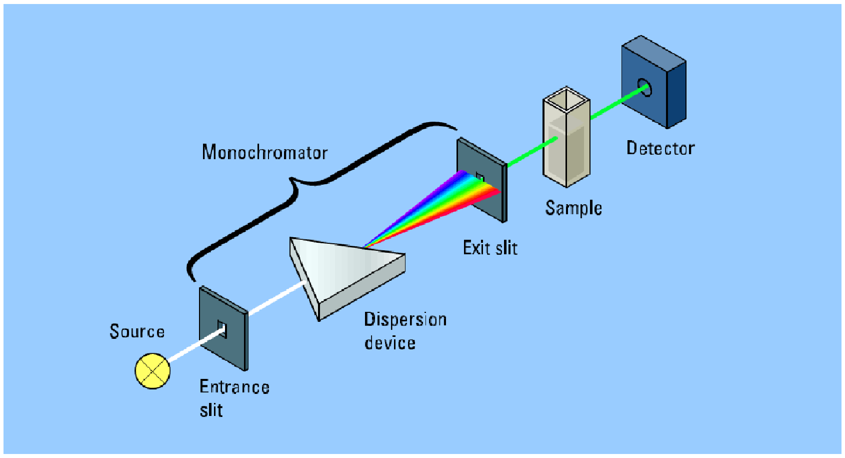


Figure 3.2: Schematic of UV-visible extinction spectrometer.

3.3: Gas Chromatography

Gas chromatography is a physical technique separating the volatile and semi-volatile substances by passing a mobile gas over the stationary phase. Separation occurs as analyte passes through the stationary phase being carried through the mobile phase. The part of the analyte which shows strong affinity towards the stationary phase comes first, while those with lower affinity appear later.

The basic components of the Gas Chromatogram are shown in Figure 3.2.

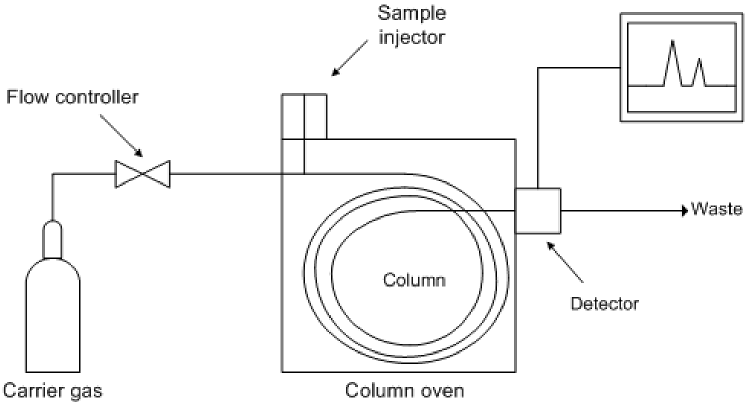


Figure 3.2: Schematic diagram of Gas Chromatograph.

The gas cylinder is the source of pure carrier gas which acts as mobile phase and carries analyte through the chromatographic system. The two stage pressure regulator serves two purposes; it checks the pressure of gas inside the cylinder and the pressure of the gas being applied to the chromatogram. The sample of the analyte is injected through the injection port for analysis. The oven regulates the temperature of the column where separation process occurs. The detector senses the analyte into the effluents coming out of the column and sends the signal to the data system which collects the signal and generates a chromatogram. A chromatogram is a plot of time *versus* output signals generated from the detector. The intensity of the output signal varies with the concentration of analyte or mass of analyte.

The analyte is injected through the hot injection port *via* a syringe where sample and solvent vaporizes. A silicon rubber septum is applied at the top of injector to avoid leak in the system. The vapors of the analyte are carried by the carrier gas over the stationary phase where various components of the analyte absorbed onto the surface of stationary phase depending on the preference of binding. The affinity of adsorption is measured by the distribution coefficient 'K', which relates the ratio of solute in the stationary phase and mobile phase. This resulted analyte separation into distinct bands in the column and is taken forward to the detector by carrier gas. At detector analyte is detected and signal is recorded by the data station, generating the chromatogram.

The distribution coefficient (K) is given by the expression,

$$K = \frac{[A]_{\mathrm{S}}}{[A]_{\mathrm{M}}}$$

where, $[A]_{\mathrm{S}}$ is the analyte concentration in stationary phase and $[\mathrm{A}]_{\mathrm{M}}$ is the analyte concentration in the mobile phase.

The higher value of K indicates the greater affinity of the analyte towards stationary phase. This suggests higher retention time for the analyte in the column.

3.4 Viscometer

The viscosity of ionic liquid systems is measured by using Brookfield viscometer. The Brookfield cone-plate viscometer precisely measures the viscosity of at different rotational speeds. The system consists of a calibrated beryllium-copper spring to a rotating cone which senses the resistance to rotation caused by the fluid between the cone and a stationary flat plate. The resistance produced by fluid in the rotation of the cone produces a torque that is proportional to the shear stress in that fluid. The magnitude of shear stress is converted into the viscosity in centipoise (cP).

"*Everything in the universe has a polar opposite; in every failure, lies a success.*" – *Laws of Polarity*

4: Thermosolvatochromism in Protic Ionic Liquids

In this chapter effect of structure and temperature on the polarity of protic ionic liquids has been studied by using the solvatochromic method. This method depends on the change in electronic transition due to the change in solvent polarity, while thermosolvatochromism is the temperature-dependent polarity. The thermal effect on the two classes of protic ionic liquids viz. 1-methylimidazolium and 1-butylimidazolium having bisulphate, formate, acetate, and propionate anions are studied between the temperature range 298.15 to 353.15 K. The dependence of polarity of protic ionic liquids on the structural components is drawn from the thermosolvatochromic study. The intermolecular interaction between cation and anion, which governs polarity of protic ionic liquid, are discussed in terms of the Kamlet-Taft parameters.

4.1: Introduction

The solvent effects of protic ionic liquids are studied by measuring their polarity. The polarity of ionic liquids is sensitive towards the nature of cation and anion and is guided by the nature and strength of Coulomb and van der Waals interaction between ions. Recent theoretical observations based on the principal component analysis for a number of aprotic ionic liquids demonstrate the influence of structural variations on polarity.[1,2] Polarity of ionic liquids can be measured by a multiparameter approach, electronic transition energy, $E_T(30)$, and Kamlet–Taft parameters, α hydrogen bond donor acidity, β hydrogen bond acceptor basicity and π^* dipolarity/polarizability.[3,4] $E_T(30)$ is measured by using Reichardt's dye, while *N,N*-diethyl-4-nitroaniline and 4-nitroaniline have been used for the measurement of Kamlet–Taft parameters. Polarity of ionic liquids has been also measured by using microwave dielectric spectroscopy as studied by Weingartner *et al.*[5] However, for low viscous fluids, the fast elementary steps of solvation dynamics and solvent-controlled chemical reactions have been probed by using FTIR spectroscopy because dielectric spectroscopy is valid for slow diffusive processes.[6,7]

The hyperpolarity of protic ionic liquids as expected due to the extended hydrogen-bonding is also supported by the microwave dielectric spectroscopy, where strong orientational correlation between dipoles can enhance dielectric polarization.[6,7] The behavior of ionic liquids and their solvation capability also depend upon the nature of the dissolved solute.[8,9] The polarity of ionic liquids obtained using a polar solute differs significantly from that obtained by using a non-polar solute. The spectroscopically active salt 1-ethyl-4-(methoxycarbonyl)pyridinium iodide, [Py]I, also indicates the higher polarity of ionic liquids due to the lower concentration of ion-pairs while higher concentration was noted in the molecular solvents of higher polarity.[8,9]

The low volatility of solvatochromic dyes makes them useful over a wide range of temperatures. A literature search reveals that a few studies exist on the thermosolvatochromism of ionic liquids and their solutions.[10-15] The variation of alkyl chain length and the introduction of functional groups on cations alter the polarity.[10,11] An earlier report from our group has shown the effect of cosolvents on the polarity of aprotic ionic liquids using a preferential solvation model.[16,17] The strong synergism between an ionic liquid and methanol results into the positive deviation from ideal mixing. A comprehensive study of polarity of ionic liquids and molecular solvents has been reported by Reichardt.[18]

Protic ionic liquids are considered to be ‘hyperpolar’ in nature due to the extensive hydrogen bonding between ions. The polarity of ionic liquids decreases with the increase in distance between ions due to decrease in effective charge density between them. In this work, we present the polarity of some protic ionic liquids with a view to ascertaining the role of anions. Herein, we represent another explanation based on the Kamlet–Taft parameters for the variation in polarity upon varying anions towards a particular cation. Polarity study using the solvatochromic technique depends on the preferential stabilization of well formed polar/apolar ground or excited states of the probe molecule. The probability of interaction between ions and the probe molecule directly depends on the extent of Coulombic interactions between them. Strong coulombic forces between ions lead to weaker interaction with the probe molecule; thereby reducing the polarity on the solvatochromic scale.

In the present study, we now investigate the thermal effect on solvatochromism of probe molecules in 1-methylimidazolium and 1-butylimidazolium classes of protic ionic liquids. We also address the question whether ‘hyperpolarity’ in protic ionic liquids is anion-dependent. The acronyms and names of protic ionic liquids used in this work have been collected in Table 4.1, while Figure 4.1 depicts the structures of these protic ionic liquids. In Figure 4.2 are shown the solvatochromic probe molecules used in this investigation.

Table 4.1: The Acronyms of Ionic Liquids Employed in the Present work.

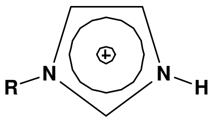
acronyms	names of ionic liquid
[BMIm][BF_4]	1-butyl-3-methylimidazolium tetrafluoroborate
[BMIm][PF_6]	1-butyl-3-methylimidazolium hexafluorophosphate
[HmIm][HSO_4]	1-methylimidazolium bisulphate
[HmIm][HCOO]	1-methylimidazolium formate
[HmIm][CH_3COO]	1-methylimidazolium acetate
[HmIm][CH_3CH_2COO]	1-methylimidazolium propionate
[HbIm][HSO_4]	1-butylimidazolium bisulphate
[HbIm][HCOO]	1-butylimidazolium formate
[HbIm][CH_3COO]	1-butylimidazolium acetate
[HbIm][CH_3CH_2COO]	1-butylimidazolium propionate

4.2: Experimental Section

4.2.1: Materials

The spectroscopic indicator dye 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)-phenolate (1) was obtained from Fluka Analytical (98.5% purity). Reichardt’s dye (2) and 4-nitroaniline (3) were used as obtained from M/s Sigma Aldrich. *N,N*-Diethyl- 4-nitroaniline (4) was purchased from Frinton laboratories (99% purity) (shown in Fig. 2). 1-Methylimidazole, 1-butylimidazole and n-butyl bromide were distilled prior to their use. Formic acid, acetic acid, propionic acid and sulfuric acid solutions all obtained from Merck were used as obtained. Sodium tetrafluoroborate and potassium hexafluorophosphate were used as purchased from Merck.

Cations

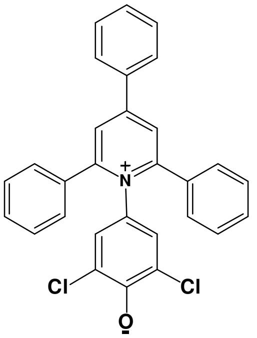


R= CH_3, C_4H_9

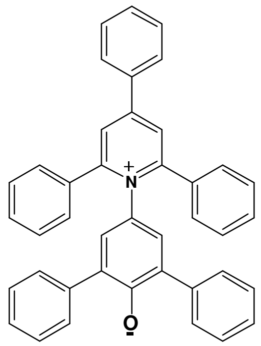
Anions

HSO_4^-, $HCOO^-$, CH_3COO^-, $CH_3CH_2COO^-$

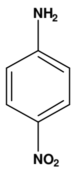
Figure 4.1: Structures of the PILs used for thermosolvatochromic studies.



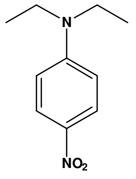
2,6-dichloro-4-(2,4,6-triphenyl-pyridinium-1-yl)phenolate (1)



Reichardt's Dye (2)



4-nitroaniline (3)



N,*N*-diethyl-4-nitroaniline (4)

Figure 4.2: Solvatochromic probe molecules.

4.2.2: Synthesis of Protic Ionic Liquids

Protic ionic liquids were synthesized by an atom-economic process by mixing equimolar amounts of acid and base.[19] Dropwise addition of base to acid was carried out for complete neutralization in an ice bath in order to avoid heat generation. The reaction mixture was stirred for 6 h at room temperature. Water formed in the neutralization was removed by using a rotavapor at 80 °C for 6 h. The last traces of water and other volatile impurities were removed from protic ionic liquids under reduced pressure at 70 °C for 10 h. The characterization and their purities were determined by NMR spectroscopy. The water content of the pure and dried protic ionic liquids as measured by Karl-Fischer coulometer analysis did not exceed 50 ppm. The halide contents were estimated using Volhard titration due to the lack of a sophisticated ion-chromatographic technique with us.[20] It may be noted that the standard Volhard titration has been validated using a chloride-selective electrode.[21] The residual halide contents (bromides) were less, >30 ppm.

4.2.3: Polarity Measurements

The stock solutions of the required dyes were prepared in methanol prior to their use. The stock solution was added dropwise to a protic ionic liquid, and the solvent was evaporated under vacuum. The protic ionic liquid was then transferred to a quartz cuvette under a nitrogen atmosphere and sealed with a septum. The λ_{max} was measured at different temperatures using a UV-visible spectrophotometer. The temperature of the cell was controlled using the single cell accessory having an accuracy of ±0.1 K.

4.3: Determination of E_T^N and Kamlet-Taft Parameters

The equations required to calculate various parameters for characterizing the polarity of ILs are given in the Table 4.2.

Table 4.2: Equations to Determine the E_T^N and Kamlet-Taft Parameters.

polarity parameters	empirical equations
Normalized Electronic Transition Energy (E_T^N)	$E_T(30)$ (kcal mol^{-1}) = $hc\nu_{max}$ = $28591/\lambda_{max}$ (nm) =2.8591 ν_{max} where λ_{max} is the maximum wavelength of lowest energy band of Reichardt's dye (2) $E_T(30)$ can be normalized between water and TMS E_T^N = [E_T (solvent) – E_T (TMS)]/ [E_T (solvent) – E_T (water)] = [E_T (solvent) – 30.7]/32.4
Hydrogen Bond Donor Acidity (α)	$\alpha = 0.0649\ E_T(30) - 0.72\ \pi^* - 2.03$
Hydrogen Bond Acceptor Basicity (β)	$\nu_{(3)max} = 1.035\nu_{(4)max} - 2.8\beta + 2.64$ where $\nu_{(3)max}$ and $\nu_{(4)max}$ are the maximum wave number of the 4-nitroaniline (probe 3) and *N,N*-diethyl-4-nitroaniline (probe 4), respectively
Polarity Index (π^*)	$\nu_{(4)\ max} = 27.52\text{-}3.182\pi^*$

Protic ionic liquids possess lower pK_a values, leading to the protonation of Reichardt's dye 30 (pK_a = 8.6) and therefore, the long-wavelength intramolecular charge transfer (ICT) absorption band disappears. The $E_T(30)$ data for all protic ionic liquids were derived from $E_T(33)$, a polarity scale of a less basic probe 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl) phenolate (pKa = 4.78). For this purpose, a simple linear regression method was used, involving eight molecular solvents and one ionic liquid as shown in Figure 4.3.

$$E_T(30) = 0.9119(\pm 0.02956)\ E_T(33) - 3.80634(\pm 1.68048) \qquad (1)$$

The calculated $E_T(30)$ values using above formula were found in good agreement with the measured $E_T(30)$ values as shown in Table 4.3.

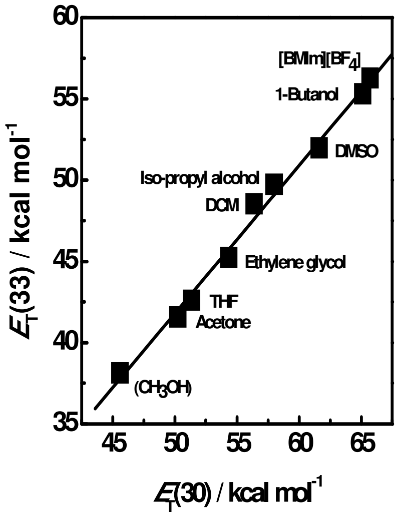


Figure 4.3: A linear regression analysis between $E_T(30)$ and $E_T(33)$. (r^2 = 0.99, SD = 0.574, n = 9, P = < 0.0001).

As suggested by earlier workers, Reichardt dye 30 (2) is not suitable for the polarity measurement of protic ionic liquids.[22] They used Nile red, the least basic solvatochromic dye that has been extensively used for the polarity measurement of weak acids and protic molecular solvent. However in our study we used Reichardt dye 33 (1) and observed the long wavelength ICT absorption band, which is absent in the case of Reichardt dye 30 (2).

4.4: Results and Discussion

The polarity parameters $E_T(30)$, α, β, and π^* for 1-methylimidazolium and 1-butylimidazolium class of protic ionic liquids were initially determined at 298.15 K as shown in Table 4.3. The measured values are in good agreement with the reported data for some ionic liquids and organic solvents. The trends in polarity for $[HmIm]^+$ and $[HbIm]^+$ classes of protic ionic liquids were found to be:

$[HmIm][HSO_4] > [HmIm][HCOO] > [HmIm][CH_3COO] >$
$[HmIm][CH_3CH_2COO]$

$[HbIm][HSO_4] > [HbIm][HCOO] > [HbIm][CH_3COO]$

$> [HbIm][CH_3CH_2COO]$

4.4.1: A Comparison of Polarity in Protic and Aprotic Ionic Liquids

It is imporatnt to understand how polarity of protic ionic liquid differ from those of aproticionic liquid. The polarity study in aprotic ionic liquids and protic ionic liquids show opposite behavior with respect to Kamlet-Taft parameters. In aprotic ionic liquids, hydrogen-bond donating (HBD) ability α has a major effect on the E_T^N value, while hydrogen-bond accepting (HBA) ability β has a negligible effect on the E_T^N.[16,18] HBD ability is solely controlled by cation while HBA ability depends on the nature of anion. Similar observations were obtained in the case of hydroxylic solvents and water, where HBD ability promotes high polarity (E_T^N). Introduction of alkyl substituent greatly affects the HBD ability. In imidazolium-based ionic liquid, the polarity decreases as the length of alkyl chain increases from ethyl to octyl. From $[EMIm][N(Tf)_2]$ to $[OMIm][N(Tf)_2]$, E_T^N decreases from 0.658 to 0.630. This decrease in E_T^N is in the same order of decreasing HBD ability (0.627 for $[EMIm][N(Tf)_2]$ and 0.595 for $[OMIm][N(Tf)_2]$).[11] Similar observations were noted for the pyridinium, pyrrolidinium and phosphonium-based ionic liquids where E_T^N values vary as the HBD ability.[11,16] Influence of substituent on α was observed similar to the influence on polarity, indicating that α is a major contributor to polarity.[10,15] Hydrogen bond accepting tendency β depends on the anion. The presence of alkyl substituent on the cation has a little effect on β value.[11]

Table 4.3: Polarity Parameters of Protic Ionic Liquids, Aprotic Ionic Liquids and Molecular Solvents at 298.15 K.

ionic liquids / solvents	$E_T(33)$ kcalmol	$E_T(30)$ kcal/mol	E_T^N	π^*	α	β
[HmIm][HSO_4]	73.89	63.6	1.02	1.17	1.225	0.61
[HmIm][HCOO]	65.62	56.0	0.78	1.10	0.812	0.81
[HmIm][CH_3COO]	59.50	50.5	0.61	1.03	0.506	0.85
[HmIm][CH_3CH_2COO]	55.70	47.0	0.50	1.50	-0.06	0.10
[HbIm][HSO_4]	76.04	65.5	1.07	1.12	1.415	0.58
[HbIm][HCOO]	66.20	56.6	0.80	0.97	0.945	0.73
[HbIm][CH_3COO]	65.01	55.5	0.77	0.88	0.938	0.73
[HbIm][CH_3CH_2COO]	64.35	54.9	0.75	1.01	0.806	0.63
[BMIm][PF_6]		53.64	0.71	1.04	0.702	0.24
		(52.4)a	(0.67)a	(1.03)a	(0.63)a	(0.21)a
[BMIm][BF_4]	61.61	52.4	0.67	1.05	0.62	0.72
		(53.6)b	(0.71)b	(1.05)b	(0.63)b	(0.34)b
Methanol	65.13	55.6	0.77	0.735	1.049	0.63
		(55.4)c	(0.76)c	(0.73)c	(1.05)c	(0.6)c
Acetone	51.34	43.0	0.38	0.71	0.250	0.54
		(42.0)d	(0.35)d	(0.70)d	(0.20)d	(0.54)d
Ethylene Glycol	65.73	56.1	0.78	1.024	0.874	0.59
		(56.3)e	(0.79)e	(0.93)e	(0.95)e	(0.51)e
Tetrahydrofuran	45.59	37.8	0.22	0.590	-0.002	0.61
		(38.1)f	(0.21)f	(0.60)f	(0.0)f	(0.54)f

Reported values are given in the parentheses [a]Ref [15] [b]Ref [15] [c]Ref [10] [d]Ref [10] [e]Ref [23] [f]Ref[24]

Contrary to aprotic ionic liquids, for which the constitutent cation governs polarity, the anion has a major contribution towards polarity (E_T^N) in protic ionic liquids. In spite of very high α value, the E_T^N of protic ionic liquids were observed low when compared to those of the molecular solvents, for which higher α value always resulted to the higher polarity (E_T^N value). This indicated the partial reduction in the cationic control on polarity by anion. The E_T^N value fluctuates according to their hydrogen bond accepting tendency (β). Variation in the polarity with anion is in the same order as that of the β value. The α has no direct effect on the polarity of PILs. However, [HmIm][HSO_4] and [HbIm][HSO_4] show high polarity due to the presence of oxyanions. HBA tendency for [HSO_4]$^-$, [HCOO]$^-$ and [CH_3COO]$^-$ anion was found as 0.61, 0.81 and 0.85, respectively, which is in the order of their decreasing polarity. In the case of [CH_3CH_2COO]$^-$ the β value was noted as 0.10, which is against the order of E_T^N value. Probably, high π^* (1.50) value controls this behavior. A substitution of -CH_3 by -C_4H_9 on imidazole ring favors high E_T^N value. It appears that the steric crowding around cation plays down the influence of anion on polarity. However, the thermosolvatochromic trend mimics the thermal effect on α than β. An increase in temperature from 298.15 to 353.15 K causes slight lowering in the α value leading to negligible or small effect on the E_T^N value.

4.4.2: E_T^N Parameter

The E_T^N values for 1-methylimidazolium and 1-butylimidazolium class of protic ionic liquids show similar trend with the variation in anion, but slightly different trend with temperature. The E_T^N value for 1-methylimidazolium class of protic ionic liquids remains unaffected with the change in temperature from 298.15 to 353.15 K. A strong stabilization of the dye molecule in ground state cannot be weakened by an increase in temperature. A very small decrease in the α and β values in the temperature range of 298.15 to 353.15 K supports strong association between protic ionic liquids and the dye molecule. The temperature dependence of the E_T^N parameters for several protic ionic liquids is shown in Figure 4.4 (a) and (b). Polarity index (π^*) depends on the interaction of dye molecule with its cybotactic environment. The strong interaction of a dye with its environment leads to the high value of π^*. High π^* value stabilizes the charge of dye molecule in the excited state and therefore influences the polarity.

The π^* value for 1-methylimidazolium class of protic ionic liquids were noted to be either constant or to decrease slowly with temperature from 298.15 to 353.15 K. The observed trends in the E_T^N values for 1-butylimidazolium class of protic ionic liquids are found slightly different with increasing temperature. The E_T^N value for [HmIm][HSO_4] was noted to be 1.02 at 298.15 K. An increase in the basicity of anion from [HSO_4]$^-$ to [HCOO]$^-$ as indicated by the increased β value from 0.61 to 0.81, respectively, leads to strong Coulombic interactions between ions in protic ionic liquids, which lowers the E_T^N value from 1.02 for [HmIm][HSO_4] to 0.78 for [HmIm][HCOO] at 298.15 K. A further increase in the β value (0.85) for $[CH_3COO]^-$ anion lowers the E_T^N value to 0.61 at 298.15 K. The β value for $[CH_3CH_2COO]^-$ was observed to be lower than $[HCOO]^-$ and $[CH_3COO]^-$ suggesting polarity should be higher for [HmIm][CH_3CH_2COO] than [HmIm][HCOO] and [HmIm][CH_3COO]. However, the polarity for [HmIm][CH_3CH_2COO] was observed to be lower than the [HmIm][HCOO] and [HmIm][CH_3COO]. This anomalistic decrease in polarity (E_T^N value) in spite of lower β value (0.10) for [HmIm][CH_3CH_2COO] is quite surprising. However, high π* value (1.50) indicates higher polarity.

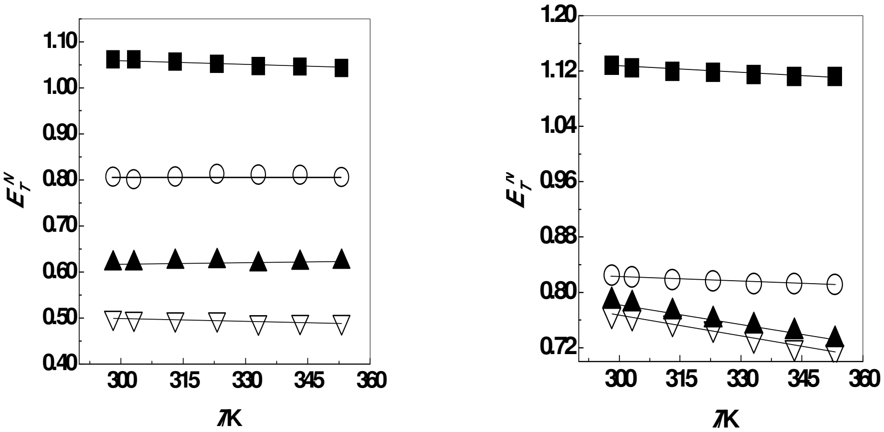


Figure 4.4: The E_T^N-T plots of (a) [HmIm][HSO_4](■), [HmIm][HCOO](○), [HmIm][CH_3COO](▲), [HmIm][CH_3CH_2COO](▽), (b) [HbIm][HSO_4](■), [HbIm][HCOO](○), [HbIm][CH_3COO](▲), [HbIm][CH_3CH_2COO](▽).

Substitution of the –CH_3 group by –C_4H_9 remarkably increases the E_T^N value of the ionic liquid. In the 1-butylimidazolium class of protic ionic liquids comparatively lower value of π* and β while higher α value decides the extent of Coulombic interaction between ions and hence polarity in protic ionic liquids. This lowering in Kamlet-Taft parameters can only be attributed due to the presence of butyl chain.

Discrepancies in the E_T^N values for 1-butylimidazolium class of protic ionic liquids were seen with an increase in the temperature from 298.15 to 353.15 K. There was no thermosolvatochromic change found in the E_T^N value for [HbIm][HSO$_4$] and [HbIm][HCOO], but the decreasing trend in the E_T^N value was observed for [HbIm][CH$_3$COO] and [HbIm][CH$_3$CH$_2$COO].

Thermosolvatochromic response for [HbIm][CH$_3$COO] and [HbIm][CH$_3$CH$_2$COO] may be due to high thermal sensitivity of the Kamlet-Taft parameter. E_T^N value was found decreasing for [HbIm][CH$_3$COO] from 0.77 to 0.71 and for [HbIm][CH$_3$CH$_2$COO] from 0.75 to 0.70 in the temperature range from 298.15 to 353.15 K. Thus, [HbIm][CH$_3$COO] and [HbIm][CH$_3$CH$_2$COO] show positive thermosolvatochromic response.

4.4.3: *α* parameter

In spite of very close similarity in the behavior of E_T^N and α in the temperature range of 298.15 to 353.15 K, it was noted that α had no direct hold on the polarity of protic ionic liquids. The α-T plots of different protic ionic liquids are shown in Figure 4.5. For 1-methylimidazolium class of protic ionic liquids α parameter was observed to be constant over the temperature change from 298.15 to 353.15 K. For 1-butylimidazolium class of protic ionic liquids, a small increase in α was noted for [HbIm][HSO$_4$] and [HbIm][HCOO] with rise in temperature, while E_T^N remained constant. However, for [HbIm][CH$_3$COO] and [HbIm][CH$_3$CH$_2$COO], α decreased from 0.938 to 0.907 and 0.806 to 0.760, respectively within the temperature range of 298.15 to 353.15 K. The exceptionally high α value for [HmIm][HSO$_4$] and [HbIm][HSO$_4$] may be due to the presence of oxyanion. Unusually higher α value makes them more polar than water. Surprisingly a negative α value for [HmIm][CH$_3$CH$_2$COO] was noted, which indicated the dominance of HBA basicity of anion over the HBD acidity of cation. Probably, a retrotransfer of quaternized proton to a more basic organic anion is responsible for this dramatic behavior.[25,26] Further, protic ionic liquids form extensive hydrogen bonding which stabilizes both cation and anion, therefore, the probability of reverse proton transfer becomes low. Due to these opposing phenomena, a very small proportion of neutral moiety exists along with the protic ionic liquid that leads to the lower α value, which is far beyond the α value for pure CH$_3$CH$_2$COOH *i.e.* 1.12.[26]

The order of HBD tendency for 1-methylimidazolium class of ionic liquids was found to be:

[HmIm][HSO_4] > [HmIm][HCOO] > [HmIm][CH_3COO] >
[HmIm][CH_3CH_2COO]

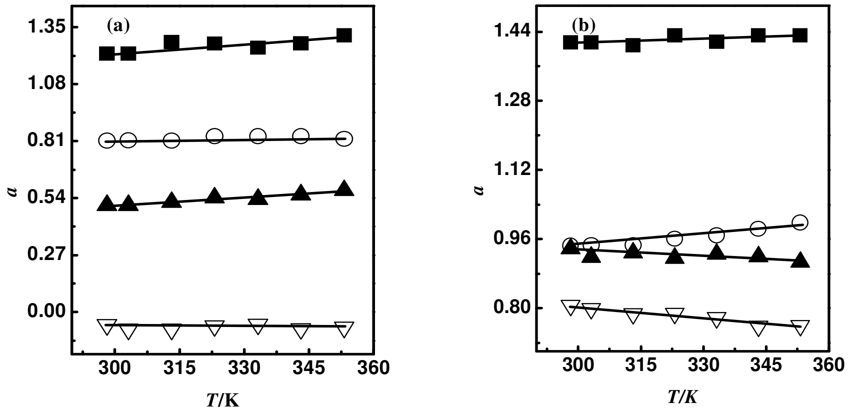


Figure 4.5: The *α-T* Plots for (a) [HmIm][HSO_4](■), [HmIm][HCOO] (○), [HmIm][CH_3COO](▲), [HmIm][CH_3CH_2COO](▽), (b) [HbIm][HSO_4](■), [HbIm][HCOO](○), [HbIm][CH_3COO](▲), [HbIm][CH_3CH_2COO](▽).

Further, HBD tendency for 1-butylimidazolium class of ionic liquids was noted slightly higher than 1-methylimidazolium class of ionic liquids as shown in Table 4.3. The presence of butyl chain in 1-butylimidazole surprisingly increases the HBD acidity. The order of HBD value for 1-butylimidazole class at 298.15 K was observed as:

[HbIm][HSO_4] > [HbIm][HCOO] > [HbIm][CH_3COO] > [HbIm][CH_3CH_2COO]

4.4.4: *β* Parameter

The hydrogen bond acceptor (HBA) basicity *β,* was observed to decrease with an increase in temperature from 298.15 to 353.15 K. The *β-T* plots of protic ionic liquids are shown in Figure 4.6. The *β* value increased with the rise in temperature from 298.15 to 353.15 K for [HmIm][HSO_4] and [HbIm][HSO_4]. Contrary to this, the *β* value for protic ionic liquids containing $[HCOO]^-$, $[CH_3COO]^-$ and $[CH_3CH_2COO]^-$ anions were found high and decreased with a rise of temperature. Exceptionally, low *β* values for [HmIm][CH_3CH_2COO] may be due to the presence of neutral moiety along with the ionic species. However, *β* for [HmIm][CH_3CH_2COO] is very small than the *β* for pure CH_3CH_2COOH (0.45). Let us consider the following equilibria:

$$HA + B = [BH^+] + A^-$$

The strong acid (low pK_a) favors the equilibrium towards right due to complete transfer of proton showing high *β* value. However, the stabilization of cation and anion by hydrogen bonding opposes the formation of neutral species. Thus, it was assumed that the presence of ionic species favors high *β* value and a combination of neutral species i.e. solvents and ionic species favors low *β* value.

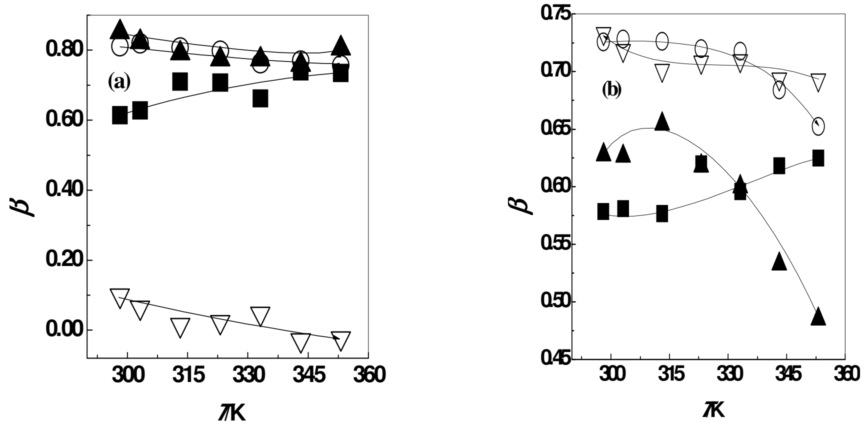


Figure 4.6: The *β*-*T* Plots for (a) [HmIm][HSO_4] (■), [HmIm][HCOO] (○), [HmIm][CH_3COO] (▲), [HmIm][CH_3CH_2COO] (▽), (b) [HbIm][HSO_4] (■), [HbIm][HCOO] (○), [HbIm][CH_3COO] (▲), [HbIm][CH_3CH_2COO] (▽).

Further the observed trends for 1-methylimidazolium and 1-butylimidazolium class of PILs were noted to be:

[HmIm][HSO_4] > [HbIm][CH_3CH_2COO] > [HbIm][HCOO] > [HbIm][CH_3COO]

[HbIm][HSO_4] > [HbIm][CH_3CH_2COO] > [HbIm][HCOO] > [HbIm][CH_3COO]

Thus, the anomalous trend in *β* values for protic ionic liquids containing [HCOO]$^-$, [CH_3COO]$^-$ and [CH_3CH_2COO]$^-$ is attributed only to the higher basicity (pK_a) and to the relative stability of of these anions by hydrogen bonding.

4.4.5: *π** Parameter

The dipolarity/polarizability parameter, *π** is based on the *π*-*π** electronic transition of *N,N*-diethyl-4-nitroaniline. Its magnitude depends upon the interactions of chromophore with its cytobactic environment. With a rise in temperature the interaction weakens, giving rise to a decrease of *π** values. The high value of dipolarity/polarizability for 1-methylimidazolium class of protic ionic liquids reveals that strong interaction occurs between probe and protic ionic liquids. With increasing temperature, non-linear decrease in the *π** values were observed as shown in Figure 4.7. As evident, the trend in *π** value is:

[HmIm][CH_3CH_2COO] > [HmIm][HSO_4] > [HmIm][HCOO] >
[HmIm][CH_3COO]

Exceptionally high dipolarity/polarizability ratio for [HmIm][CH_3CH_2COO] was recorded. Very low *β* value (0.10) and moderate *α* value (0.66) can be attributed to the strong interactions between dye and [HmIm][CH_3CH_2COO].

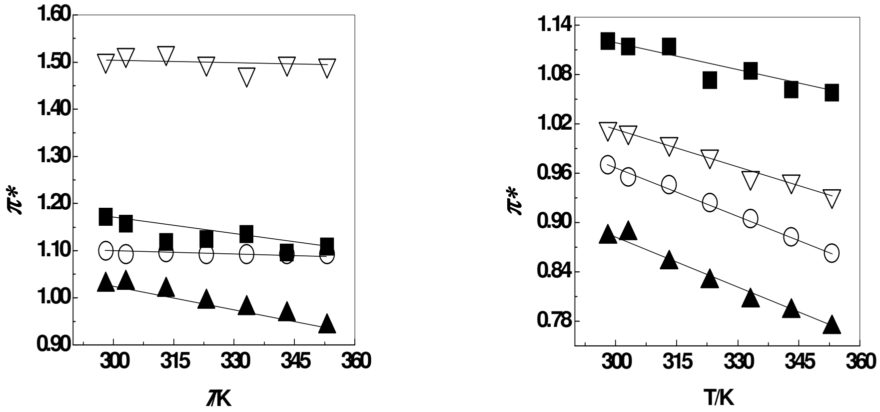


Figure 4.7: The Plots of *π**-*T* for **(a)** [HmIm][HSO_4] (■), [HmIm][HCOO] (○), [HmIm][CH_3COO] (▲), [HmIm][CH_3CH_2COO] (▽) **(b)** [HbIm][HSO_4] (■), [HbIm][HCOO] (○), [HbIm][CH_3COO] (▲), [HbIm][CH_3CH_2COO] (▽).

The *π** value for 1-butylimidazolium class of protic ionic liquids were found slightly lower than the 1-methylimidazolium class of protic ionic liquids. The introduction of butyl chain on imidazolium ring makes it more asymmetric, allowing a close approach of cation to create the nanoscale regions of aliphatic character in which probe molecule may partition.[27] This leads to the lower dipolarity/polarizability ratio for 1-butylimidazolium class of protic ionic liquids. With a rise in temperature, π^* values decrease linearly. The observed trend in π^* values for 1-butylimidazolium class of protic ionic liquids are as:

$$[HbIm][CH_3CH_2COO] > [HbIm][HSO_4] > [HbIm][HCOO] > [HbIm][CH_3COO]$$

Thus, polarity measurement (E_T^N value and Kamlet-Taft parameters) in protic ionic liquids depend on the Coulombic interaction which is governed by the basicity of anion and dipolarity/polarizability. The cation has a very small effect on the polarity of protic ionic liquid.

4.5: Fajans' Rule and Polarity of Ionic Liquids: Reverse Polarization

In 1923, Fajans developed his quanticule theory called as "Fajans' rule" to explain the development of partial covalent character in ionic bond.[28] According to this theory a small, highly charged cation pulls the electron cloud of an anion, thereby developing covalent character in ionic bond. Interaction of a cation of high charge density (hard) with anion of high polarizability (soft) generates a covalent character between the ions in which cation penetrates the electron cloud of anion. Polarization of a large anion by small cation is very frequent phenomena. However, is it possible to see the polarization of a large cation by a small anion? This turnaround of interaction between ions leading covalent character is known as reverse polarization. However, practically, it seems difficult because a soft cation holds its electron cloud, while a hard anion cannot repel its electron cloud to become a nucleus. For reverse polarization both the requirements are essential.

Ionic liquids are composed entirely of bigger ions and there is always a possibility to develop covalent character between them. Polarity study in different classes of aprotic ionic liquids suggests them to be of low polarity, comparable to short chain alcohol. In all these classes of ionic liquids it is difficult to correlate the polarity with cation and anion. In order to make an ionic liquid, it is desirable to incorporate a bulky cation having diffuse positive charge with various kinds of anion. A bulky cation with diffused charge behaves as a polarizable cation that can be easily distorted by anion. In this condition there is a possibility of reverse polarization in ionic liquid. Hardness of anions, therefore, acts as guiding criteria to develop the covalent character in ionic liquid changing polarity. A strong interaction between ions creates more covalent character and therefore changes the polarity as measured by solvatochromic method. Among various class of ionic liquids it was observed that soft anions such as $[NTf_2]^-$, $[PF_6]^-$ interact weakly with soft cation (such as alkylimidazolium) while hard anions such as $[BF_4]^-$, $[N(CN)_2]^-$ come much closer approach towards the soft cation. The magnitude of this interaction governs the development of covalent character and thereby polarity of ionic liquids. The E_T^N values for $[BMIm][N(Tf)_2]$ and $[BMIm][PF_6]$ were measured as 0.645 and 0.669, respectively while for $[BMIm][N(CN)_2]$ as 0.629.[29-31] This small difference in E_T^N value arises due to the strong interactions of $[N(CN)_2]^-$ towards $[BMIm]^+$ as compared to those of $[N(Tf)_2]^-$ and $[PF_6]^-$ offering less interactions for $[BMIm]^+$. Similarly, for $[EMIm][N(Tf)_2]$, $[EMIm][PF_6]$ and $[EMIm][N(CN)_2]$, the E_T^N values were observed 0.658, 0.676 and 0.648, respectively.[29,32] In the pyridinium-based ionic liquids *i.e.* $[BP][BF_4]$ and $[BP][N(Tf)_2]$, the E_T^N values recorded were 0.639 and 0.648, respectively.[16] This again confirms the role of anion as a guiding factor to determine the polarity. An increase in the alkyl chain length bears the similar effect on the E_T^N value for $[OP][BF_4]$ and $[OP][N(Tf)_2]$ to be 0.606 and 0.617, respectively.[16]

PILs due to the extensive hydrogen bonding act as hyperpolar media. A transfer of proton from Brønsted acid to Brønsted base generates the conjugate counterpart of acid and base. The relative basicity of an anion for a cation controls the development of covalent character. However, oxyanions such as $[HSO_4]^-$, $[NO_3]^-$, $[H_2PO_4]^-$ etc. due to the extensive network of hydrogen bonding generate highly polar PILs. The current polarity study in 1-methylimidazolium and 1-butylimidazolim class of PIL with $[HSO_4]^-$, $[HCOO]^-$, $[CH_3COO]^-$ and $[CH_3CH_2COO]^-$ as a counter anions shows exceptionally low E_T^N value except for $[HSO_4^-]$. The lower polarity arises due to the increasing polarizability of anion. The stronger interaction of 1-methylimidazolium with the increasing polarizability of anion ($[HCOO]^-$, $[CH_3COO]^-$ and $[CH_3CH_2COO]^-$) leads to the greater degree of polarization and hence, the E_T^N value becomes exceptionally low. The E_T^N values for [HmIm][HCOO], [HmIm][CH_3COO] and [HmIm][CH_3CH_2COO] were noted as 0.78, 0.61 and 0.50, respectively. The lowest value for [HmIm][CH_3CH_2COO] is close to that of dimethylsulphoxide (0.444), acetonitrile (0.46) and 2-propanol (0.50) acting as non-polar media. Similarly, for 1-butylimidazolium-based protic ionic liquids with $[HCOO]^-$, $[CH_3COO]^-$ and $[CH_3CH_2COO]^-$ anions, the E_T^N values were found 0.80, 0.77 and 0.75, respectively. The presence of $-C_4H_9$ lowers the polarizing power of cationic core thereby decreasing the E_T^N value due to partial development of covalent character.

A correlation between the polarity (E_T^N value) and polarization of ions prompts us to develop a concept dealing with the polarizing power and polarizability of cation/anion. However, it is difficult to discuss the Kamlet-Taft parameters (α, β and π^*) and polarization of ions on the similar grounds. Only hydrogen bond donor tendency (α) was observed to depend on the nature of anion. More polarizable anion leads to the lower α value than less polarizable anion. The α value for [BMIM][$N(CN)_2$] was observed 0.464, while for [BMIM][NTf_2] and [BMIM][PF_6] the values were 0.617 and 0.634, respectively.[29-31]

4.6: Conclusions

In conclusion, the polarity in protic ionic liquids is anion specific. The protic ionic liquids having organic anions play a crucial role in deciding the interaction of dye and ions in ionic liquids due to their large hydrogen bond acceptor tendency β. The relative stabilization of the ions by hydrogen bonding and the reverse proton transfer between cation and anion controls the α and β. The thermosolvatochromic study shows a constant polarity for protic ionic liquids over wide range of temperature. It suggests that protic ionic liquids can be used as a media for those processes, where constant polarity is needed at higher temperatures. Further investigations are required to explore the data on the thermosolvatochromic study in other classes of protic ionic liquids.

4.7: References

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"*… a sober evaluation of the data suggests the phenomena warrants further scrutiny*" *– Kenny Young*

5. Determination of Hammett Acidity of Carboxylic Acids in Protic Ionic Liquids, Water, and Their Binary Mixtures

In this chapter, the Hammett acidity (H_0) of HCOOH, CH_3COOH, and CH_3CH_2COOH has been determined in protic ionic liquids, water, and their binary mixtures. In Section 5.1, the H_0 for carboxylic acids was measured in water and alkylimidazolium-, pyrrolidinium-, and piperidinium-based protic ionic liquids possessing formate and acetate anions. The ability of protic ionic liquids and water in the dissociation of carboxylic acids was discussed in terms of the solute-solvent interactions between them. In Section 5.2, different proportions of protic ionic liquids mixed in water were used to measure the H_0 of carboxylic acids. The role of solvent on the dissociation of carboxylic acids in binary mixtures is discussed in terms of complex ionic liquid-cosolvent systems.

5.1: Hammett Acidity of Carboxylic Acids in Protic Ionic Liquids and Water: Mechanism of Dissociation

5.1.1: Introduction

Protic ionic liquids have been used as media to carry out many acid-catalyzed reactions due to the presence of acidic proton.[1] In spite of being a subject of extensive investigation in various applications from very early development of protic ionic liquids; a little research has been carried out on the acidity formulation of these non-aqueous media. Their use in various processes such as pharmacological application, reaction mechanism, properties of new materials, changing molecular structure, etc requires the precise information about the acidity level. Several attempts have been made to estimate the acidity of protic ionic liquids using different acidity scales.[2,3] Though protic ionic liquid contain an acidic proton, their acidity can further be tuned by mixing Brønsted acid.

Acid-base notion for a variety of compounds was based on their p*K*a values. Since p*K*a is more useful only for aqueous medium alternate methods such as potentiometric titration and acidity functions have been used for nonaqueous media. By using potentiometric titration and acidity functions pH value, which ranges from $1 < pH < 13$ can be extended on either end in aqueous/nonaqueous solvents.[4,5] Unlike pH, which indicates the total strength of proton, unconventional method like Hammett function observes the variation of any physical property due to the protonation. Acidity determination of weak acids and bases in non-aqueous medium by spectroscopic method depends on the isolation of spectral changes due to the protonated/non-protonated forms of the indicator. For most of the indicators isosbestic point was observed which points out the appearance of protonated/non-protonated forms.[6] A large number of acidity functions depending on the acidity and basicity of the medium are available in the literature. The determination of acidity function based on the primary nitroaniline as a base is well established because of high accuracy in its measurement.

The first report on acidity determination in ionic liquids was published by Thomazeau, Oliviér-Bourbigou, Magna, Luts and Gilbert who measured the acidity of bistriflylimide acid ($HN(Tf)_2$) and triflic acid (HOTf) in the imidazolium-based aprotic ionic liquids.[7] They observed the same acidity level for $HNTf_2$ and HOTf in 1-butyl-3-methylimidazolium bistriflimide, $[BMIm][N(Tf)_2]$. However, $HN(Tf)_2$ showed higher acidity level in 1-butyl-3-methylimidazolium tetrafluoroborate, $[BMIm][BF_4]$ than that in $[BMIm][N(Tf)_2]$ because of the lesser solvation of proton (H^+) by BF_4^- than that of NTf_2^-.The role of C2-H (most acidic proton on ring) on the acidity of $HN(Tf)_2$ was negligible, as similar H_0 values were noted in $[BMIm][BF_4]$ and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate, $[BMMIm][BF_4]$. Recently, a general account on the acidity of different carboxylic acids in 1-butyl-2,3-dimethylimidazolium bistriflimide, $[BMMIm][N(Tf)_2]$ and *N*-butyl-*N*-methyl pyrrolidinium bistriflimide, $[BMPyrr][N(Tf)_2]$, using spectrophotometric titration in terms of protonation equilibrium (*K*) has been published by Noto & coworkers.[8,9]

In the current investigation we address the issue of the acidity determination of carboxylic acids in the imidazolium-based protic ionic liquids using Hammett equation. We also attempt to establish a correlation between the acidity of these acids with the structural component of ionic liquids. The carboxylic acids were chosen in order of the relative basicity of their conjugate anion in gas phase. The acronyms for ionic liquids used in the present study are summarized in Table 5.1.1. The structures of protic ionic liquids used in the study are shown in Figure 5.1.1. All protic ionic liquids were synthesiszed by the method discussed in Chapter 4, Section 4.2.2.

Table 5.1.1 The Acronyms of Protic Ionic Liquids Employed in the Present Work.

Acronyms	**names of ionic liquid**
[HmIm][HCOO]	1-methylimidazolium formate
[HmIm][CH_3COO]	1-methylimidazolium acetate
[HbIm][HCOO]	1-butylimidazolium formate
[HbIm][CH_3COO]	1-butylimidazolium acetate
[HPyrr][HCOO]	1-methylpyrrolidinium formate
[HPyrd][HCOO]	1-methylpiperidinium formate

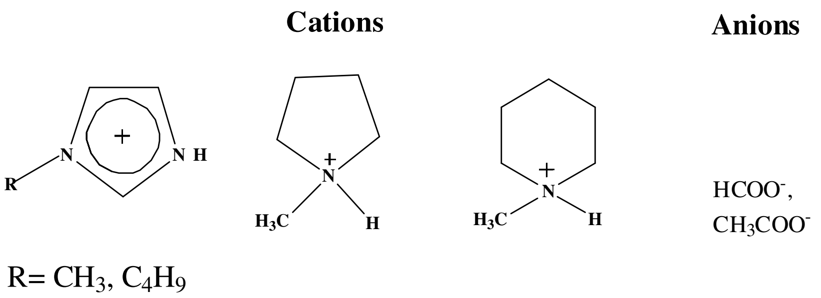


Figure 5.1.1: The structure of protic ionic liquids used in the study.

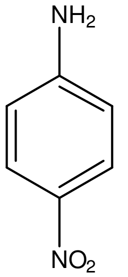
5.1.2: Experimental Section:

5.1.2.1: Materials:

Spectroscopic indicator dye 4-nitroaniline was obtained from Sigma Aldrich. 1-methylimidazole, 1-butylimidazole, 1-methylpyrrolidine and 1-methylpiperidine were purchased from Sigma and distilled prior to use. Formic acid, acetic acid and propionic acid solutions were obtained from Merck and use as obtained. Deionized water possessing conductivity < 18.2 Ω was used throughout the work.

5.1.2.2: Measurement of Acidity Using Hammett Equation

A dilute solution (10^{-4} M) of 4-nitroaniline dye (Figure 5.1.2) in methanol was prepared and used as a stock solution throughout the experiments. All the acids were used as an equimolar solution in water.[10] Any contribution towards the maximum optical density by the medium was set zero by using baseline. A small amount of dye solution was dissolved in 1 ml of protic ionic liquid and methanol was removed by placing it under high vacuum. The whole sample was now filled inside the quartz cuvette and the UV-visible spectrum was recorded. The maximum optical density/absorbance (A_{max}) for protic ionic liquid + dye solution was used as a reference for each protic ionic liquid. An addition of acid in protic ionic liquid + dye content protonates the dye, thereby decreasing the maximum optical density. Similarly, A_{max} after each addition of acid was recorded and again compared with the A_{max} of protic ionic liquid + dye solution. This relative comparison between A_{max} of protic ionic liquid + dye solution and protic ionic liquid + dye + acid solution gave the relative abundance of protonated and non-protonated form of the dye.



4-nitroaniline

Figure 5.1.2. The acidity probe 4-nitroaniline (pK_a = 0.99).

The acidity of the solution can be calculated by using Hammett equation in the form of H_0, the acidity function as given:

$$H_0 = pK(I)_{aq.} + \log [I]_s/[HI^+]_s \qquad (1)$$

where $pK(I)_{aq.}$ is the protonation constant of the dye in aqueous solution. For 4-nitroaniline $pK(I)_{aq.}$ = 0.99 and $[I]_s$ and $[HI^+]_s$ are the concentrations of solvated non-protonated and protonated form of the indicator. From eq. (1) it is clear that strong acid leads to the lower H_0 values.

Equation (1) can also be written as,

$$H_0 = -\log a(H^+_{aq.}) - \log \gamma(I) / \gamma(HI^+) - \log \Gamma(I) / \Gamma(HI^+) \qquad (2)$$

where $\gamma(I)$ and $\gamma(HI^+)$ are the activity coefficients of non-protonated and protonated form of indicator and $\Gamma(I)$ and $\Gamma(HI)$ are the transfer activity coefficients from water to the protic ionic liquid.

For a very dilute solution of indicator, the ratio of activity coefficient of protonated and nonprotonated forms of indicator remains constant. The ratio of the transfer activity coefficient of the two forms of indicator depends on their solvation. This difficulty can be resolved by assuming that this ratio is unity and does not depend on the choice of the solvent. However, it is difficult to meet this demand as different solvent solvate these two forms of the indicator to different extent. In the case of the structurally similar indicator molecule, it can be assumed that this ratio remains constant.

The H_0 of protic ionic liquids and water has been carried out by the method shown in Table 5.1.2.

Table 5.1.2. Calculation of Hammett function for Acetic acid in [HmIm][CH_3COO].

acid concentration (M)	**A_{max}**	**$[I]_s\%$**	**$[HI^+]_s\%$**	**H_0**
0	1.454	100	0	0.990
0.48	1.378	94.8	5.2	2.248
0.64	1.344	92.4	7.6	2.077
0.79	1.319	90.7	9.3	1.980
0.91	1.287	88.5	11.5	1.877
1.07	1.251	86.0	14.0	1.780
1.22	1.223	84.1	15.9	1.714
1.40	1.184	81.4	18.6	1.632

For 4-nitroaniline $pK(I)_{aq.} = 0.99$

5.1.3: Results and Discussion

In order to obtain the acidity, a suitable and specific indicator is required. The p*K*$(\mathrm{I})_{\mathrm{aq.}}$ is a critical parameter for an indicator in the acidity determination. The acidity level of a medium and its variation can be probed only by an indicator of suitable basicity (p*K*$(\mathrm{I})_{\mathrm{aq.}}$). An improper selection of indicator molecule will lead either to the disappearance of intramolecular charge transfer (ICT) spectra due to the protonation of indicator or to the protonation of water by added acid instead of protonating indicator. Normally, in the case of strong acid, indicators having low p*K*$(\mathrm{I})_{\mathrm{aq}}$ was found suitable. 2,4-dinitroaniline is commonly used for strong acid (p*K*$(\mathrm{I})_{\mathrm{aq}}$ = -4.53) due to its much lower basicity. 4-nitroaniline (p*K*$(\mathrm{I})_{\mathrm{aq}}$ = 0.99) and 2,5-dichloro-4-nitroaniline (p*K*$(\mathrm{I})_{\mathrm{aq}}$ = -1.18) always remained in protonated form when used for acidity determination of strong acids. The use of 2,4-dinitroaniline and 2,5-dichloro-4-nitroaniline for weak acid is also not very much effective as the protonation level of indicator is noted too weak and only a very small decrease in A_{max} is observed during addition of acid. Therefore, an appropriate pairing between the basicity of indicator and the nature of acid is required before measurement. Based on our observations, we selected 4-nitroaniline as a suitable indicator for acidity determination of weak organic acid.

Strength of an acid (acidity level) in a medium depends on the availability of proton (H^+) furnished by acid rather than the amounts of proton in strong acid.[11] The dilution of the acid shifts the acidity level from its original value. It was observed that all strong acids had similar strength when the ratio of acid to water exceeded 1:6. However, this behavior was not expected during the dilution of weak acid because dissociation of weak acid prevailed over the solvation with increase in dilution. However, it is interesting to observe the behavior of organic acids in water and protic ionic liquids, as the interaction of proton is different in water than that in protic ionic liquids. The relative order of acidity of HCOOH, CH_3COOH and CH_3CH_2COOH in water (Figure 5.1.3 (a)) and in four different protic ionic liquid was observed opposite when examined on Hammett scale, H_0.

The relative order of acidity in water was observed as:

$$\mathrm{HCOOH} > \mathrm{CH_3COOH} > \mathrm{CH_3CH_2COOH}$$

whereas, the acidity order was reversed in all protic ionic liquids shown in Figure 5.1.3 (b) and (c) to summarize:

$$CH_3CH_2COOH > CH_3COOH > HCOOH$$

The values of H_0 for all protic ionic liquids and water system are given in Table 5.1.3.

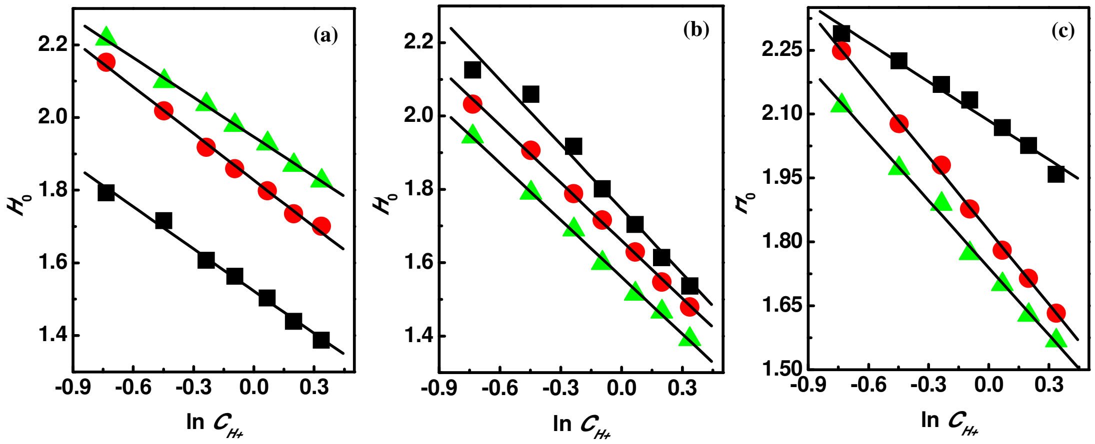


Figure 5.1.3: The H_0 *versus* ln C_{H+} plots of HCOOH (■), CH_3COOH (●), CH_3CH_2COOH (▲) in (a) water, (b) [HmIm][HCOO], and (c) [HmIm][CH_3COO].

Table 5.1.3: Hammett Function of HCOOH, CH_3COOH and CH_3CH_2COOH in Water and Protic Ionic Liquids.

water/ PILs	organic acid	concentration / M						
		0.48	0.64	0.79	0.91	1.07	1.22	1.40
H_2O	HCOOH	1.792	1.716	1.607	1.563	1.503	1.439	1.387
	CH_3COOH	2.152	2.018	1.918	1.859	1.798	1.735	1.701
	CH_3CH_2COOH	2.217	2.100	2.036	1.979	1.928	1.869	1.826
[HmIm][HCOO]	HCOOH	2.050	2.004	1.926	1.886	1.812	1.784	1.751

	CH_3COOH	2.032	1.906	1.788	1.716	1.629	1.547	1.479
	CH_3CH_2COOH	1.944	1.790	1.690	1.599	1.515	1.466	1.391
[HmIm][CH_3COO]	HCOOH	2.289	2.225	2.169	2.133	2.068	2.026	1.958
	CH_3COOH	2.248	2.077	1.980	1.877	1.780	1.714	1.632
	CH_3CH_2COOH	2.120	1.973	1.889	1.773	1.700	1.628	1.568
[HbIm][HCOO]	HCOOH	2.313	2.204	2.119	2.051	1.995	1.946	1.908
	CH_3COOH	2.235	2.042	1.919	1.815	1.735	1.663	1.591
	CH_3CH_2COOH	2.157	1.987	1.856	1.758	1.678	1.613	1.546
[HbIm][CH_3COO]	HCOOH	2.384	2.281	2.202	2.149	2.066	2.017	1.979
	CH_3COOH	2.264	2.076	1.946	1.852	1.779	1.705	1.629
	CH_3CH_2COOH	2.099	1.940	1.824	1.734	1.655	1.596	1.532
[HPyrr][HCOO]	HCOOH	2.245	2.118	2.045	1.949	1.865	1.817	1.757
	CH_3COOH	2.194	1.981	1.837	1.727	1.641	1.558	1.479
	CH_3CH_2COOH	2.118	1.923	1.784	1.686	1.592	1.517	1.447
[HPyrd][HCOO]	HCOOH	2.153	2.067	1.967	1.896	1.860	1.785	1.737
	CH_3COOH	2.178	1.984	1.832	1.734	1.637	1.561	1.476
	CH_3CH_2COOH	2.144	1.937	1.814	1.728	1.652	1.557	1.482

The H_0 for HCOOH is less in water than in protic ionic liquids. However, the H_0 values for CH_3COOH and CH_3CH_2COOH in protic ionic liquids are obtained lower than that in water. These observations for HCOOH, CH_3COOH and CH_3CH_2COOH are very similar to those reported by MacFarlane *et al.* on aprotic ionic liquid having anion of variable basicity than water.[12,13] Based on their observations; they suggested that the relative basicity of water and ionic liquid anion are the controlling factor for the dissociation of acid. Thus, highly basic anion promotes the dissociation of acid in ionic liquid more than that in water and *vice-versa*. Contrary to this any of the protic ionic liquid was observed to be sufficient to differentiate the organic acids in spite of the same anion. Thus, this assumption seems to fairly applicable for predicting the acidity level in ionic liquid and water but, the acidity order of weak acids in a given protic ionic liquid cannot be accounted by using the same criterion. Therefore, the basicity of ionic liquid anion is only useful in classifying an acid more/less acidic as water. A more basic anion than water will always stabilize the acidic form of an indicator up to the same extent and *vice-versa*. The different acidity values for organic acids in all protic ionic liquids cannot be explained on the similar grounds. This indicates the involvement of protic ionic liquid cation along with anion in acidity determination. A detail investigation on the acidity of weak acids in protic ionic liquids having anion of varying basicity should be helpful to reach further conclusion.

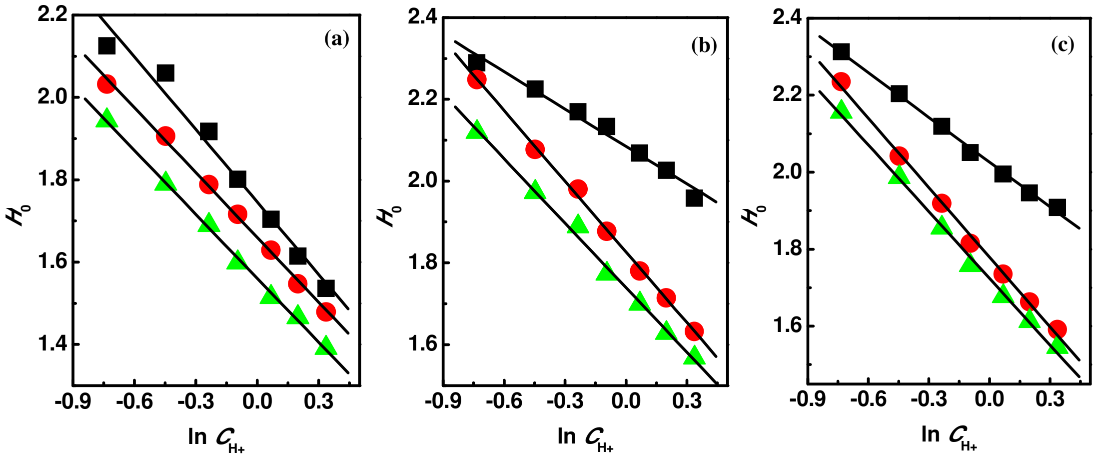


Figure 5.1.4: The H_0 *versus* ln C_{H+} plots of HCOOH (■), CH_3COOH (●), CH_3CH_2COOH (▲) in (a) [HmIm][HCOO], (b) [HmIm][CH_3COO], and (c) [HbIm][HCOO].

A comparison of protic ionic liquid in promoting the acidity either due to the change in anion or due to the increase in alkyl chain length on cation enable us to know about the structural variations that affect the H_0 values (Figure 5.1.4). From the Figure 5.1.4, it is evident that the acidity level for all organic acid is maximum in [HmIm][HCOO] than in other protic ionic liquid. This unique behavior of [HmIm][HCOO] in promoting acidity suggests greater dissociation of acid in medium and this can be accounted either because of the lower solvation of proton or higher stabilization of conjugate base in protic ionic liquid.

Acidic behavior of an acid in a medium depends on the stabilization of its conjugate anion (X^-) by the medium.

$$HX \longrightarrow H^+ + X^-$$

Different H_0 values therefore indicate different level of stabilization of anions $[HCOO]^-$, $[CH_3COO]^-$ and $[CH_3CH_2COO]^-$ in water and in protic ionic liquids. The different level of anion stabilization may be either due to the structural differences between water and protic ionic liquid or due to the preferential stabilization of anion by the medium. Protic ionic liquids are entirely different from water in structural aspects due to the presence of aromatic ring, alkyl chain and Coulomb interactions between ions. It is therefore, obvious that these structural features can influence the dissociation of organic acid. In order to confirm this, we plotted H_0-H_2O *versus* H_0-protic ionic liquid for all the three acids (Figure 5.1.5).

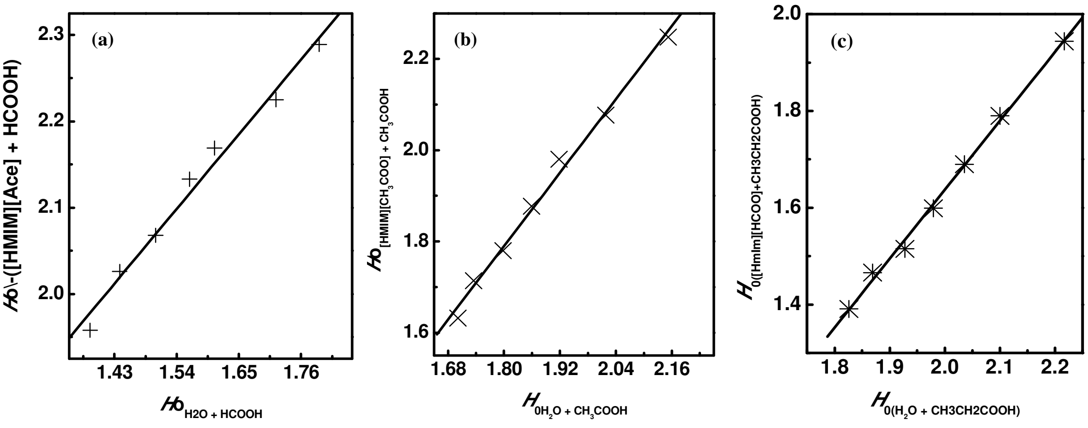


Figure 5.1.5: A linear correlation between H_0-H_2O and H_0-[HmIm][HCOO] for (a) HCOOH (+), (b) CH_3COOH (×) and (c) CH_3CH_2COOH (∗).

A linear correlation between these two (Figure 5.1.5) confirms that the structural features of protic ionic liquid do not influence the dissociation of acid or the protonation of indicator and they act similar to water. However, the slope of linear correlation increases with the increase in number of carbon in acid molecule. This shows the higher protonation of indicator in protic ionic liquid with the increase in number of carbon in acid than in water.

Preferential stabilization of conjugate anion of acid in protic ionic liquid favors the dissociation of acid, thereby, influencing the acidity. The ratio between H_0 values of organic acids in water and in protic ionic liquid, say, 1-methylimidazolium acetate indicates the preferential stabilization by protic ionic liquid for higher carboxylic acid. In water, the ratio was observed 1: 1.20: 1.24, while in protic ionic liquid it was 1.08: 1.06: 1 for HCOOH, CH_3COOH and CH_3CH_2COOH, respectively. This reversal in H_0 ratio clearly indicates the preferential dissociation of CH_3COOH and CH_3CH_2COOH in protic ionic liquid. This preferential dissociation can be correlated by using Pearson's hard and soft acid base (HSAB) principle.[14,15]

According to HSAB principle hard acid (low polarizability) bind preferentially with hard base and soft acid (high polarizability) bind with soft base. Carboxylic acids are weak acids but its conjugate anion acts as strong base. The relative hardness/basicity of carboxylate anions are in the order

$$[HCOO]^- < [CH_3COO]^- < [CH_3CH_2COO]^-$$

The precursor of protic ionic liquids *i.e.* alkylimidazole is a weaker base (pK_a = 6.95) than water (pK_a = 15.7). Transfer of proton from carboxylic acid to alkylimidazole results strong conjugate acid. Since strong conjugate acid always prefers strong base, therefore, alkylimidazolium cation binds preferentially with strongest base available. The preferential binding of alkylimidazolium cation follows the order of basicity of anion. Exceptionally higher acidity level in [HmIm][HCOO] than other protic ionic liquids can be explained as:

$$[HmIm][HCOO] + HCOO^- \rightarrow \text{No reaction/equilibrium}$$
$$[HmIm][HCOO] + CH_3COO^- \rightarrow [HmIm][CH_3COO] + HCOO^-$$
$$[HmIm][HCOO] + CH_3CH_2COO^- \rightarrow [HmIm][CH_3CH_2COO] + HCOO^-$$

Thus, a preferential binding of CH_3COO^- and $CH_3CH_2COO^-$ anion with $[HmIm]^+$ will shift the above equilibrium in the forward direction, thereby promoting the acidity. Steric effect due to $-C_4H_9$ inhibits the preferential binding of $[HbIm]^+$ with basic anions inspite of slightly lower basicity (p*K*a = 6.91), therefore acidity in 1-butylimidazolium-based protic ionic liquids was noted to be lower than that of 1-methylimidazolium-based protic ionic liquids.

To ensure the validity of above observations in determining the acidity order, we measured the H_0 in different classes of protic ionic liquids having different cationic backbone combined with the $HCOO^-$ anion. The precursors of these protic ionic liquids are 1-methylpyrrolidine (p*K*a = 10.55) and 1- methylpiperidine (p*K*a = 10.08). Therefore, the relative basicity order of their conjugate cations along with 1-methylimidazole (*p*Ka = 6.95) is as;

$$[HmIm]^+ > [HPyrd]^+ > [HPyrr]^+ \qquad (4)$$

The relative stabilization of conjugate anion of organic acids and hence the acidity order in these protic ionic liquids are shown in Figure 5.1.6 (a), (b), and (c).

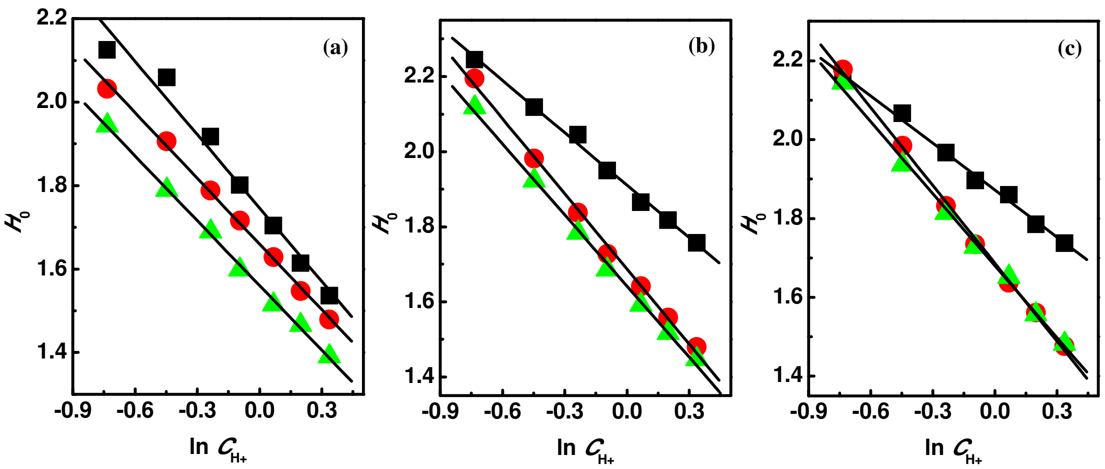


Figure 5.1.6: The acidity profiles of HCOOH (■), CH_3COOH (●), and CH_3CH_2COOH (▲) in (a) [HmIm][HCOO] (b), [HPyrr][HCOO], and (c) [HPyrd][HCOO].

These plots reveal the influence of different protic ionic liquid cations in determining the acidity level of organic acids due to preferential stabilization of conjugate base of acids. Figure 5.1.6(a) strongly supports the involvement of favorable HSAB interactions between the protic ionic liquid cation and $HCOO^-$ anion. The acidity of HCOOH in these protic ionic liquids was found according to their conjugate acidity of protic ionic liquid cation as shown in equation (4). Figure 5.1.6(b) also indicates the favorable interactions *via* the HSAB principle.

However, for CH_3COOH the acidity order in [HPyrd][HCOO] and [HPyrr][HCOO] is not clearly differentiated in plots as compared to that for HCOOH. The H_0 value of CH_3COOH [HPyrd][HCOO] is slightly higher than that in [HPyrr][HCOO]. This anomalous behavior in case of CH_3COOH may be due to the beginning of steric repulsion between larger CH_3COO^- anion and more crowded $[HPyrd]^+$ than the less crowded $[HPyrr]^+$ which in turn opposes the favorable HSAB interaction. Figure 5.1.6(c) further supports this view where steric repulsion completely dominates over HSAB interaction and the acidity of CH_3CH_2COOH in [HPyrr][HCOO] was noted more than that in [HPyrd][HCOO] in spite of the higher conjugate acidity of $[HPyrd]^+$ than $[HPyrr]^+$. From the above evidences, it is obvious that though HSAB interactions are the prime reason for higher dissociation of organic acids in protic ionic liquids, steric repulsion has a large and opposite influence on these favorable interactions.

5.1.4: Conclusions

A detailed investigation on the acidity in protic ionic liquids and water on the protonation/deprotonation equilibria was carried out from which the following conclusions could be drawn:

(1) A reversal in acidity order of HCOOH, CH_3COOH, and CH_3CH_2COOH in water and protic ionic liquids is observed. The higher acidity level of CH_3COOH and CH_3CH_2COOH in protic ionic liquids is because of the preferential stabilization of the conjugate anion of acid with the cation of protic ionic liquid according to the HSAB principle.

(2) The ability of the protic ionic liquids to promote the acidity was noted to be higher in [HmIm][HCOO] than other protic ionic liquids.

(3) The increased steric hindrance can outplay the HSAB interaction.

5.2: Determination of Hammett Acidity of Carboxylic Acids in Binary Mixtures of Protic Ionic Liquids and Water

5.2.1: Introduction

Acidity of a medium is an intrinsic number. However, the strength of an acid in a medium varies with i) the nature of the acidic species and ii) the ability of the solvent to dissociate it. The solvation behavior of ionic liquids is quite different in comparison to water because of the various specific and non-specific interactions. In spite of the different structural and electronic features, protic ionic liquid mimics water in a sense of extensive hydrogen bonding.[16] MacFarlane *et al.* have shown that the strength/acidity level of an acid in water and ionic liquid is mainly guided by their relative basicity.[13]

Prompted by the similarity between protic ionic liquids and water in terms of hydrogen bonding; we now address an issue whether the ability of protic ionic liquids in dissociating carboxylic acids differ in binary mixture with water. The different behavior of protic ionic liquids in binary mixture arises due to the complex solvent-cosolvent interactions. The relationship between acid dissociation and solvent composition in mixed solvents is complex and it relies either on the preferential solvation of acid by any of the solvents present in the mixture and or on solvent-solvent interactions or both. This relationship is extremely useful in some liquid chromatography technique. Therefore, an equation relating the acidity change with the composition of binary mixture will be of significant importance. Several models relating change in the pH and pKa with composition of binary mixtures are available, but, unfortunately such developments are not applicable in case of the Hammett acidity, H_0.[17]

In the present work, we investigate the strength of carboxylic acids (HCOOH, CH_3COOH and CH_3CH_2COOH) at different molar concentrations (0.48, 0.79, 1.07, and 1.4 M) in binary mixtures of protic ionic liquids and water. The concentration (x_{IL}) of protic ionic liquid in water varied from 0.2-0.8. All protic ionic liquids were resistant towards hydrolysis. The Hammett acidity of carboxylic acids in binary mixtures of protic ionic liquids was measured by the procedure described in 5.1.2.3.

5.2.2: Results and Discussion

A reverse acidity order of HCOOH, CH_3COOH and CH_3CH_2COOH in water and protic ionic liquid encouraged us to find out the acidity level in binary mixture of these two solvents. The recent studies in binary composition depicts that the nature of solute-solvent interaction is completely different from that of the pure solvent.[18] Any change in the composition of solvation shell of solute by adding other solvent leads to the change in the property. The overall interactions between solvents either change the interactions between solute and solvent or may results into a new medium called “pseudo-solvent”. The pseudo-solvent having the property of both the solvent leads to the abrupt change in the magnitude of property than that of pure components. The purpose of this observation in binary mixtures is to locate the component that controls the acidity level, since both protic ionic liquids and water are hyperpolar in nature. A polar solvent makes the dissociation easy and hence promotes the acidity level in binary mixtures. However, the outcome is quite interesting and indicates the participation of both, synergetic effect as well as preferential solvation. The dominance of synergetic effect over preferential solvation and *vice versa* stems due to the complex protic ionic liquid-water-acid interaction. A detailed investigation using deuterated NMR technique can be helpful to find out the real picture of this complex interaction. The scarcity of acidity models based on the Hammett function further makes understanding difficult. Earlier reports on binary mixtures show that the measured properties distribute between the pure components and they were found much higher than the pure component on certain occasions due to cooperative/synergetic behavior.[17] The deviation in measured quantities from the pure component may be positive/negative. The Hammett function for binary mixture follows the similar trend. In addition, there are also some oddities in the observations that are discussed in the detail.

The H_0 values of HCOOH in the binary mixtures of different protic ionic liquids are given in Table 5.2.1. The Hammett acidity profiles of HCOOH in binary mixtures of protic ionic liquids are given in Figure 5.2.1. The H_0 values for HCOOH in the binary mixture of all protic ionic liquids were noted to increase, thereby decreasing the acidity level. A sudden increase in the H_0 value with addition of protic ionic liquids suggests that protic ionic liquid have a dominating role in determining the protonation of indicator. However, the H_0 value in binary mixtures was noted to be higher than that of its pure components. Therefore, the generation of an intermediate solvent/pseudo-solvent is suspected to have similar characteristic to the protic ionic liquids. The effect of intermediate solvent/pseudo-solvent on the H_0 value becomes intense as the difference in the H_0 value of the pure component becomes low. However, at a given composition of water and protic ionic liquids, increase in concentration of acid lowers the magnitude of H_0, thereby increasing the acidity level.

Table 5.2.1: Hammett Acidity of HCOOH as a Function of Mole Fraction, x_{IL}, in Binary Mixtures of Protic Ionic Liquids and Water.

ionic liquids	concentration (M)	x_{IL}			
		$x_{IL} = 0.2$	$x_{IL} = 0.4$	$x_{IL} = 0.6$	$x_{IL} = 0.8$
	0.48	2.205	2.257	2.243	2.303
[HmIm][HCOO]	0.79	2.006	2.021	2.069	2.128
	1.07	1.895	1.916	1.970	2.021
	1.4	1.779	1.804	1.849	1.871
	0.48	2.371	2.371	2.415	2.421
[HmIm][CH_3COO]	0.79	2.218	2.197	2.209	2.226
	1.07	2.080	2.094	2.102	2.086
	1.4	1.958	1.959	1.989	1.995
	0.48	2.331	2.387	2.385	2.331
[HbIm][HCOO]	0.79	2.183	2.219	2.195	2.178
	1.07	2.061	2.085	2.042	2.053
	1.4	1.936	1.962	1.954	1.950
	0.48	2.474	2.438	2.403	2.402
[HbIm][CH_3COO]	0.79	2.247	2.213	2.224	2.212
	1.07	2.134	2.112	2.107	2.111
	1.4	2.007	1.990	1.975	2.000

This observation indicates the steady behavior of the pseudo-solvent over all the concentrations of acid. The H_0 value for HCOOH shows positive deviation. The magnitude of the deviation being higher than the pure component clearly indicates the synergetic behavior of pseudo-solvent for HCOOH.

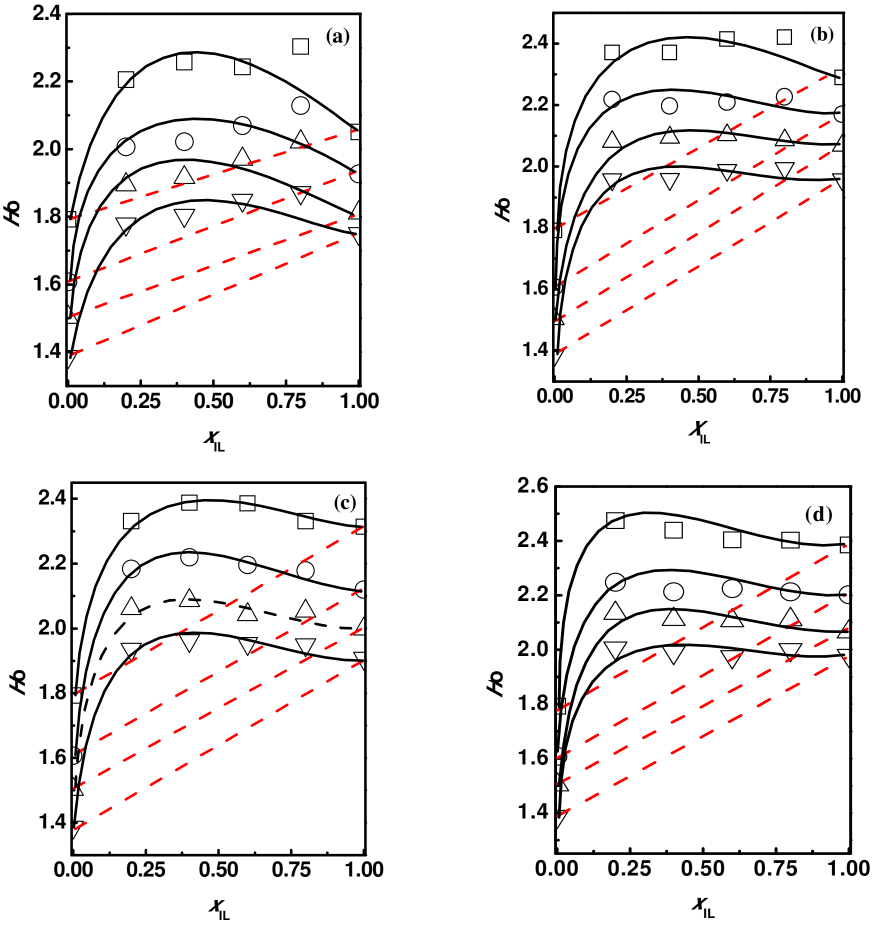


Figure 5.2.1: The plots of H_0-x_{IL} for HCOOH in (a) [HmIm][HCOO], (b) [HmIm][CH_3COO], (c) [HbIm][HCOO] and (d) [HbIm][CH_3COO] at 0.48 M (□), 0.79 M (○), 1.07 M (Δ) and 1.4 M (▽). The dashed lines are shown to bring out the contrast from non-linearity.

The H_0 of CH_3COOH in the binary mixtures of protic ionic liquids and water are shown in Table 5.2.2. The Hammett acidity profiles of CH_3COOH in binary mixtures of protic ionic liquids are given in Figure 5.2.2. The H_0 values for the CH_3COOH in binary compositions also reveal the presence of pseudo-solvent that has the similar characteristics to the protic ionic liquids. However, except for the [HmIm][HCOO], all other protic ionic liquids have higher H_0 value for CH_3COOH than that of water. The relative H_0 value for water and protic ionic liquid modifies the nature of the pseudo-solvent which influences the deviations in H_0 value for binary mixtures.

Table 5.2.2: Hammett Acidity of CH_3COOH as a Function of Mole Fraction, x_{IL}, in Binary Mixtures of Protic Ionic Liquids and Water.

ionic liquids	**concentration (M)**	x_{IL}			
		$x_{IL} = 0.2$	$x_{IL} = 0.4$	$x_{IL} = 0.6$	$x_{IL} = 0.8$
	0.48	2.201	2.139	2.169	2.219
[HmIm][HCOO]	0.79	1.846	1.819	1.793	1.834
	1.07	1.644	1.626	1.603	1.660
	1.4	1.498	1.456	1.423	1.489
	0.48	2.370	2.396	2.350	2.279
[HmIm][CH_3COO]	0.79	2.034	2.017	1.971	1.935
	1.07	1.883	1.843	1.792	1.757
	1.4	1.721	1.701	1.654	1.613
	0.48	2.304	2.246	2.272	2.272
[HbIm][HCOO]	0.79	1.950	1.924	1.948	1.948
	1.07	1.778	1.748	1.756	1.756
	1.4	1.628	1.616	1.605	1.605
	0.48	2.404	2.325	2.339	2.318
[HbIm][CH_3COO]	0.79	2.056	1.992	1.981	1.978
	1.07	1.848	1.795	1.798	1.800
	1.4	1.701	1.658	1.652	1.649

In [HmIm][HCOO], the positive deviation at lower concentration of acid becomes negative with the increase in the concentration of acid. The reversal in the H_0 value indicates that the behavior of the pseudo-solvent at lower concentration is similar to water and at higher concentration it behaves like the [HmIm][HCOO]. However, for other protic ionic liquids, change in the behavior of pseudo-solvent appeared at higher concentrations. For [HmIm][HCOO], the H_0 value changes from positive to negative as the concentration of acid increases, thereby, increasing the acidity level, while for other protic ionic liquids, a reversal in the nature from positive to negative are rarely observed. Unlike, HCOOH, CH_3COOH has lower positive deviation over the entire water-protic ionic liquid compositions. Synergetic behavior of the pseudo-solvent can only be witnessed where positive deviations take place. Evidently, it is clear that CH_3COOH is characterized by higher acidity level than HCOOH in pure protic ionic liquids and binary mixtures.

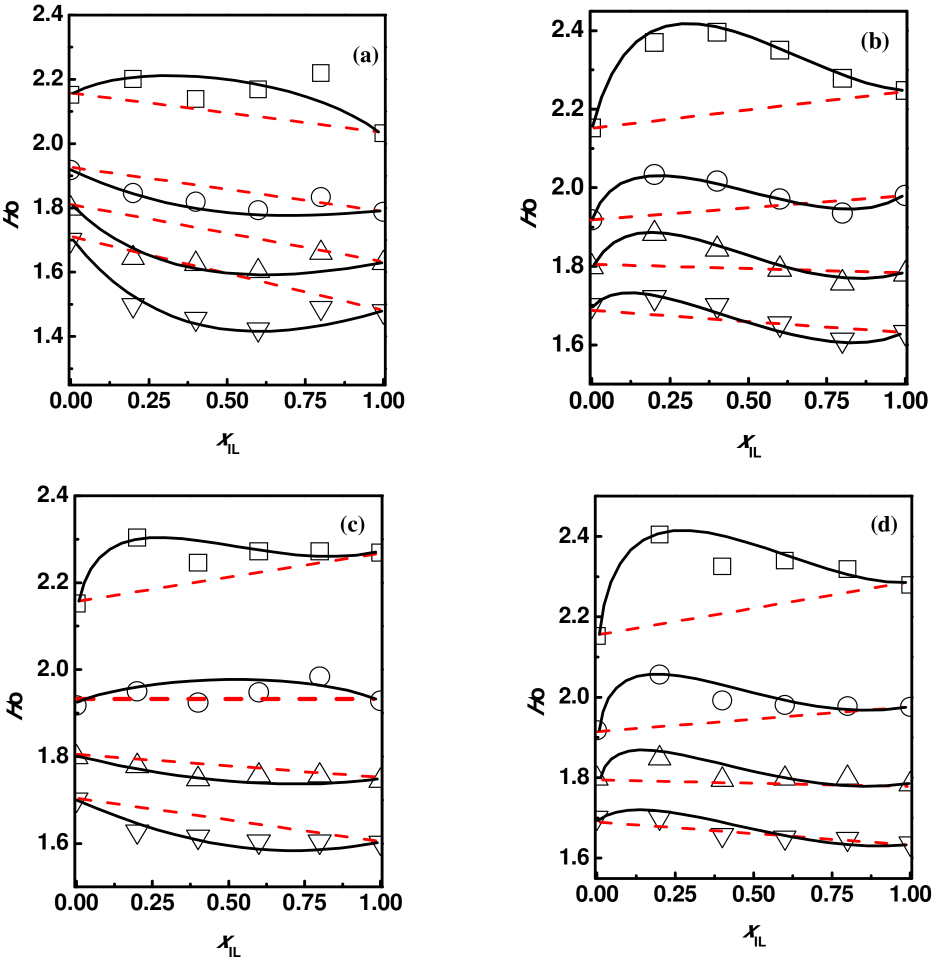


Figure 5.2.2: The plots of H_0-x_{IL} for CH_3COOH in (a) [HmIm][HCOO], (b) [HmIm][CH_3COO], (c) [HbIm][HCOO] and (d) [HbIm][CH_3COO] at 0.48 M (□), 0.79 M (○), 1.07 M (Δ) and 1.4 M (▽). The dotted lines are shown to bring out the contrast from non-linearity.

The H_0 values of CH_3CH_2COOH in binary mixtures of protic ionic liquids and water are given in Table 5.2.3. The Hammett acidity profiles of CH_3CH_2COOH in binary mixtures of protic ionic liquids are given in Figure 5.2.3. As shown in Figure 5.2.3, H_0 values for CH_3CH_2COOH in all protic ionic liquids are lower than that in water. Therefore, the characteristic of pseudo-solvent is similar to the protic ionic liquids. However, it is also observed that the difference in H_0 value decides the deviation pattern with the rise in concentration of CH_3CH_2COOH. In [HmIm][HCOO], a large difference in H_0 value casts a permanent effect on the behavior of pseudo-solvent and only the negative deviation in H_0 value is observed over the entire concentration change. The magnitude of this deviation is higher than for other protic ionic liquids. Thus, [HmIm][HCOO] is the most suitable protic ionic liquids to promote the acidity in binary mixture as well as in pure state.

Table 5.2.3: Hammett Acidity of CH_3CH_2COOH in Binary Mixtures of Protic Ionic Liquids and Water.

ionic liquids	**concentration (M)**	x_{IL}			
		$x_{IL} = 0.2$	$x_{IL} = 0.4$	$x_{IL} = 0.6$	$x_{IL} = 0.8$
	0.48	2.138	1.910	2.062	2.120
[HmIm][HCOO]	0.79	1.802	1.623	1.732	1.753
	1.07	1.623	1.456	1.546	1.555
	1.4	1.470	1.339	1.399	1.401
	0.48	2.314	2.291	2.239	2.206
[HmIm][CH_3COO]	0.79	1.992	1.928	1.919	1.886
	1.07	1.801	1.732	1.725	1.691
	1.4	1.670	1.611	1.595	1.564
	0.48	2.211	2.224	2.207	2.189
[HbIm][HCOO]	0.79	1.904	1.897	1.867	1.907
	1.07	1.727	1.708	1.713	1.715
	1.4	1.591	1.576	1.565	1.587
	0.48	2.174	2.271	2.241	2.207
[HbIm][CH_3COO]	0.79	1.875	1.914	1.876	1.862
	1.07	1.707	1.734	1.684	1.680
	1.4	1.584	1.601	1.556	1.546

The other protic ionic liquids show positive deviation at lower concentration that becomes negative with the rise in the acid concentration. However, unlike positive deviation, where synergetic feature of the pseudo-solvent is common, most of the protic ionic liquids negative deviations are devoid of synergetic behavior, except for the [HmIm][HCOO], where a small decrease in H_0 value at $x_{IL} = 0.4$ was observed.

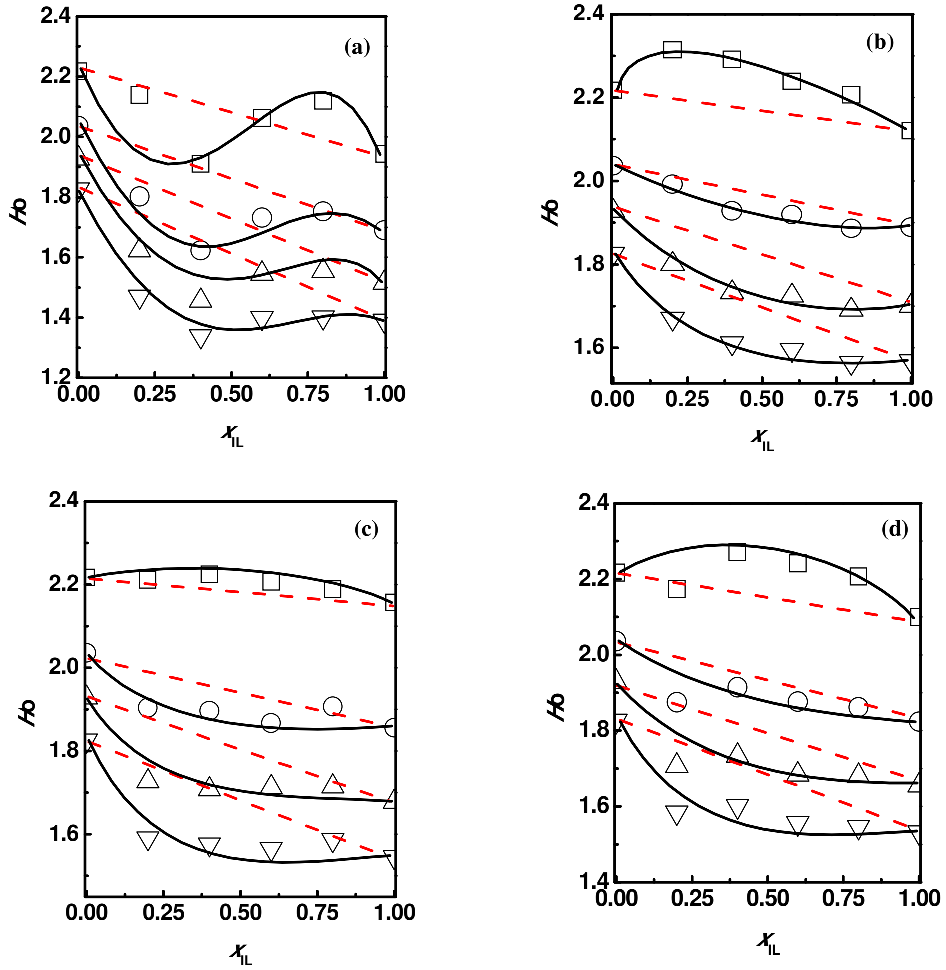


Figure 5.2.3: The plots of H_0-x_{IL} for CH_3CH_2COOH in (a) [HmIm][HCOO], (b) [HmIm][CH_3COO], (c) [HbIm][HCOO] and (d) [HbIm][CH_3COO] at 0.48 M (□), 0.79 M (○), 1.07 M (Δ) and 1.4 M (▽). The dashed lines are shown to bring out the contrast from non-linearity.

5.2.3: Conclusions

Based on the detailed investigation in binary mixtures of protic ionic liquid and water following observations are drawn;

(1) The complex behavior of protic ionic liquids and water on the dissociation of carboxylic acids was observed.

(2) The H_0 value in the binary mixture clearly indicates the presence of an intermediate solvent/pseudosolvent.

(3) The behavior of pseudosolvent varies with the nature of acid and concentration.

(4) The synergetic characteristic of the pseudosolvent is more common for HCOOH and is rarely observed for CH_3COOH and CH_3CH_2COOH.

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10. However, a suggestion has been made that in a different mechanism if anions of protic ionic liquids are highly solvating it is likely that higher level of acidity will never be reached. With due acknowledgement of the suggestion, we noted higher acidity for carboxylic acids in protic ionic liquids and a suggestion say that presence of small amount of water can only promote the acidity of fluorous ionic liquid drastically due to the hydrolysis of anion. (for example see Cui, X.; Zhang, S.; Shi, F.; Zhang, Q.; Ma, X.; Lu, L.; Deng Y. *Chem. Sus. Chem.* **2010**, *3*, 1043.) Therefore, higher acidity of long chain carboxylic acid in presence of small amount of water in protic ionic liquids can only be attributed to the more facile stabilization of lower carboxylate anion which in turn promotes the higher acidity because of more favorable HSAB pairing.

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"*The process of scientific discovery is, in effect, a continual flight from wonder.*" – *Albert Einstein*

6. Effect of Ionic Strength and Temperature on the Hammett Acidity of Carboxylic Acids

In this chapter, effects of neutral salts and temperature on the Hammett acidity (H_0) of carboxylic acids in different protic ionic liquids and binary mixtures with water have been investigated. In Section 6.1, effect of NaCl, Na_2SO_4, $MgCl_2$, and $MgSO_4$ on the H_0 of CH_3COOH in binary mixtures of imidazolium-, pyrrolidinium-, and piperidinium-based protic ionic liquids containing formate anion with water is studied. The behavior of salts in influencing the H_0 changes with the concentration of protic ionic liquids in water. The efficiency of different salts in affecting the H_0 was correlated with the "free" ion concentration rather than the total ion concentration. In Section 6.2, effect of temperature on the H_0 of carboxylic acids in protic and aprotic class of ionic liquids was studied. The efficiency of ionic liquids in dissociating of carboxylic acids has been explained in terms of the solute-solvent interactions and was discussed by using thermodynamic parameters ($\Delta H^0, \Delta S^0$), activation energy of proton transfer ($E_{a,H+}$), and polarity parameters of these ionic liquids.

6.1: How Does Speciation Assist in Revalidating the Hofmeister Series?

6.1.1: Introduction

Ion induced effects are ubiquitous in biology and various physical and chemical transformations in chemistry. These effects emerge through the alteration in the hydrogen bonding network of water by salt ion.[1] Acidity function, which has been employed in extending the pH scale, can be manipulated by altering the ionic strength and temperature. These factors determine the protonation equilibrium of the indicator, which in turn regulates Hammett acidity (H_0); however, the fundamental mode of action by these effects is quite different. Unlike thermal effect which affects dissociation of acid and solubility of indicator, salt effect only alters the availability of indicator.

Hammett and Deyrup have measured the H_0 for different combinations of aqueous H_2SO_4 using a series of basic indicators[2] and observed a parallelism amongst the H_0 values obtained from different indicators. The importance of zero point energy for an infinitely dilute acid is given by Hammett and Paul.[3] At zero point, H_0 becomes equal to pH. The ionizable salts were found to influence the zero point energy more than that of the non-ionizable salts. Paul has measured the H_0 of HCl in LiCl, NaCl, and KCl solutions and obtained higher H_0 for the bulkier indicator diphenylamine than smaller base 4-nitroaniline.[4] Though, the variation in the H_0 was primarily discussed owing to the perturbation of the protonation equilibria of indicator, several reports have accounted change in the H_0 due to the change in water activity.[5,6] Therefore, a correction term is applied in this case to the activity coefficients of indicator ratio based on the solubility measurements and the activity of water was calculated in presence of salt. However, the change in the H_0 at molecular level was reported by considering the different number of water molecules (n_{H2O} =1-4).[7]

Salting effects are of immense importance in regulating the chemical kinetics and reaction equilibria. The varying acidity level/strength in the presence of salt has remarkable effects on various processes. The bleaching action of chlorine dioxide (ClO_2), produced during addition of $NaClO_3$ in H_2SO_4, depends on the strength of medium and is tuned by addition of Na_2SO_4.[8] Salt effect assists in determining the mechanism of acid-catalyzed reaction and also influences the outcome of depolymerization reaction. The acid-catalyzed hydrolysis rate of the 3-diazo-l-methoxycarbonyloxy-l-phenylacetone violates "Zucker-Hammett" hypothesis in presence of $HClO_4$, but varies linearly with $-H_0$ in $NaClO_4$.[9] This observation helped in concluding that the rate determining step was bimolecular and hydrolysis follow A_2 mechanism. The acid-catalyzed depolymerization reaction was prone to the size of salt cation and polymer and the highest rate was observed for the smallest polymer in presence of salt having smaller cation.[10] Nafion films are used as a proton conductor for proton exchange membrane (PEM) fuel cells. The acidity of the nafion film, which is due to the change in conformation of the terminal sulphonate group, was found to increases by the alkali metal halide, while tetraalkylammonium halides were observed to decrease the acidity.[11]

Table 6.1.1: The Gibbs' Free Energy of Hydration ($\Delta_{hyd}G$)[12] and Molar Entropy of Hydration ($\Delta_{hyd}S$)[13] of Different Ions.

ion	$\Delta_{hyd}G$/ kJ mol^{-1}	$\Delta_{hyd}S$/ J K^{-1} mol^{-1}
Na^+	-365	-117
K^+	-295	-80
Mg^{2+}	-1830	-331
Ca^{2+}	-1505	-252
Al^{3+}	-4525	-553
Cl^-	-340	-87
OH^-	-430	-161
SO_4^{2-}	-1080	-199

The ions in bold are only for the comparison.

The proficiency of salt ions in curbing the solvation equilibria of indicator can be rationaled with their ranks in the Hofmeister series. Hofmeister series effects are based on the ability of salt ions to induce change in the physical properties of protein/non-electrolyte from solution. Initially, salting effects were explained owing to the influence of salt ions on the structure of water, but later several reports appeared which negate the above explanation and suggest that the salt-induced effect is not primarily due to the variation in water structure, but is guided by the more specific ion-solute interactions. The potency of different ions in influencing the solvation equilibria of indicator can be correlated with the Gibbs free energy of hydration ($\Delta_{hyd}G$) or molar entropy of hydration ($\Delta_{hyd}S$) of salt ions (Table 6.1.1).

Ionic liquid behaves as a poor media towards the salting phenomena of nonpolar molecules owing to their amphiphilic nature. The presence of low dielectric domain also forbids solubility of salt. An adequate blending of high dielectric medium, such as water, with ionic liquids enhances the solubility of salt. In a recent development on the kinetics of Diels-Alder reaction, it is noted that in highly aqueous solutions ionic liquids act as co-solvent and promotes the rate of Diels-Alder reaction because of the stabilization of the transition state.[14]

In the present work, we aimed to study the salting effects of strong electrolytes NaCl, Na_2SO_4, $MgCl_2$ and $MgSO_4$ on the H_0 of CH_3COOH at very low concentration of protic ionic liquids (x_{IL} = 0.02, 0.05, and 0.08) in water. Through this work we attempt to address the following questions: (1) How protic ionic liquid addition alters salt effect on Hammett acidity? (2) Do ions affect H_0 in the same order as they affect water?

The protic ionic liquids used in the current work include [HmIm][HCOO], [HPyrr][HCOO] and [HPyrd][HCOO]. All protic ionic liquids were synthesized by the methods used in Chapter 4, Section 4.2.2. The Hammett acidity of equimolar mixture of acetic acid and water in the binary mixture of protic ionic liquid and water was measured by the procedure followed in Chapter 5, Section 5.1.2.2. The reference absorbance was recorded by adding the calculated amount of salt in binary mixture of protic ionic liquid and water and absorbance after the addition of acid was compared with the reference absorbance.

6.1.2: Experimental Section

6.1.2.1: Materials

The salts, NaCl, Na_2SO_4, $MgCl_2$, and $MgSO_4$ were obtained from the Sigma Aldrich and were dried at 80 ^{0}C under high vacuum for 6 h before use.

6.1.2.2: Ion Speciation

A thermodynamic speciation model VisualMINTEQ (version 3.0) which is based on the MinteqA2 software with the Minteq database is employed to calculate the salt ion speciation at different concentrations.[15] In this thermodynamic calculation, concentration of salt in the binary mixtures of protic ionic liquid and water were used as the input. The pH of the mixture was always < 6 in all calculations.

6.1.3: Results and Discussion

Salt induced effects on Hammett acidity is extensively explored in water and in mixtures of solvents; however, to the best of our knowledge, this is the first report on the salting effects on the H_0 using protic ionic liquid mixtures. An addition of small amount of protic ionic liquid (x_{IL} = 0.02) in salt solution causes an anomalous shift in the Hammett acidity function, H_0. The variation in $H_{0,\mathrm{rel}}$ also depends on the protic ionic liquid concentration in addition to the salt effect as shown in Figure 6.1.1. A reversal in the $H_{0,\mathrm{rel}}$ values at different concentrations of protic ionic liquid for aqueous salt solution was also observed. Several reporters have witnessed the influence of inorganic salts on the liquid-liquid phase diagram of aqueous solution of ionic liquids.[16,17] A biphasic solution of ionic liquid and water forms due to demixing caused by inorganic salts. However, in our case no demixing of the protic ionic liquid in aqueous salt solution was noted for all salts within experimental concentration range.

Addition of salt in water causes electrostriction of water molecules around ions and consequently lowers the number of hydrogen bonding sites for indicator.[18] Due to the electrostriction of water molecules, cost of cavitation for indicator increases and consequently solubility of indicator decreases.[5,6] Although ionic liquid consists of oppositely charged ions, they form diffused hydration shell in water due to the delocalized charge on ions.[19]

6.1.3.1: Effect of Protic Ionic Liquids

In the present work imidazolium-, pyrrolidinium-, and piperidinium-based protic ionic liquids with formate anion are employed to measure the H_0 of CH_3COOH in salt solution. In the ionic liquid family, protic ionic liquids are known as emblem of "hyperpolarity" owing to their extensive network of hydrogen bonding similar to water.[20] A very high relative permittivity (ε_s) close to water and high $E_T(30)$ value for tetraalkylammonium nitrate, $[R_4N][NO_3]$ further support this.[21] These reports suggest that protic ionic liquid in water might act as a weak electrolyte and partially shift the indicator ratio, $[I]_s/[HI^+]_s$. However, several other reports indicate that the availability of indicator in binary solution of ionic liquid violate "dielectric enrichment model of solvation" and is rather directed by the specific interactions between the probe and ionic liquid.[22] These contradictory reports pose difficulty in assigning the role of protic ionic liquid on the H_0. In spite of these conflicting reports, H_0 was observed to vary with the increasing concentration of protic ionic liquid.

From Figure 6.1.1, it is apparent that the H_0 decreases with increasing concentration of protic ionic liquid in terms of mole fraction (x_{PIL}) from 0.02 to 0.08. Thus, addition of protic ionic liquid in water aids in the dissociation of carboxylic acid. The higher strength of acetic acid with the increasing concentration of protic ionic liquid is owing to the lower solubility of indicator in salt solution. This observation further corroborates the electrolytic nature of protic ionic liquids.[19]

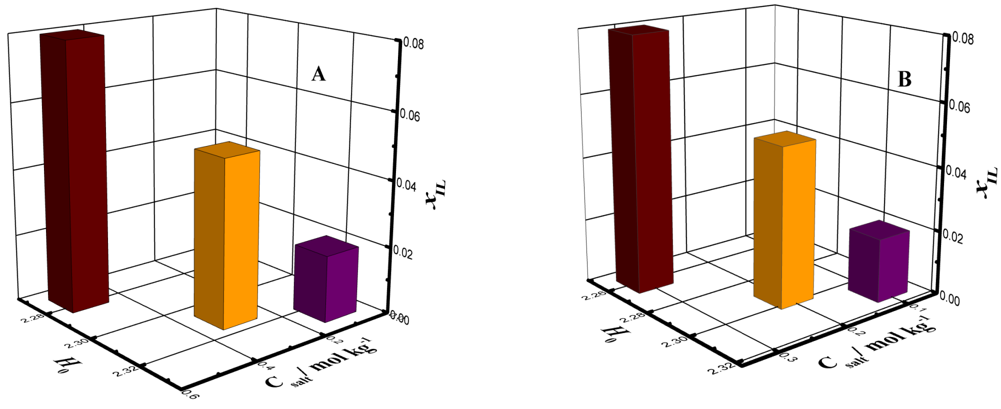


Figure 6.1.1: The 3D plots showing effects of salt and protic ionic liquid on the H_0 for NaCl in (a) [HmIm][HCOO] and (b) [HPyrr][HCOO].

Unlike aprotic ionic liquid which reveals salting phenomena in aqueous electrolyte solutions, no such report is available dealing with the salting phenomena in protic ionic liquid solution.[23] However, according to a recent development on the dissolution of polyol in salt solutions and ionic liquids, it is observed that the ability of ionic liquid to form hydrogen bond with protic solvents depend on the basicity of anion.[24] The studied protic ionic liquids have a common “formate” anion (β = 0.81), therefore change in $H_{0,\mathrm{rel}}$ remains independent from the anion and is solely contributed by the cation. Two different trends in the $H_{0,\mathrm{rel}}$ for $MgSO_4$ and NaCl solutions were observed depending on the concentration of protic ionic liquid (Figure 6.1.2). This also suggests that though the availability of indicator is mainly guided by the salt, protic ionic liquid interrupt indicator equilibria in some way. At $x_{\mathrm{IL}} = 0.02$, two trends in $H_{0,\mathrm{rel}}$ were noted for the studied salts. For NaCl and $MgSO_4$ salts, $H_{0,\mathrm{rel}}$ was observed to increase depending on the protic ionic liquid, however, for Na_2SO_4 and $MgCl_2$, $H_{0,\mathrm{rel}}$ was noted to decrease in all protic ionic liquids. At higher ionic liquid concentrations (x_{IL} = 0.05 and 0.08), the lower $H_{0,\mathrm{rel}}$ was obtained for all salts in protic ionic liquid solutions. This turnaround in the behavior of NaCl and $MgSO_4$ will be addressed in detail in the next section.

6.1.3.2: Effect of Salt:

The amount of added salt and their nature affects the $H_{0,\mathrm{rel}}$ significantly. Salts, such as Na_2SO_4 and $MgCl_2$ were noted to decrease the $H_{0,\mathrm{rel}}$ values in protic ionic liquid solution, while NaCl and $MgSO_4$ were observed to increase the $H_{0,\mathrm{rel}}$ at lower concentration of protic ionic liquid. The influence of different salts on the $H_{0,\mathrm{rel}}$ is shown in Figure 6.1.2. At lower concentration, *i.e.* $x_{\mathrm{IL}} = 0.02$, different salts influence $H_{0,\mathrm{rel}}$ depending on the ion-solute interactions at a fixed concentration of acetic acid, 0.64 M. At $x_{[\mathrm{HmIm}][\mathrm{HCOO}]} = 0.02$ in water, $MgSO_4$ was noted to increase the $H_{0,\mathrm{rel}}$, while NaCl, Na_2SO_4, and $MgCl_2$ were found to decrease the $H_{0,\mathrm{rel}}$. These observations signify that, while $MgSO_4$ increases the solubility of indicator; NaCl, Na_2SO_4, and $MgCl_2$ decrease the solubility of indicator in aqueous protic ionic liquid solution. This alteration in the solubility of indicator in presence of different salts governs the magnitude of $H_{0,\mathrm{rel}}$ indirectly. At $x_{[\mathrm{HPyrr}][\mathrm{HCOO}]} = 0.02$, NaCl and $MgSO_4$ act as salting-in salt and incresaes the $H_{0,\mathrm{rel}}$, while, Na_2SO_4 and $MgCl_2$ behave as salting-out salt and decreases the $H_{0,\mathrm{rel}}$.

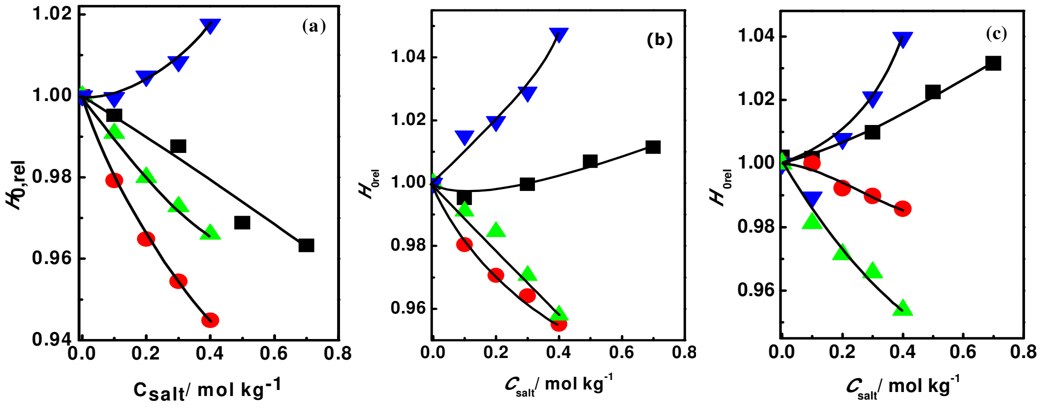


Figure 6.1.2: The $H_{0,\mathrm{rel}}$ *versus* C_{salt} plots in aqueous (a) [HMIm][HCOO], (b) [HPyrd][HCOO], and (c) [HPyrr][HCOO] at $x_{\mathrm{IL}} = 0.02$ for NaCl (■), Na_2SO_4 (●), $MgCl_2$ (▲), and $MgSO_4$ (▼).

Similarly, at $x_{[\mathrm{HPyrd}][\mathrm{HCOO}]} = 0.02$, NaCl and $MgSO_4$ acts as chaotrope, while, Na_2SO_4 and $MgCl_2$ behave like kosmotrope. Thus, the behavior of different salts toward the $H_{0,\mathrm{rel}}$ also depends on the characteristic of protic ionic liquid in solution. For example, NaCl acts as a salting-out salt in [HmIm][HCOO], but transforms into salting-in salt in [HPyrr][HCOO] and [HPyrd][HCOO]. Nature of protic ionic liquid therefore governs the magnitude of the $H_{0,\mathrm{rel}}$ for a given salt. The salting-in ability of $MgSO_4$ in different protic ionic liquids at $x_{\mathrm{IL}} = 0.02$ was noted to increase in the order,

$$[\mathrm{HmIm}][\mathrm{HCOO}] < [\mathrm{HPyrr}][\mathrm{HCOO}] < [\mathrm{HPyrd}][\mathrm{HCOO}]$$

However, the above trend of protic ionic liquids in promoting the $H_{0,\mathrm{rel}}$ was not followed by the Na_2SO_4 and $MgCl_2$, but clearly weak conjugate acids $[\mathrm{HPyrr}]^+$ and $[\mathrm{HPyrd}]^+$ were observed to promote the $H_{0,\mathrm{rel}}$ more than that of the strong conjugate acid $[\mathrm{HmIm}]^+$ as reported previously.[25]

The influence of salt on the $H_{0,\mathrm{rel}}$ values changes rapidly with the change in protic ionic liquid concentration. The behavior of different salts on the $H_{0,\mathrm{rel}}$ at $x_{\mathrm{IL}} = 0.05$ is shown in Figure 6.1.3.

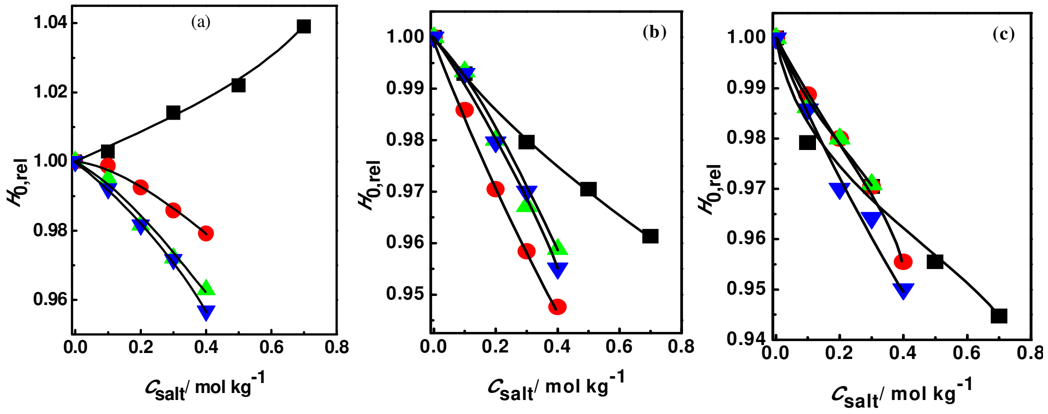


Figure 6.1.3: The $H_{0,\mathrm{rel}}$ *versus* C_{salt} plots in aqueous (a) [HMIm][HCOO], (b) [HPyrd][HCOO], and (c) [HPyrr][HCOO] at $x_{\mathrm{IL}} = 0.05$ for NaCl (■), Na_2SO_4 (●), $MgCl_2$ (▲), and $MgSO_4$ (▼).

All salts were found predominantly to act like salting-out salt at $x_{\mathrm{IL}} = 0.05$. However, the magnitude of influence by the [HmIm][HCOO] on $H_{0,\mathrm{rel}}$ was lower than that of the [HPyrr][HCOO] and [HPyrd][HCOO]. In other words, salting-out behavior of different salts was less apparent in [HmIm][HCOO] and was more evident in [HPyrr][HCOO] and [HPyrd][HCOO]. All salts were found to increase the $H_{0,\mathrm{rel}}$, except NaCl in [HmIm][HCOO]. This unusual behavior of NaCl on $H_{0,\mathrm{rel}}$, is quite surprising and cannot be justified on the grounds of solubility change of indicator in solution. Another problem related with different salts is to arrange them in an order similar to Hofmeister series based on their influence on the $H_{0,\mathrm{rel}}$.

Similarly at $x_{\mathrm{IL}} = 0.08$, all the salts have displayed salting-out behavior and $H_{0,\mathrm{rel}}$ decreases with the salt concentration as revealed in Figure 6.1.4.

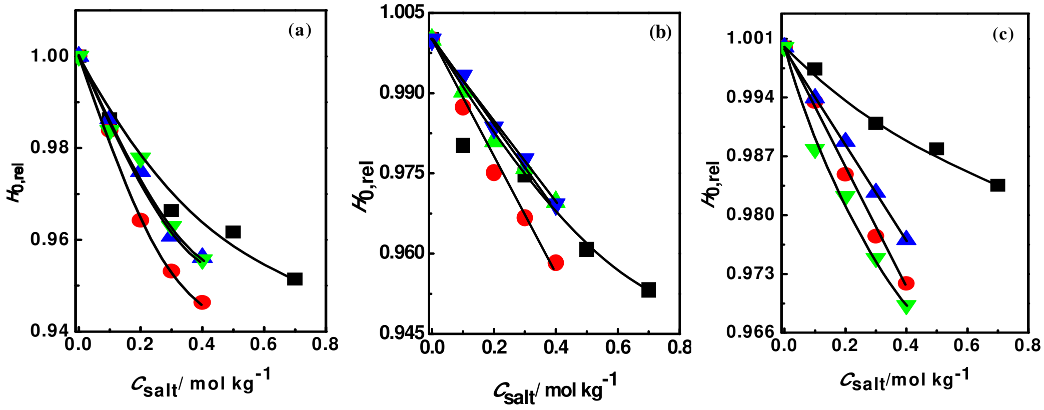


Figure 6.1.4: The $H_{0,\mathrm{rel}}$ *versus* C_{salt} plots in aqueous (a) [HmIm][HCOO], (b) [HPyrd][HCOO], and (c) [HPyrr][HCOO] at $x_{\mathrm{IL}} = 0.08$ for NaCl (■), Na_2SO_4 (●), $MgCl_2$ (▲), and $MgSO_4$ (▼).

Though these results are indicative of the strong salting-out behavior, their order of influence on the availability of indicator as predicted by the Hofmeister series is not obeyed as evident by the $H_{0,\mathrm{rel}}$. According to the Hofmeister series, efficiency of ions in salting-out the indicator from water should follow the order,

$$SO_4^{2-} > Cl^-$$

$$Mg^{2+} > Na^+$$

These ordering of salt ions are based on the hydration enthalpies and hydration entropies in water. The free energy of hydration, $\Delta_{\mathrm{hyd}}G$, of Mg^{2+} (-1830 kJ mol^{-1}) is higher than that of Na^+ (-365 kJ mol^{-1}). Similarly, $\Delta_{\mathrm{hyd}}G$ of SO_4^{2-} (-1080 kJ mol^{-1}) is higher than that of Cl^- (-340 kJ mol^{-1}). This contradiction in salt ion-induced consequences is noted by several workers. They have found that the order of influence of ions on non-electrolyte in water is different from the order of the $\Delta_{\mathrm{hyd}}G$.

Shahriari *et al.* have shown that the ability of ions to act as salting-out agent follows the order of hydration entropies.[26] Several reports suggest that the salting-out effect is mainly due to the entropic factor and operates through ion-dipole interactions.

The efficiency of a salt in producing ion-induced effects depends on the amount of salt required to promote the $H_{0,\mathrm{rel}}$ up to a certain level. The most effective salt needs least amount of salt for lowering the $H_{0,\mathrm{rel}}$. It is evident that the influence of salts on the $H_{0,\mathrm{rel}}$ vary with the concentration of ionic liquid. At $x_{\mathrm{IL}} = 0.02$, $MgSO_4$ acts as a strong salting-in agent in spite of very high $\Delta_{\mathrm{hyd}}G$ values of ions. Similarly, at higher concentrations of ionic liquids different ions regulate the availability of indicator differently irrespective of their $\Delta_{\mathrm{hyd}}G$ values. At $x_{\mathrm{IL}} = 0.02$, Na^+ has higher influence on the $H_{0,\mathrm{rel}}$ than that of Mg^{2+} having same anion. Even at higher concentration of protic ionic liquid ($x_{\mathrm{IL}} = 0.08$), the order of ions in promoting $H_{0,\mathrm{rel}}$ violates the Hofmeister ordering. Thus, it is apparent that the salt ions are following different mechanism, than that applies for the Hofmeister ordering, in promoting the $H_{0,\mathrm{rel}}$. While Figure 6.1.2, 6.1.3, and 6.1.4 reveals the dependency of the $H_{0,\mathrm{rel}}$ on salt concentration (C_{salt}), it does not give any idea about the dependency of the $H_{0,\mathrm{rel}}$ on the salt ion concentration. A plot of the $H_{0,\mathrm{rel}}$ against the salt-ion concentration shows a different trend when compared with the C_{salt}. Figure 6.1.5 showed a better ordering of salt ion influence on the $H_{0,\mathrm{rel}}$. From both the plots (6.1.5 (a) and (b)) it is evident that salts having higher valence of ions promote Hammett acidity more as compared to the salt ions of lower valence.

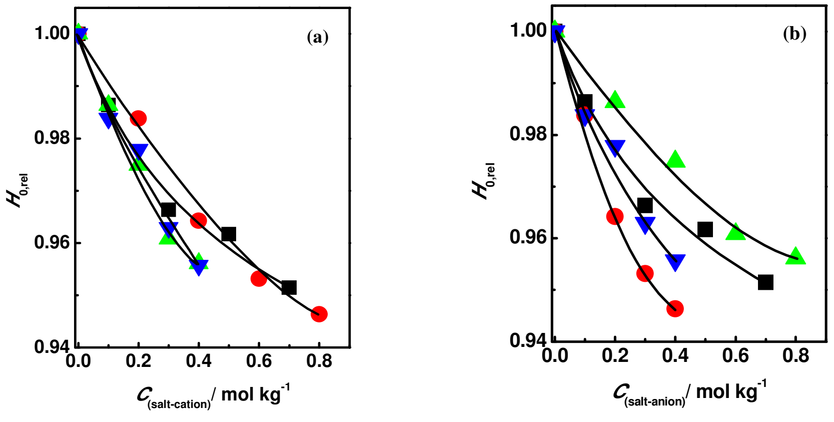


Figure 6.1.5: The plots of $H_{0,\mathrm{rel}}$ *versus* (a) $C_{\mathrm{(salt-cation)}}$ and (b) $C_{\mathrm{(salt-anion)}}$ of salts NaCl (■), Na_2SO_4 (●), $MgCl_2$ (▲), and $MgSO_4$ (▼).

The influence of anions on the $H_{0,\mathrm{rel}}$ is more evident, while effects of cation on the $H_{0,\mathrm{rel}}$ is still unambiguous. It is established through several studies that in aqueous salt systems; salt ions having similar water affinity exhibit different ion-pairing tendency. This ion-pairing tendency reduces the number of "effective/free" ions for salting-out and hence arranges them different from the Hofmeister series. Therefore, it is irrelevant to correlate the ion influence on the $H_{0,\mathrm{rel}}$ based on their order in Hofmeister series without considering the fraction of "free" ions. Rudolph et al. have shown that at higher $MgSO_4$ concentration, SO_4^{2-} anion exists as ion-pair with Mg^{2+}.[27] A detailed investigation of H_2SO_4 solution using dielectric relaxation spectroscopy along with Raman spectroscopy has shown that a simple, higher-valent and completely dissociated salt in fact is a mixture several complex species, whose distribution varies with the concentration of salt.[28] Thus, it is imperative to calculate the speciation of salts in aqueous solution as this might help in coordinating ion-induced changes on the Hammett acidity.

Ion speciation in aqueous solution was measured by the VisualMINTEQ. Speciation provides distribution of ionic species along with their concentrations. The speciation profiles of different salts at $x_{[\mathrm{HmIm}][\mathrm{HCOO}]} = 0.02$ are shown in Figure 6.1.6. It is assumed that the presence of a very small amount of protic ionic liquid does not affect the speciation calculations significantly.

From the depicted profiles (Figure 6.1.6) it is clear that the ion speciation varies with the nature of salts. The simplest 1:1 salt NaCl does not completely dissociated form even at 0.1 mol kg^{-1}. A small fraction of associated form exist as ion pair whose proportion further increases with the increasing concentration of NaCl. Similarly, Na_2SO_4 reveals more complicated ion speciation in aqueous protic ionic liquid ($x_{\mathrm{IL}} = 0.02$). It produces four different species; free ions Na^+ and SO_4^{2-}, ion pairs $NaSO_4^-$ and a small fraction of HSO_4^- due to the acid hydrolysis of anion in presence of acid. The $MgCl_2$ contains two ions Mg^{2+} and two Cl^-, but in solution it produces ion pair $MgCl^+$. At 0.4 mol kg^{-1} $MgCl_2$, 27 % Mg^{2+} remain in the form of ion pair. The $MgSO_4$ shows very complex behavior in aqueous solution. Apart from Mg^{2+} and SO_4^{2-} ions, it also contains a very large fraction of undissociated $MgSO_4$ and almost a negligible fraction of HSO_4^-. These speciation profiles of NaCl,

Na_2SO_4, $MgCl_2$, and $MgSO_4$ suggest that in comparison to 1:1 salt, 1:2 and 2:2 salts exhibit more complex ion speciation in aqueous solutions.

At higher protic ionic liquid concentrations (x_{IL} = 0.05 and 0.08) pH of the solution did not vary significantly, therefore almost negligible change in the ion speciation was noticed.

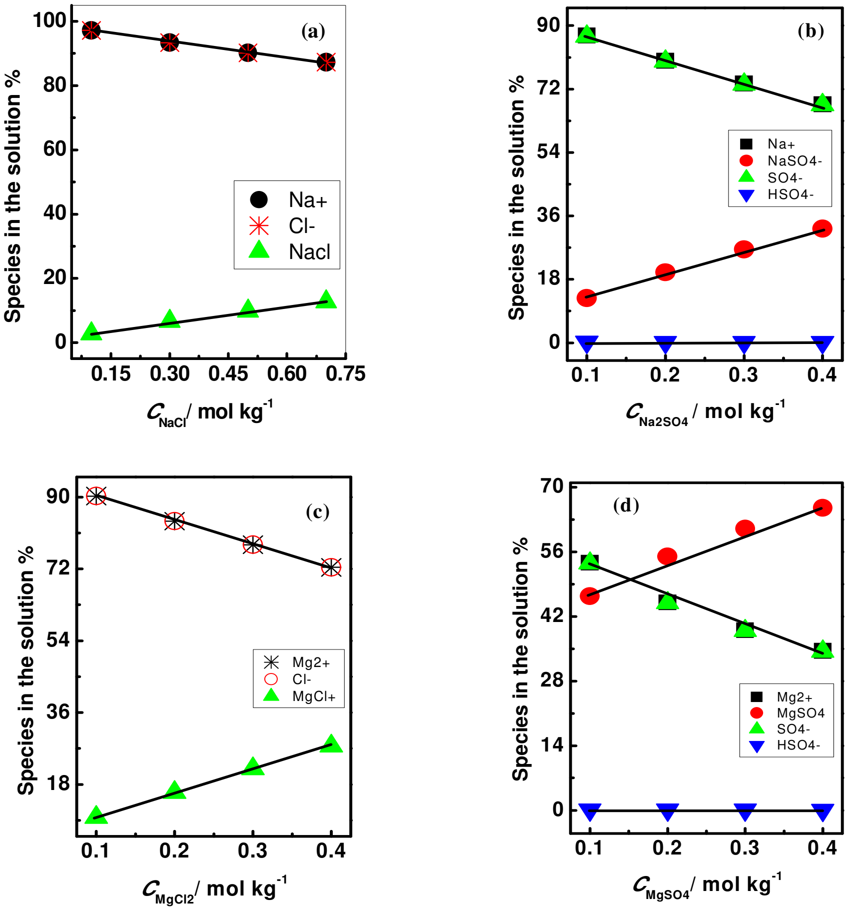


Figure 6.1.6: Ion speciation profiles of different salts in aqueous protic ionic liquid solution (x_{IL} = 0.02) at 298 K at measured pH = 5.37 for (a) NaCl, (b) Na_2SO_4, (c) $MgCl_2$, and (d) $MgSO_4$.

Ion speciation depends on the pH of the protic ionic liquid solution. It is observed that at lower pH (< 6), a divalent anion undergoes acid hydrolysis preferably than monovalent anion. Similarly, at pH > 8, cation of higher valence forms hydroxide due to alkaline hydrolysis more as compared to the monovalent metal cation. Since we have used 0.64 M CH_3COOH throughout the experiment for the Hammett acidity measurement in protic ionic liquid solutions, pH of the solutions were always < 6. This lower pH does not alter ion speciation significantly. Similarly, changing protic ionic liquid does not cause any shift in the pH of the solution (pH < 6). Thus, for a given salt in different ionic liquids, ion speciation remains unaltered. In short, speciation profiles of studied salts are independent of the nature and concentration of the protic ionic liquids used and only depends on the pH values of the medium.

Collins law of "Matching Water Affinity", which is based on the hydration enthalpies of ions, is used for predicting the ion pair formation in solution.[29] This law arises when hydration enthalpy of ion-water interactions become similar to the ion-ion interaction. Interaction of a small ion with a large counterion causes less enthalpic gain during the inner sphere ion pair formation than dehydrating the same ion from water. According to this law, in a salt solution the decreasing order of interactions is as follows:

kosmotrope-kosmotrope > kosmotrope-water > water-water
> chaotrope-water > chaotrope-chaotrope

Thus, ion pair formation in water depends on the relative magnitude of the hydration enthalpy and lattice enthalpy. These developments inferred that the solubility of ions in water is directly related to their tendency to form ion pair.

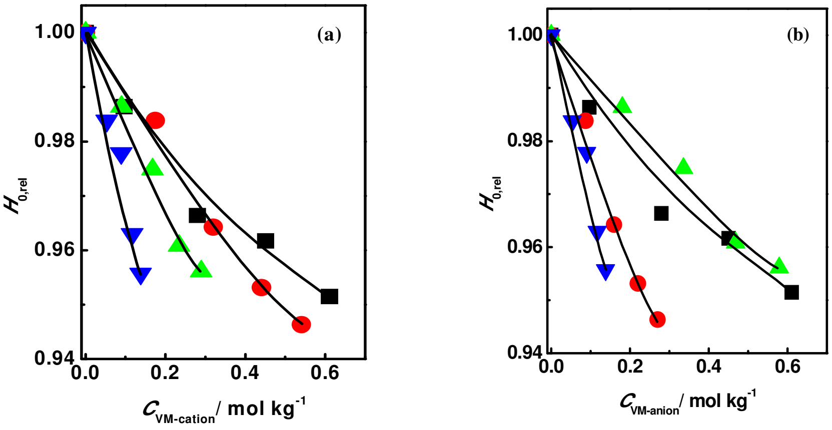


Figure 6.1.7: The plots of $H_{0,rel}$ *versus* (a) $C_{(VM-cation)}$ and (b) $C_{(VM-anion)}$ of salts NaCl (■), Na_2SO_4 (●), $MgCl_2$ (▲), and $MgSO_4$ (▼).

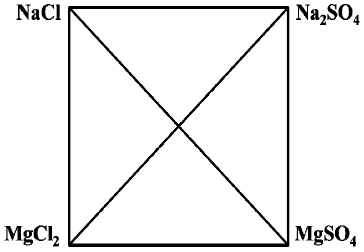
The estimation of ion speciation of salts in solution assists in correlating the $H_{0,\mathrm{rel}}$ with the "free" ion concentration and helps in developing the explicit order of ion influence on the $H_{0,\mathrm{rel}}$. Figure 6.1.7 reveals the correlation of the $H_{0,\mathrm{rel}}$ on the "free" ion concentration instead of the total ion concentration. From Figure 6.1.7, it is evident that the dependence of $H_{0,\mathrm{rel}}$ on the salt concentration can be resolved by considering the "free" ion concentration. The salting-out trends among the cations and anions are more apparent than that shown in Figure 6.1.5. The divalent Mg^{2+} cation causes more salting-out to the indicator than the monovalent Na^{+} cation. Similarly, salting-out by the divalent SO_4^{2-} is higher as compared to the monovalent Cl^{-}. The tendency of cations and anions to salt out the indicator corroborate very well with their order of free energy of hydration ($\Delta_{\mathrm{hyd}}G$) values shown in Table 6.1.1. This conformity between $\Delta_{\mathrm{hyd}}G$ values of ions and their influence on $H_{0,\mathrm{rel}}$ also nullify the changes due to the small amount of protic ionic liquid. From Figure 6.1.7, it is evident that $MgSO_4$ is the strongest salting-out agent amongst the studied salts as it remains close to the origin. Thus, even a very small amount of $MgSO_4$ causes a large change in the $H_{0,\mathrm{rel}}$.

Though, both cation and anion change $H_{0,\mathrm{rel}}$, but the question arises that which of these ions influence the $H_{0,\mathrm{rel}}$ predominantly? This can be analyzed by considering the Gibb's free energy of ion hydration ($\Delta_{\mathrm{hyd}}G$) as it assists in guiding the effect of ion on the $H_{0,\mathrm{rel}}$. Generally, monovalent anion shows higher $\Delta_{\mathrm{hyd}}G$ than monovalent cation owing to the higher polarizability of former over later. However, divalent SO_4^{2-} anion possess lower $\Delta_{\mathrm{hyd}}G$ (-1080 kJ mol^{-1}) than divalent cation Mg^{2+} (-1830 kJ mol^{-1}), which becomes more evident for the trivalent cation. These comparisons point out the difficulty in assigning the contribution of oppositely charged ions on $H_{0,\mathrm{rel}}$. Therefore, it can be imagined that both ions act cooperatively in promoting $H_{0,\mathrm{rel}}$. These discussions suggest that the $H_{0,\mathrm{rel}}$ is not a function of salt concentration, and it works better when speciation of salt ions in the solution is considered.

In addition to the salt solution a combined effect of the ions and salts can be of extreme importance in calculating the Hammett acidity in protic ionic liquid solutions. This can be facilitated by examining the Young's cross square rule (YCSR).[30] Originally, this rule was proposed by Young, Wu, and Krawetz based on their enthalpy measurements.[31] This rule states that the sum of the common-ion mixings (the mixings around the square) is equal to the sum of the non-common-ion mixings (the two cross-mixings). The six possible reciprocal pairs for Na^+, Mg^{2+}, Cl^-, and SO_4^{2-} are represented below.

According to the YCSR rule, $\partial H_{0,m}$ for binary salt mixtures with common ions should be equal to the $\partial H_{0,m}$ for the salt mixtures with uncommon ions.

$$\partial H_{0,m}(NaCl\text{-}Na_2SO_4) + \partial H_{0,m}(Na_2SO_4\text{-}MgSO_4) + \partial H_{0,m}(MgSO_4\text{-}MgCl_2) + \partial H_{0,m}(MgCl_2\text{-}NaCl) = \partial H_{0,m}(NaCl\text{-}MgSO_4) + \partial H_{0,m}(Na_2SO_4\text{-}MgCl_2) \quad (1)$$



Note that $\partial H_{0,m}$ for binary mixtures are obtained from the individual $H_{0,salt}$ values. The $H_{0,salt}$ represents the change in Hammett acidity caused by added salt and was obtained by eliminating the solvent contribution to H_0 values. Previously, YCSR rule is validated on the nucleation temperature, T_H, in the binary mixture of salts.[32]

Table 6.1.2: Validity of the YCSR Rule and Its Application in Calculating $\partial H_{0,m}$ at yB = 0.5 and I = 1 mol kg^{-1} Aqueous Solution of [HmIm][HCOO] at $x_{[HmIm][HCOO]}$ = 0.05.

mixture, x_{IL} = 0.05	$\partial H_{0,m}$	mixture, x_{IL} = 0.05	$\partial H_{0,m}$
$NaCl\text{-}Na_2SO_4$	-0.037	$NaCl\text{-}MgSO_4$	-0.096
$Na_2SO_4\text{-}MgSO_4$	-0.067	$Na_2SO_4\text{-}MgCl_2$	-0.064
$MgSO_4\text{-}MgCl_2$	-0.051		
$MgCl_2\text{-}NaCl$	-0.011		
sum	-0.166		-0.16

The $\partial H_{0,m}$ values for all the six possible binary salt mixtures are measured in the imidazolium-, pyrrolidinium-, and piperidinium-based protic ionic liquid at different x_{ILs}. The application of YCSR rule in Hammett acidity is shown in Table 6.1.2.

Table 6.1.2 conforms the validity of the YCSR rule for Hammett acidity in binary mixtures of salt. The sum of $\partial H_{0,\mathrm{m}}$ values for the salt mixtures with a common ion is -0.166, which is close to that obtained (-0.16) for the salt mixtures with uncommon ions. The validity of the YCSR rule facilitates in predicting the Hammett acidity in binary salt mixtures with uncommon ion, by using the knowledge of the Hammett acidity change in binary salt mixtures with a common ion.

6.1.4: Conclusions

In summary, ion-induced effects on the relative Hammett acidity ($H_{0,\mathrm{rel}}$) in binary mixtures of protic ionic liquid and water were different than that of water. A reversal in the behavior of salts on the relative Hammett acidity was revealed upon varying the concentration of protic ionic liquid. The aptitude of salt ions to influence the Hammett acidity does not follow the Hofmeister series and their hydration ability. The deviation occurs in the influence of salt on the Hammett acidity owing to the coulombic interactions and ion speciation in binary mixtures of protic ionic liquids. A better correlation between the relative Hammett acidity and salt concentrations was observed when the concentration of "free" ion was used in place of the total concentration of ions. The speciation of salt ions thus assists in reviving the Hofmeister ordering. In binary salt mixtures, Young's cross square rule is certified. In addition, a linear relation is developed between different salts, based on their influence on the Hammett acidity, and a single parameter is derived to calculate the Hammett acidity at higher concentrations.

6.2: Effect of Temperature on Hammett Acidity: Thermodynamic Parameters and Activation Energy of Proton Transfer

6.2.1: Introduction

The concept of acid-base catalysis has played a key role in the understanding and the development of many organic and biological processes.[33] The development of Hammett structure-activity equation and Brønsted catalysis equation, which laid the foundation of physical-organic chemistry are based on the pK_a scale of acidity measurement.[34,35] The strength of an acid in a medium depends on the solvation of proton.[36] Thus, the magnitude of solute-solvent interactions regulates the dissociation of an acid in a medium. The knowledge of the solute-solvent interactions between acid and solvent can be of significant value in constructing the efficient media for attaining the maximum strength even for weak acids.

Thermodynamic parameters have been used to predict the nature of solute-solvent interactions in the dissociation of weak acid.[37] Thermal change directly affects the magnitude of solute-solvent interactions. Thus, the thermal effect on a physical change can be used to comprehend the nature of the solute-solvent interactions involved in the process. The thermodynamic parameters are obtained from the measurements of dissociation constant (K_a) weak acids at different temperatures. The K_a values of weak acids are measured either by the potentiometry or EMF method. The EMF method fails in the case of strong acids, while the potentiometry does not yield reliable values of the K_a values for weak acids and bases.[38]

In this section, we propose a method based on the "indicator overlapping method" for the determination of K_a of weak acids. This method depends on the protonation of indicator at different temperatures. The general criterion for the selection of indicator is that its pK_a should be at least two units less than that of the acid to avoid complete protonation of the indicator.

In the present investigation, we address the issue of the acidity determination of carboxylic acids in protic ionic liquid and aprotic ionic liquid using the Hammett acidity relation. We have attempted to relate the Hammett acidity change in different ionic liquids in terms of the solute-solvent interactions operates between acid and ionic liquid. The efforts have also been made for accounting the principal reason for the large difference in the H_0 values for carboxylic acids in protic ionic liquid and aprotic ionic liquid. We have attempted to solve these issues by measuring the H_0 for carboxylic acids in protic ionic liquid and aprotic ionic liquid, determining thermodynamic parameters, activation energy of proton transfer, and polarity.

The polarity of ionic liquids was determined as measured in Chapter 4, Section 4.2.3. The Hammett acidity of carboxylic acids was determined by the procedure used in Chapter 5, Section 5.1.2.2. The ionic liquids employed in this work are 1-butyl-3-methylimidazolium formate [BMIm][HCOO], [HmIm][HCOO], [HPyrr][HCOO] and [HPyrd][HCOO]. All ionic liquids were synthesized by the mode given in Chapter 4, Section 4.2.2.

6.2.2: Experimental Section

6.2.2.1: Determination of Activation Energy of Proton Transfer, $E_{a,H+}$

The activation energy of proton transfer was calculated from the temperature-dependent H_0 measurements of carboxylic acids in ionic liquids. A linear plot was noticed between the $\ln H_0$ and $1/T$ as shown in Figure 6.2.1.

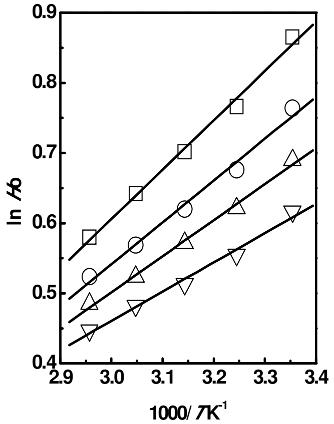


Figure 6.2.1: The Arrhenius-type plots for CH_3COOH in 1-methylimidazolium acetate at 0.48 M (□), 0.79 M (○), 1.07 M (Δ) and 1.4 M (▽).

The activation energy of proton transfer ($E_{a,H+}$) was calculated by using the Arrhenius-type equation.

$$H_0 = (H_0)_0 e - E_{a,H+}/RT \qquad (2)$$

where, $(H_0)_0$ is the Hammett acidity at room temperature, $E_{a,H+}$ is the activation energy of proton transfer and R is the universal gas constant.

Taking the natural log of equation 2,

$$\ln H_0 = \ln(H_0)_0 - E_{a,H+}/RT \qquad (3)$$

In a medium, the availability of a proton depends on the interaction of the proton with the medium, i.e., solvation. An increase in temperature favors the availability of a proton by weakening the proton-solvent interactions. The energy required to release the proton from the solvated form to the free form is equal to the activation energy of proton transfer ($E_{a,H+}$). Generally, weakly solvated protons have a lower value of $E_{a,H+}$, while strongly solvated protons have a higher $E_{a,H+}$.

6.2.2.2: pH Measurement

The pH of equimolar mixture of carboxylic acids and water in ionic liquids was measured by using the calibrated pH meter (DPH 504).

6.2.2.3: Determination of Thermodynamic Parameters by Indicator Overlapping Method

A small volume of 4-nitroaniline (10^{-4} M) prepared in methanol was added in a round bottom flask and methanol was removed using high vacuum prior to the addition of 1 ml of ionic liquid. The sample was filled inside the cuvette and absorbance was recorded at 298 K. This absorbance was taken as reference value. The reference absorbance denotes the presence of the 100% unprotonated form of indicator and thus negates any aid provided by the medium on the H_0. All acids were mixed in equimolar proportion with deionized water. The H_0 of carboxylic acids in ionic liquids was independent of the presence of small amount of water as dissociation is guided by the basicity (β) of medium and the β of studied ionic liquids (Table 6.2.5) is higher than that of water (β = 0.49).[39] The calculated amount of acid was added inside the cuvette and absorbance was noted at different temperatures ranging from 298 to 338 K. Similarly, the absorbance at different concentrations in the temperature range from 298 to 338 K was also recorded. The indicator ratio ($[HI^+]/[\mathrm{I}]$) was calculated by the procedure given in Table 6.2.1.

Table 6.2.1: Calculation of the Equilibrium Constants for HCOOH in [HPyrr][HCOO] at 0.48 M in the Temperature Range from 298 to 338 K by Indicator Overlapping Method.

T/K	A_{max}	$[I]$%	$[HI^+]$%	$[HI^+]/[I]$	K^a_{eq}
298	1.420	100.0	0	0	0
298	1.334	93.9	6.1	0.064	0.13
308	1.301	91.6	8.4	0.091	0.19
318	1.269	89.4	10.6	0.119	0.25
328	1.230	86.6	13.4	0.154	0.32
338	1.190	83.8	16.2	0.193	0.40

[a]K_{eq} values are precise to ± 0.03

The protonation equilibrium of indicator is as,

$$I + HX \leftrightarrow HI^+ + X^- \tag{4}$$

The equilibrium constant (K_{eq}) for the dissociation of weak acids is given as,

$$K_{eq} = \frac{[HI^+][X^-]}{[I][HX]} \tag{5}$$

The ratio $[HI^+]/[\mathrm{I}]$ was obtained by comparing the optical density/absorbance of the protonated form of indicator against the reference value. The ratio $[X^-]/[HX]$ was calculated from the pH data of carboxylic acids in protic ionic liquids. However, a very small extent of carboxylic acid remains in the dissociated form in protic ionic liquids as suggested by their degree of dissociation (α) values calculated from the pH measurements (Table 6.2.2). The degree of dissociation for HCOOH, CH_3COOH, and CH_3CH_2COOH in [HmIm][HCOO] and [HPyrr][HCOO] was in the order of ~10^{-7}, while in [HPyrd][HCOO] and [BMIm][HCOO] it was noted to be in the order of ~ 10^{-6} between the experimental temperature range of 298 to 338 K. The equilibrium constant was calculated as shown in Table 6.2.1.

Table 6.2.2: Degree of Dissociation (α) Values for HCOOH, CH_3COOH, and CH_3CH_2COOH in Ionic Liquids.

ionic liquids	**carboxylic acids**	**10^7x α (0.48 M)**	**10^7x α (0.79 M)**	**10^7x α (1.07 M)**	**10^7x α (1.4 M)**
[HmIm][HCOO]	HCOOH	3.7	2.5	2.1	1.7
	CH_3COOH	5.2	3.0	2	1.6
	CH_3CH_2COOH	6.8	5.8	5.5	5.3
[HPyrr][HCOO]	HCOOH	1.5	1.3	1.3	1.5
	CH_3COOH	1.2	1.0	1.0	1.0
	CH_3CH_2COOH	1.0	0.9	0.9	0.9
[HPyrd][HCOO]	HCOOH	24.0	20.1	19.0	27.0
	CH_3COOH	23.0	20.0	20.0	19.0
	CH_3CH_2COOH	22.0	19.0	19.0	17.0
[BMIm][HCOO]	HCOOH	29.0	30.0	63.0	180.0
	CH_3COOH	5.7	3.2	4.9	7.1
	CH_3CH_2COOH	2.9	3.5	6.5	8.9

Similarly, the temperature-dependent K_{eq} was obtained at different concentrations of carboxylic acid (0.79, 1.07, and 1.4 M) and were further used for the determination of the thermodynamic parameters.

The linear dependence of K_{eq} on temperature is given by the van't Hoff equation.

$$\Delta G^0 = -RT ln K_{eq} \tag{6}$$

or,

$$ln K_{eq} = -\frac{\Delta G^0}{RT} \tag{7}$$

At a given temperature, ΔG^0 depends on the ΔH^0 and ΔS^0 as,

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{8}$$

Substituting equation (8) into (7) leads to van't Hoff equation,

$$ln K_{eq} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{10}$$

A plot of the lnK_{eq} against $1/T$ gives a straight line with slope = $-\Delta H^0/R$ and intercept = $\Delta S^0/R$.

A negative slope between the lnK_{eq} and $1/T$ signifies endothermic nature of carboxylic acid dissociation, while a positive slope implies exothermic nature of dissociation process as suggested by the equation 9. In protic ionic liquids and aprotic ionic liquid, dissociation of carboxylic acids were endothermic in nature. A typical plot of lnK_{eq} against $1/T$ for carboxylic acid is shown in Figure 6.2.2. The thermodynamic parameters, ΔH^0 and ΔS^0, for the dissociation of carboxylic acids were calculated from the slope and intercept values, respectively.

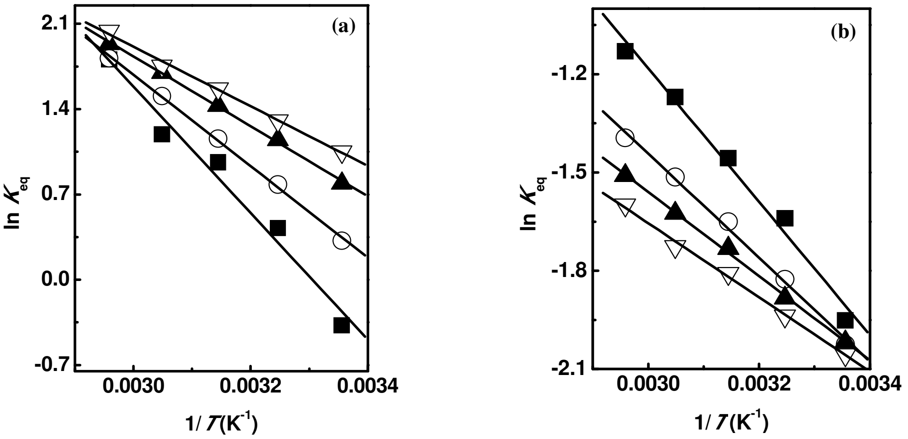


Figure 6.2.2: A plot of $ln\ K_{eq}$ *versus* $1/T$ for CH_3COOH in (a) [HPyrr][HCOO] and (b) [BMIm][HCOO] at 0.48 M (■), 0.79 M (○), 1.07 M (▲), and 1.4 M (▽).

6.2.3: Results and Discussion

The solvation behavior of protic and aprotic ionic liquids is different from each other as indicated by their polarity values.[40-42] For aprotic class of ionic liquids polarity ($E_T(30)$) ranges from 47 – 59 kcal mol^{-1} which is similar to those of alcohols, however, the $E_T(30)$ for protic class of ionic liquids varies from 50 – 65 kcal mol^{-1} which is comparable to water.[43,44] In the polar Diels-Alder reactions, the electrophilic character of the dienophile was observed significantly higher in protic ionic liquids than that of the aprotic ionic liquid as evidenced from the higher reactivity and regioselectivity of the product in protic ionic liquids.[45] The high polarity of protic ionic liquid helps in the aggregation of surfactant than that of aprotic ionic liquids.[46]

Thus, the Hammett acidity, which measures the ability of a solvent to donate a proton towards a base, would be different for a protic acid in protic ionic liquids and aprotic ionic liquids. The lower H_0 values for HCOOH, CH_3COOH, and CH_3CH_2COOH were obtained in protic ionic liquids than that of aprotic ionic liquid (Figure 6.2.3). The C_{H+} values denote the concentrations of added carboxylic acid. This suggests the greater dissociation of carboxylic acids in protic ionic liquid in comparison with aprotic ionic liquid. For comparison, the H_0 values of HCOOH, CH_3COOH, and CH_3CH_2COOH in protic ionic liquids is taken from our earlier work.[25]

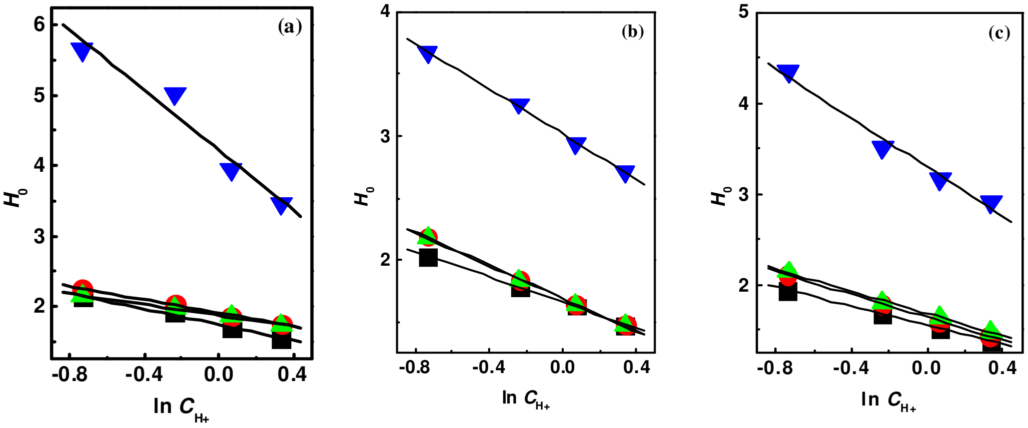


Figure 6.2.3: The plots of H_0 *versus* ln C_{H+} for (a) HCOOH, (b) CH_3COOH, and (c) CH_3CH_2COOH in [HmIm][HCOO] (■), [HPyrr][HCOO] (●), [HPyrd][HCOO] (▲), and [BMIm][HCOO] (▼).

From these plots, it is evident that the H_0 for all carboxylic acids are higher in protic ionic liquids as compared to that in aprotic ionic liquid. The higher dissociation of carboxylic acids in protic ionic liquids is independent of their hyperpolarity as lower H_0 values were obtained in the polar protic ionic liquids. For example, the maximum dissociation for all carboxylic acids is obtained in [HmIm][HCOO] ($E_T(30)$ = 56 kcal mol^{-1}) than that in [HPyrd][HCOO] ($E_T(30)$ = 61.4 kcal mol^{-1}) in spite of the lower polarity of former protic ionic liquid. This indicates involvement of non-electrostatic interactions between protic ionic liquid and carboxylic acid. Recently, it is reported that the dissociation of carboxylic acid in protic ionic liquids is facilitated by the hard-soft acid-base (HSAB) combination between the protic ionic liquid cation and conjugate anion of acid.[25] The increasing strength of carboxylic acids in protic ionic liquids follows the order,

$$CH_3CH_2COOH > CH_3COOH > HCOOH$$

Thus, conjugate acidity of protic ionic liquid cation act as a decisive factor in controlling the H_0 of carboxylic acids. The order of conjugate acidity of 1-methylimidazole (pK_a = 6.95), 1-methylpyrrolidine (pK_a = 10.5), and 1-methylpiperidine (pK_a = 10.08) bases, $[HmIm]^+$, $[HPyrr]^+$, and $[HPyrd]^+$, respectively are

$$[HmIm]^+ > [HPyrd]^+ > [HPyrr]^+$$

The strength of HCOOH in protic ionic liquids varies according to the conjugate acidity of the protic ionic liquid cations. The maximum strength for HCOOH was achieved in [HmIm][HCOO] and minimum in [HPyrr][HCOO]. Similarly, the strength of CH_3COOH in protic ionic liquids was noted to follow the order of the conjugate acidity of cations. However, a very small difference in the H_0 values was observed for CH_3COOH in [HPyrd][HCOO] and [HPyrr][HCOO]. The small difference in H_0 is probably due to the onset of steric repulsion between the larger $[HPyrd]^+$ (six membered) and CH_3COO^- which opposes the HSAB interaction and therefore lowers the H_0. The strength of CH_3CH_2COOH in protic ionic liquids was noted to follow the order,

$$[HmIm]^+ > [HPyrr]^+ > [HPyrd]^+$$

The above ordering suggests the dominance of steric repulsion between $CH_3CH_2COO^-$ and $[HPyrd]^+$over the favorable HSAB interactions.

Contrary to the protic ionic liquid which causes higher dissociation of carboxylic acids (lower H_0 value), the lower dissociation was observed in [BMIm][HCOO] for all carboxylic acids (higher H_0 value) as evidenced from Figure 6.2.3. This suggests the minor contribution of any conducive mechanism involved in the dissociation of carboxylic acid in aprotic ionic liquid. The lower strength of acid albeit of the presence of basic anion ($HCOO^-$) indicates the dominant role of ionic liquid cation in the dissociation of acid. Therefore, it can be presumed that the H_0 in ionic liquids is a function of the conjugate acidity of cation. In other words, higher dissociation of carboxylic acids in ionic liquids is because of the greater stabilization of the conjugate base of carboxylic acids rather than the stabilization of proton.

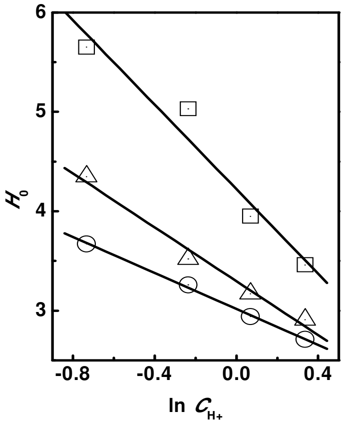


Figure 6.2.4: The plots of H_0 *versus* ln C_{H+} for HCOOH (⊡), CH_3COOH (⊙), and CH_3CH_2COOH (△) in [BMIm][HCOO].

The order of the H_0 for HCOOH, CH_3COOH, and CH_3CH_2COOH in [BMIm][HCOOH] is shown in Figure 6.2.4. The H_0 values for HCOOH, CH_3COOH, and CH_3CH_2COOH in [BMIm][HCOO] are noted to vary in the order,

$$CH_3COOH > CH_3CH_2COOH > HCOOH$$

The above arrangement of carboxylic acid dissociation in [BMIm][HCOO] reveals neither the complete dominance of the electrostatic interactions nor the specific interactions. The higher H_0 for CH_3COOH in [BMIm][HCOO] than that of the HCOOH indicates involvement of the specific interactions in the dissociation. Since [BMIm][HCOO] is synthesized *via* quaternization of base rather than the transfer of proton, its cation ($[BMIm]^+$) is expected to possess the lower ability to bind with the conjugate base of carboxylic acids than that of protic ionic liquid cation. A higher H_0 for CH_3COOH ahead of the CH_3CH_2COOH can be explained due to the steric repulsion between the $[BMIm]^+$ and $CH_3CH_2COO^-$.[25] The steric repulsion opposes the specific interaction between the $[BMIm]^+$ and $CH_3CH_2COO^-$ and hence results the lower H_0 for CH_3CH_2COOH. The above analysis implies that although ionic liquid acts as strong Coulomb media, specific interaction plays a significant role in governing the solute-solvent interactions. The strength of specific interactions is noted to depend on the activation energy of proton transfer, $E_{a,H+}$, which relies on the viscosity of medium.

6.2.3.1: Activation Energy of Proton Transfer, $E_{a,H+}$

The activation energy of proton transfer ($E_{a,H+}$) is a measure of the hindrance provided by the medium in the protonation of indicator. Numerically, it is equivalent to the amount of energy required to release the proton from the solvated state. The high viscosity of ionic liquid retards the diffusion of reacting species and thereby lowers the protonation of indicator. Thus, $E_{a,H+}$ increases with the viscosity of medium. The $E_{a,H+}$ was obtained from the temperature-dependent H_0 measurements. The temperature-dependent H_0 when fitted in the Arrhenius-type equation, a linear relation was observed between the ln H_0 and $1/T$ with a negative slope as revealed in Figure 6.2.5. The $E_{a,H+}$ was calculated from the slope of linear fit.

$$\ln H_0 = \ln (H_0)_0 - E_{a,H+}/RT \qquad (9)$$

where $(H_0)_0$ is the Hammett acidity at room temperature, $E_{a,H+}$ is the activation energy of proton transfer, and R is the universal gas constant.

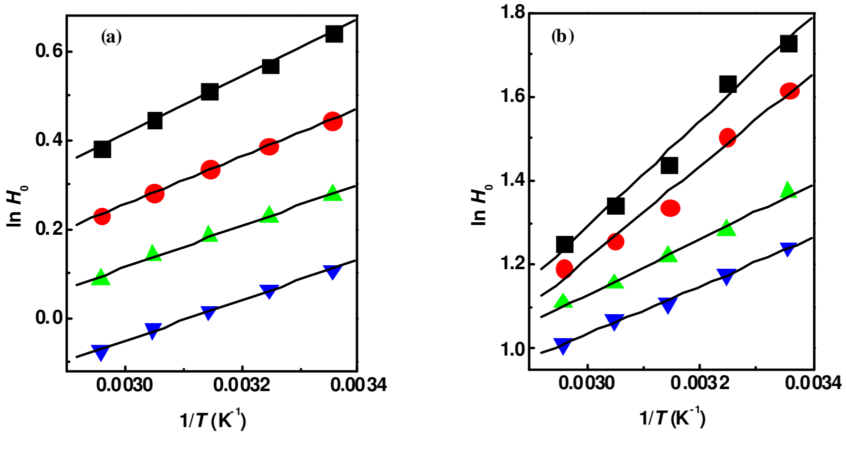


Figure 6.2.5: The Arrhenius-type plots for HCOOH in (a) [HmIm][HCOO] and [BMIm][HCOO] at 0.48 M (■), 0.79 M (●), 1.07 M (▲), and 1.4 M (▼).

The $E_{a,H+}$ for HCOOH in different ionic liquids are given in Table 6.2.3. As shown in Table 6.2.3, $E_{a,H+}$ for HCOOH in all protic ionic liquids do not vary significantly, but for aprotic ionic liquid it is nearly two-fold. The high $E_{a,H+}$ value for HCOOH in [BMIm][HCOO] denotes the greater hindrance in the diffusion of reacting species that lowers the protonation of indicator and thus lower strength for HCOOH (higher H_0). Similar observations were noted for CH_3COOH and CH_3CH_2COOH in protic ionic liquids and aprotic ionic liquid. It is noticed by several workers that the diffusion controlled process depends on the viscosity of medium.[47,48] Thus, the high $E_{a,H+}$ value in a medium indicates the highly viscous nature of medium.

Table 6.2.3: Activation Energy ($E_{a,H+}$) for HCOOH in Protic Ionic Liquids and Aprotic Ionic Liquid.

ionic liquids	**$E_{a,H+}$ (kJ mol^{-1})**			
	0.48 M	0.79 M	1.07 M	1.4 M
[HmIm][HCOO]	5.37	4.46	3.87	3.80
[HPyrr][HCOO]	5.14	4.06	3.44	3.12
[HPyrd][HCOO]	5.47	4.09	3.49	3.12
[BMIm][HCOO]	10.49	9.21	5.53	4.75

Generally, aprotic ionic liquids posses' higher viscosity than that of protic ionic liquids. For aprotic ionic liquids, viscosity ranges between 60 – 10000 cP (1 cP = 1 mPa·s), while for protic ionic liquids it varies between 6 – 30 cP. Hence, the different H_0 values for HCOOH, CH_3COOH, and CH_3CH_2COOH in protic ionic liquids and aprotic ionic liquid are also confirmed by the $E_{a,H+}$ in these media. The presence of intermolecular solute-solvent interactions between carboxylic acids and ionic liquids can also be shown by the thermodynamic parameters (ΔH^o, ΔS^o).

6.2.3.2: Thermodynamic Parameters and Dissociation of Carboxylic Acids in Ionic Liquids

Thermodynamic parameters (ΔH^o, ΔS^o), arise from solute-solvent interactions, help in comprehending the interactions at molecular level. The value of the thermodynamic parameters also helps in predicting the feasibility of protonation of indicator. The driving force for the protonation of indicator in a medium depends on the affinity of solute by medium. The magnitudes of the ΔH^o and ΔS^o were observed to vary with the nature of ionic liquids. The ΔH^0 and ΔS^0 values at different concentrations of HCOOH, CH_3COOH, and CH_3CH_2COOH in [HmIm][HCOO], [HPyrr][HCOO], [HPyrd][HCOO], and [BMIm][HCOO] are given in Table 6.2.5.

A linear relation was observed between the ΔH^0 and ΔS^0 against lnC_{H+} (Figure 6.2.6). This indicates that the nature of carboxylic acid- ionic liquid interactions remain independent of the concentration of acid. The efficacy of the thermodynamic parameters in the dissociation of carboxylic acids is discussed in different classes of ionic liquids.

The standard entropy change, ΔS^0, refers to the entropy change during the protonation of indicator. In protic ionic liquids, all carboxylic acids have positive ΔS^0. A large ΔS^0 for carboxylic acids in protic ionic liquids are in contradiction with the generalization that “all ionization of uncharged acids in aqueous solution leads standard entropy change, ΔS^0, nearly -22 cal K^{-1} mol^{-1}.”[49] A large ΔS^0 indicates the higher dissociation of carboxylic acids in protic ionic liquids than that in aqueous solutions. However, the contribution of ΔS^0 in promoting the dissociation of carboxylic acids is very small in comparison to the ΔH^0, *i.e.* dissociation of acids is guided by the ΔH^0 values.

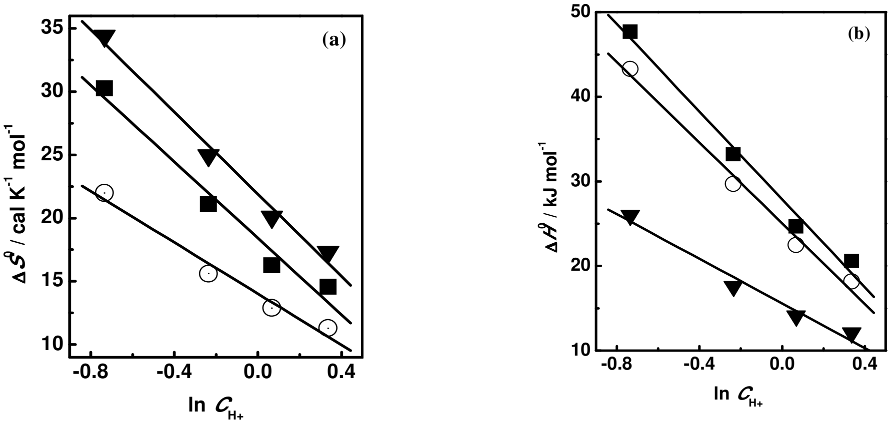


Figure 6.2.6: The plots of (a) ΔS^0 *versus* ln C_{H+} and (b) ΔH^0 *versus* ln C_{H+} for HCOOH in [HmIm][HCOO] (■), [HPyrr][HCOO] (○), and [HPyrd][HCOO] (▼).

The dissociation of carboxylic acids in protic ionic liquids is mainly governed by the enthalpy change rather than the entropy change. Further, the solute-solvent interactions can be perceived more accurately by the enthalpy change rather than the entropy change and hence are employed in the detection of intermolecular interactions. The enthalpy required in the dissociation of carboxylic acids varies with the nature of protic ionic liquids as shown in Table 6.2.4.

Table 6.2.4: Thermodynamic Parameters for the Dissociation of HCOOH, CH_3COOH, and CH_3CH_2COOH in Ionic Liquids at Different Concentrations.

ionic liquids	**carboxylic acid**	**thermodynamic parameters***	**0.48 M**	**0.79 M**	**1.07 M**	**1.4 M**
[HmIm][HCOO]	HCOOH	ΔH^0	47.7	33.2	24.7	20.6
		ΔS^0	0.13	0.09	0.07	0.06
	CH_3COOH	ΔH^0	38.7	30.4	27.6	23.0
		ΔS^0	0.10	0.08	0.07	0.06
	CH_3CH_2COOH	ΔH^0	49.0	35.9	30.3	26.9
		ΔS^0	0.13	0.10	0.08	0.07
[HPyrr][HCOO]	HCOOH	ΔH^0	43.3	29.7	22.5	18.2
		ΔS^0	0.14	0.10	0.08	0.07
	CH_3COOH	ΔH^0	43.1	31.2	23.9	20.3
		ΔS^0	0.14	0.11	0.09	0.08
	CH_3CH_2COOH	ΔH^0	52.3	26.8	21.4	15.6
		ΔS^0	0.13	0.10	0.08	0.06
[HPyrd][HCOO]	HCOOH	ΔH^0	26.0	17.6	14.1	12.1
		ΔS^0	0.09	0.07	0.05	0.04
	CH_3COOH	ΔH^0	44.3	36.8	33.8	31.3
		ΔS^0	0.15	0.12	0.11	0.10
	CH_3CH_2COOH	ΔH^0	38.6	26.5	20.9	20.8
		ΔS^0	0.13	0.09	0.08	0.07
[BMIM][HCOO]	HCOOH	ΔH^0	46.0	37.2	19.0	14.8
		ΔS^0	0.12	0.09	0.04	0.03
	CH_3COOH	ΔH^0	16.9	13.2	10.7	9.4
		ΔS^0	0.04	0.03	0.02	0.01
	CH_3CH_2COOH	ΔH^0	26.4	14.0	12.3	10.8
		ΔS^0	0.07	0.03	0.02	0.01

*Units for ΔH^0 in kJ K^{-1} mol^{-1} and for ΔS^0 in kJ mol^{-1}

The protic ionic liquids which assist in the dissociation of carboxylic acids require the lower ΔH^0. Thus, different protic ionic liquids can be arranged in the order based on their ability to dissociate carboxylic acids. The dissociation of carboxylic acids in protic ionic liquid is favored either by the greater stabilization of the conjugate anion of acid or by the dissociation of proton.

The order of different protic ionic liquids in promoting the dissociation of HCOOH, CH_3COOH, and CH_3CH_2COOH based on the ΔH^0 values are as,

$[HPyrd]^+ > [HPyrr]^+ > [HmIm]^+$
$[HmIm]^+ > [HPyrr]^+ > [HPyrd]^+$
$[HPyrd]^+ > [HPyrr]^+ > [HmIm]^+$

As apparent from these arrangements of protic ionic liquids based on the ΔH^0 values, there is no definite order of protic ionic liquids in which they interact with carboxylic acids. The potential of protic ionic liquids based on the ΔH^0 values are different than those obtained from the H_0 values for HCOOH, CH_3COOH, and CH_3CH_2COOH at 298 K. This discrepancy in the dissociating carboxylic acids in protic ionic liquids might be due to the thermal effects which were not accounted in the determination of the H_0.

However, unexpectedly very low ΔH^0 values for all carboxylic acids were obtained in [BMIm][HCOO]. This points out that the nature of intermolecular interactions between carboxylic acids and [BMIm][HCOO] is similar to protic ionic liquids and carboxylic acids based on the ΔH^0 values. The unusual behavior of [BMIm][HCOO] is in contradiction with the very large H_0 values for all carboxylic acids. Thus, the intermolecular force between the [BMIm][HCOO] and carboxylic acids cannot be predicted from the ΔH^0 values. The ambiguous behavior of [BMIm][HCOO] can be explained by employing the polarity parameters which controls the solute-solvent interactions. The polarity parameters of ionic liquids represent the solvation characteristics and can therefore be used for delineating the intermolecular interactions with solute.

6.2.3.3: Thermodynamic Parameters and Polarity of Ionic Liquids

The different arrangements of protic ionic liquids in the dissociation of HCOOH, CH_3COOH, and CH_3CH_2COOH based on the ΔH^0 values indicate specific interactions between carboxylic acid and protic ionic liquids. The solvation ability of protic ionic liquids is represented by the polarity parameters. The polarity parameters which are used to define solvation behavior of ionic liquids are the normalized electronic transition energy (E_T^N), hydrogen bond donor acidity (α), hydrogen bond acceptor basicity (β) and dipolarity/polarizability or polarity index (π*). The E_T^N value denotes overall polarity exhibited by medium, while α, β, and π* represents the hydrogen bond donating ability of cation, hydrogen bond accepting ability of anion, and electrostatic strength of medium, respectively. The polarity parameters of different ionic liquids are shown in Table 6.2.5. The standard enthalpy change, ΔH^0, which measures solute-solvent interactions can be correlated with the polarity parameters of ionic liquids. The arrangements of protic ionic liquids in dissociating the HCOOH and CH_3CH_2COOH is in the inverse order of polarity index (π*), while for CH_3COOH it is in the increasing order of π*. The efficiency of protic ionic liquids in controlling the ΔH^0 for HCOOH and CH_3CH_2COOH is in the opposite order of π* which suggests the lower relevance of the electrostatic field effect in controlling the dissociation of acid. This implies the involvement of specific interactions in the dissociation of carboxylic acids. The polarity parameters which represent specific interactions are α and β, though, direct dependence either on the α or β in the dissociation of HCOOH and CH_3CH_2COOH is not revealed by the arrangements of protic ionic liquids. However, the dependence of the ΔH^0 on α or β can be explained in an alternate way.

Table 6.2.5: Polarity Parameters of Protic Ionic Liquids at 298.15 K.

ionic liquids	**[a]E_T^N**	**π***	**α**	**β**
[b][HmIm][HCOO]	56.0	1.10	0.81	0.81
[HPyrr][HCOO]	49.3	0.99	0.45	0.78
[HPyrd][HCOO]	61.4	0.98	1.25	0.88
[BMIm][HCOO]	51.4	1.17	0.46	0.68

[a]The uncertainty in the E_T^N values as reported was ± 0.04 [b]Ref [50].

It is proposed by several workers that in ionic liquids the hydrogen bond donor ability of cation (α) and hydrogen bond acceptor ability of anion (β) remains in equilibrium with eachother.[51,52] The resultant of these two determines the behavior of ionic liquid. Therefore, a solute will always experience the lesser affinity either towards the cation or anion than that predicted by the Kamlet-Taft parameters (α, β, π^*). In other words, α is partially reduced by β and *vice-versa*. Thus, in all ionic liquids, a competition exist between the α and β values in presence of solute.

In view of these counter-balanced interactions present in ionic liquids, the arrangement of different protic ionic liquids in affecting the ΔH^0 values should be correlated with the relative α and β values. The higher dissociation of carboxylic acids in protic ionic liquids is either due to the stabilization of proton (H^+) or due to the stabilization of conjugate base of acid.

In [HPyrd][HCOO], α is higher than β, thus the dissociation of HCOOH and CH_3CH_2COOH is controlled by α. In [HPyrr][HCOO], α is lower than β, hence dissociation of HCOOH and CH_3CH_2COOH is favored by β. In [HmIm][HCOO] both α and β are equal in magnitude therefore the least dissociation of carboxylic acids and consequently the higher ΔH^0 for HCOOH and CH_3CH_2COOH is observed in [HmIm][HCOO]. Hence, the arrangement of different protic ionic liquids based on the ΔH^0 for HCOOH and CH_3CH_2COOH is according to their ability to bind with carboxylic acids by specific interactions. Surprisingly, a different order of protic ionic liquids in the increasing order of their π^* values was noted effective in the dissociation of CH_3COOH. This indicates the involvement of Coulombic forces in the dissociation of CH_3COOH which seems highly improbable. The arrangement of protic ionic liquids for CH_3COOH in the increasing order of π^* value might be due to the higher dipole moment of CH_3COOH (1.74 D) than that of HCOOH (1.41 D) and CH_3CH_2COOH (0.63 D). The strong bond dipoles present in the CH_3COOH combine well with the Coulombic region created inside protic ionic liquids.

However, similar observations could not made for the aprotic ionic liquids; as except the 1-butyl-3-methylimidazolium formate ([BMIm][HCOO]) other ionic liquids *e.g.* 1-butyl-3-methylpyrrolidinium formate ([BMPyrr][HCOO]) and 1-butyl-3-methylpiperidine formate ([BMPyrd][HCOO]) were solid at room temperature. However, as can be seen from the polarity parameters for [BMIm][HCOO], α and β are small as compared to that of protic ionic liquids. A small difference in the α and β indicates the lower tendency of [BMIm][HCOO] towards the specific interactions with solute than that of protic ionic liquids. So, the polarity parameters of

[BMIm][HCOO] also supports the lower strength of carboxylic acids. Further investigations are required to explore the role of different protic and aprotic ionic liquids having similar cation/anion in the dissociation of weak acids.

6.2.4: Conclusions

In conclusion, we have compared the potential of protic and aprotic ionic liquids in the dissociation of HCOOH, CH_3COOH, and CH_3CH_2COOH measured by the Hammett acidity function. Protic ionic liquids were observed as promising candidates in the dissociation of carboxylic acids because of higher acidic strength than their aprotic counterparts. The greater dissociation of carboxylic acids in protic ionic liquids was noted to depend on the intensity of specific interactions between them. Activation energy of proton transfer ($E_{a,H+}$) further fortifies this view. Higher $E_{a,H+}$ for carboxylic acids was obtained in aprotic ionic liquid than protic ionic liquid lowers the possibility of specific interactions. Thermodynamic parameters (ΔH^0, ΔS^0), calculated by novel "indicator overlapping method", also signifies the participation of specific solute-solvent interactions in the dissociation of carboxylic acids. The ability of different protic ionic liquids as observed by ΔH^0 value in dissociating carboxylic acids was observed to depend on the relative hydrogen bond donor (α) and hydrogen bond acceptor (β) tendencies.

The observations drawn above will be useful in designing efficient media for weak acids. This will help in avoiding the use of corrosive acids for various applications. To the best of our knowledge this is the first report comparing the potential of protic ionic liquid and aprotic ionic liquid in the dissociation of carboxylic acids.

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"*Be a physical chemist, an organic chemist, an analytical chemist, if you will; but above all be a chemist*" – *Ira Remsen*

7: Diels-Alder Reaction in Protic Ionic Liquids: Trans-Dipolar Interactions are Dominant over the Hydrogen Bonding Effects

7.1: Introduction

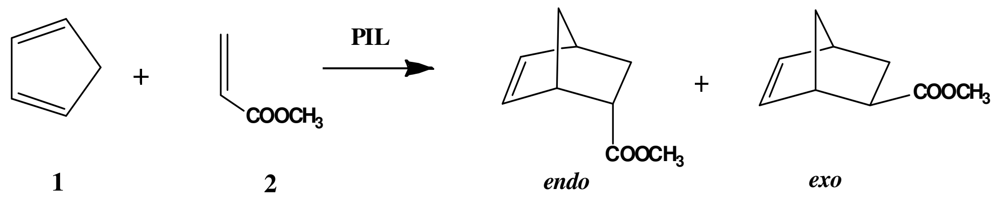
Specular effects of water on cycloaddition reactions, especially on the Diels-Alder reaction by Rideout and Breslow, have upsurged interest among chemists to explore water and other polar solvents as a medium.[1] The accelerating nature of water on the Diels-Alder reaction was attributed to their hydrophoboicity which brings non-polar molecule together into the close proximity. This observation has triggered an incresae in investigating the promoting role of water for several organic reactions.[2,3]

The strong emphasis on hydrophobicity in catalyzing the Diels-Alder reaction merely outshines other equally important factors like hydrogen bonding,[4,5] solvent pressure,[6] and solvent polarity[7]. The presence of a small amount of Lewis acid catalyst in water improves yield and selectivity.[8] The computational studies on Diels-Alder reaction suggest nearly similar contribution of the hydrophobicity and hydrogen bonding in the free energy of hydration ($\Delta_{\text{hyd}}G$).[9],[10]

Protic ionic liquids represent fascinating subclass of ionic liquid because of their extended network of hydrogen bonding similar to water.[11] Very high rate and selectivity is reported for the Diels-Alder reaction in $[EtNH_3][NO_3]$ because of the hydrogen bonding effects.[12] Later, chloroaluminate-based ionic liquids were explored as powerful media in promoting the kinetics of Diels-Alder reaction.[13] The kinetics of Diels-Alder reaction in viscous solvents, such as aprotic ionic liquids, have shown rate 10-times lower than that in water.[14] The higher viscosity of ionic liquids are observed to retards the translational and rotational motions of reactant molecules, therby lowering the rate of Diels-Alder reactions.[15]

In the present study, we address the relative importance of the hydrogen bond donor acidity (α), hydrogen bond basicity (β) and viscosity (η) on the rates and stereoselectivity of Diels-Alder reaction in Protic ionic liquid systems. Diels-Alder reaction between the cyclopentadiene (**1**) and methylacrylate (**2**) was carried out in protic ionic liquid systems as depicted in Scheme 7.1. The protic ionic liquids which were involed in this work are [HmIm][HCOO], [HPyrr][HCOO], [HPyrd][HCOO], [HmIm][HSO_4] and [HbIm][HCOO]. All protic ionic liquids were synthesiszed by the procedure mentioned in Chapter 4, Section 4.2.2.

Scheme 7.1: Reaction of Cyclopentadiene 1 with Methyl Acrylate 2



7.2: Experimental Section

7.2.1: Materials

A spectroscopic grade methanol was procured from Merck and absorbed moisture was freed by keeping with dehydrated molecular sieve overnight. Cyclopentadiene was obtained as dimerized dicyclopentadiene from Merck and was cracked into the monomer form before reaction and stored at freezing temperature of water. Methylacrylate was obtained from Sigma Aldrich and used after distillation.

7.2.2: Kinetic Measurements

In a standard kinetic run, the reaction was initiated by adding the freshly cracked cyclopentadiene **1** (1 M) into methyl acrylate **2** (1 M) and was allowed to equilibrate at 25 ^{O}C by Julabo, a constant temperarure bath, with accuracy ±0.01 K. The reaction progress was examined by GC (Varion CP-3800 Gas chromatograph) by withdrawing 1 ml of reaction mixture after a certain period of time followed by extraction with ether. The second order rate constant, k_2, was derived from the relative peak area of the product at different times.

7.2.3: Viscosity Measurements

Viscosity of protic ionic liquid systems are measured at 25°C by Brookfield (DV-III ULTRA) cone-plate viscometer at different rotational speed.

7.3: Results and Discussion

The conviction that ionic liquid decelerate the kinetics of Diels-Alder reaction can be investigated by exploring other useful properties such as hydrogen bond donor acidity, α and hydrogen bond accepter basicity, β.[7] The higher rate and selectivity for the Diels-Alder reaction in ionic liquid was obtained because of their hydrogen bonding capability than that of the molecular solvents. However, the moderate acceleration in the rate and selectivity was achieved in protic ionic liquids than that in water. Diels-Alder reaction between **1** and **2** is carried out in different protic ionic liquids and the endo/exo ratio, the k_2 values, Kamlet-Taft polarity parameters (α, and β), and viscosity of protic ionic liquids are given in Table 7.2.

The substantial increase in the endoselectivity and associated rate constants is reported by Welton *et al.* in ionic liquids having high α and low β.[8] Surprisingly, in protic ionic liquids, the endoselectivity was observed independent of the large α value. A very small endo/exo ratio was observed in [HmIm][HSO_4] and [HPyrd][HCOO] irrespective of their high α values. However, we have noted a linear correlation between the log (endo/exo) and α-β (difference between acidity and basicity) as shown in Figure 7.2.

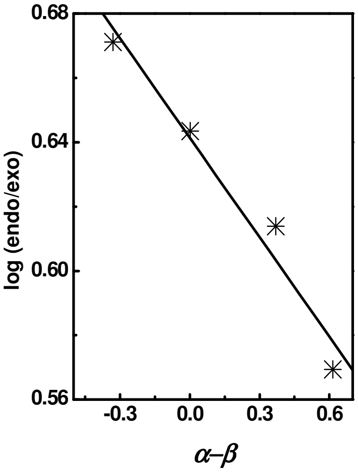


Figure 7.2: The log (endo/exo) versus α-β plot in protic ionic liquids.

This linearity is used as a tool to unravel other possible interactions related with endoselectivity. From Figure 7.2 it is evident that the endoselectivity in protic ionic liquids increases with β which shows a strong dependency on α.

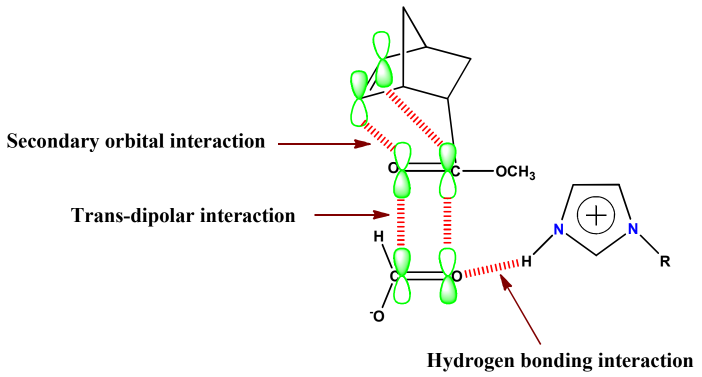
Table 7.2. Rate Constants (k_2) and endo/exo Ratios for the Reaction of 1 with 2 in Different Protic Ionic Liquids Along with Their Viscosity Values and Polarity Parameters (α, and β).

solvent systems	$10^5 \times k_2/M^{-1}\ s^{-1}$	endo /exo	α	β	η/cP
[HmIm][HCOO]	1.30	4.40	0.812	0.81	6.70
[HPyrr][HCOO]	0.29	4.69	0.45	0.78	9.55
[HPyrd][HCOO]	2.20	4.11	1.25	0.88	15.5
[HbIm][HCOO]	1.14	3.73	0.945	0.73	12.1
[HmIm][HSO_4]	0.22	3.71	1.225	0.61	406
[HPyrr][HCOO] + CH_3OH	0.43	4.94	1.11	0.33	4.28
[HmIm][HSO_4] + CH_3OH	11.0	4.4	1.21	0.49	88.4

This atypical behavior of anion in controlling endoselectivity is not solely due to β and probably arises due to the structural analogy of protic ionic liquid anion and dienophile. This analogy between anion and dienophile fortifies secondary orbital interaction in which dipoles orient themselves in trans-dipolar interaction for maximum stability. The strength of trans-dipolar interaction varies inversely with hydrogen bonding strength between cation and anion. In the current work, formate and bisulphate anions-based protic ionic liquids are used, which contain dipolar groups (C=O and S=O) and thus stabilizes secondary orbital overlap (Scheme 7.2). The higher endo/exo selectivity in formate anion-based protic ionic liquids than that of bisulphate anion-based protic ionic liquid is because of the suitable matching between the overlapping orbitals on dienophile and anion.

In order to establish the role of α and β on the endoselectivity, Diels-Alder reaction in [BMIm][N(Tf)$_2$] and [BMIm][OTf], which contain dipolar group (S=O), is analyzed in terms of the acidity and basicity of cation and anions, respectively. The higher endoselectivity in [BMIm][OTf] (4.5) as compared to [BMIm][N(Tf)$_2$] (4.3) corroborate well with their α-β value, instead of higher α for [BMIm][N(Tf)$_2$] than that of [BMIm][OTf].[8] However, the trans-dipolar interaction was absent in Br^-, BF_4^- and PF_6^- anions-based ionic liquids. In these ionic liquids, hydrogen bonding effect was operative in governing the endoselectivity similar to that in protic molecular solvents (Scheme 7.3). However, the noteworthy trans-dipolar interaction was not operative in binary mixture of [HmIm][HSO$_4$] and [HPyrr][HCOO] with methanol and hydrogen bonding effect was effective in endo/exo selectivity.

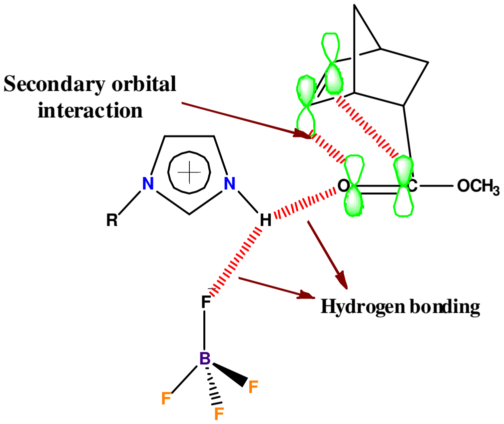
Scheme 7.2: Proposed Scheme for the Trans-Dipolar Interaction



The kinetics of Diels-Alder reaction reveals strong dependency on the viscosity of medium as shown by Firestone and Vitale and others.[16,17] It was observed that the k_2 and selectivity of Diels-Alder reaction in molecular solvents increased up to the viscosity 1.2 cP and above 12 cP a drop in the k_2 was evident.[18] In an endeavor to explore the possibility of Diels-Alder reaction in ionic liquid, Tiwari and Kumar have noted lower rate in ionic liquids than that in water.[14]

Asymmetric dienophile creates asynchronicity in the transition state of the Diels-Alder reaction and therefore increases its dependency on solvent and catalyst.[7,19] Protic ionic liquid acts as strong solvating media owing to multiple interactions including hydrogen bond, coulombic, and van der Waal forces[20] and therefore can be employed for executing the Diels-Alder reaction.

Scheme 7.3: Hydrogen Bonding Influence on Endoselectivity



However, the k_2 in protic ionic liquids were observed to vary with the change in α and viscosity. The kinetic result in [HmIm][HCOO] is taken as a reference because of its lower viscosity and negligible difference between α and β values. Compared to the [HmIm][HCOO], a lower k_2 is obtained in [HPyrr][HCOO]. The decrease in k_2 can be attributed to the dominance of β over α and increased viscosity (9.55 cP). Surprisingly, a modest increase in k_2 is obtained in [HPyrd][HCOO] than that of [HmIm][HCOO], despite very high α than β. This signifies the domination of viscous effects over α in governing the kinetics of Diels-Alder reaction. The lower k_2 in [HbIm][HCOO] can be justified in the similar manner. [HmIm][HSO_4] possess very high viscosity (406 cP) and its hydrogen bonding ability (α) is least influenced by anion (β). Even though, nearly 6-fold decrease in k_2 is obtained as compared to that of [HmIm][HCOO]. This strongly validates the viscous control over α in determining k_2 for the Diels-Alder reaction.

For conformity, k_2 in [BMIm][BF_4], [BMIm][PF_6], and [OMIm][PF_6] for the Diels-Alder reaction between **1** and **2** are analyzed in terms of α, β, and viscosity.[14] Higher k_2 in [BMIm][BF_4] ($4.5\text{x}10^{-5}$ M^{-1} s^{-1}) than that in [BMIm][PF_6] ($3.9\text{x}10^{-5}$ M^{-1} s^{-1}) was obtained regardless of the lower ability of cation (α =0.63 and β = 0.38) in former than that in later (α =0.63 and β = 0.19). The lower k_2 in [BMIm][PF$_6$] is due to the higher viscosity (450 cP) as compared to that of [BMIm][BF$_4$] (219 cP) which impedes the diffusion of **1** and **2** through it. Similarly, very high viscosity for [OMIm][PF$_6$] (866 cP at 20^{0}C) masks the hydrogen bonding ability of [OMIm]$^+$ (α =0.58 and β = 0.46) and therefore causes lower k_2 (3.1x10^{-5}). These discussions suggest that hydrogen bonding effect in a medium remain into play only when reactant molecules diffuse normally. A barrier in the diffusion of reactant molecules due to the high viscosity does not allow the hydrogen bonding between them.

Similarly, k_2 in an equimolar solution (x_{IL} = 0.5) of [HPyrr][HCOO] and [HmIm][HSO$_4$] with methanol (Table 7.2). Methanol acts as an excellent viscosity reducer and also has potential to tune the Kamlet-Taft parameters. The HBD acidity, HBA basicity and, viscosity of methanol are 1.05, 0.625 and 0.56 cP, respectively.[20]

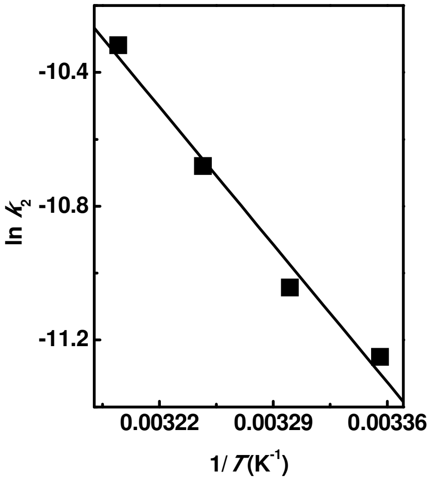


Figure 7.3. The ln k_2 versus 1/T plot for the reaction of **1** and **2** in [HmIm][HCOO].

The increased endo/exo ratio and k_2 for the Diels-Alder reaction in binary solutions can be ascribed to the simultaneous increase in α and decrease in viscosity. At x_{IL} = 0.5, k_2 slightly increases for [HPyrr][HCOO] despite the large increase in α even at viscosity 4.28 cP. Unlike [HPyrr][HCOO] which causes slight increase in k_2, [HmIm][HSO$_4$] at x_{IL} = 0.5 produces 50 fold enhancement in the k_2 as compared to that in the [HmIm][HSO$_4$] due to the decrease in viscosity from 406 cP to 88.4 cP.

The higher activation energy (E_a) required for carrying out the Diels-Alder reaction in protic ionic liquids than that of water also support lower rate in former than later. The activation energy (E_a) in [HmIm][HCOO] was obtained as 48.89 kJ mol^{-1}.The higher activation barrier for the Diels-Alder reaction in [HmIm][HCOO] (Figure 7.3) than that in water (E_a = 38.6 kJ mol^{-1}) albeit of the similar hydrogen bonding ability confirms the intervention in catalytic performance of protic ionic liquids. The higher E_a in protic ionic liquids indicates more difficulty in the diffusion of reactant molecules due to their large viscosity than that of water (η = 0.894 cP).

7.4: Conclusions

In conclusion, we have observed an unusual behavior of the protic ionic liquid anions on the selectivity of the Diels-Alder reaction. The structural analogy between ionic liquid anion and dienophile was unnoticed till the present work and is accounted for consolidating the secondary orbital interaction through the trans-dipolar interaction and an increase in the endoselectivity. The anomalous behavior of anion on governing the endoselectivity was observed in other ionic liquids, but was absent in BF_4^- and PF_6^- anions-based ionic liquids. The lower rate constant in protic ionic liquids than that in the water makes them inappropriate media for the Diels-Alder reaction. The diffusion barrier in protic ionic liquid retards the movement of reactant molecules towards the hydrogen bonding sites in medium.

7.5: References

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"*I think and think for month and years. Ninety-nine times, the conclusion is false. The hundredth time I am right.*" – *Albert Einstein*

8: Conclusions

The work presented in the current thesis enumerates the physico-chemical properties of protic ionic liquids and their implication on the Hammett acidity of carboxylic acids and kinetics of the Diels-Alder reaction. To carry out these investigations, a series of protic ionic liquids with different combinations of cations and anions were prepared with their possible effect on physico-chemical properties. The "green approach" was strictly employed by adopting the solventless condition during the synthesis of protic ionic liquids. The relevance of the results for the environmentally benign solvent systems is duly emphasized from the experimental and theoretical perspectives. The solvent property/polarity of protic ionic liquids is measured by the thermosolvatochromic method, which observes change in the electronic transition upon the variation of polarity of solvent at different temperatures. The thermosolvatochromic response in two classes of protic ionic liquids, namely, 1-methylimidazolium- and 1-butylimidazolium cation with bisulphate, formate, acetate, and propionate anions were similar and polarity was observed to be independent of the temperature change from 298 to 353 K. This suggests a strong interaction between the protic ionic liquid and probe molecule that cannot be weaken within the experimental temperature range. However, a strong hold of the hydrogen bond acceptor basicity (β) of anion on the polarity, $E_T(30)$ was observed. The anion with higher β value competes with dye molecule for the hydrogen bonding interactions present on cation. Thus, the strongly basic anion binds with the hydrogen bond donor sites present on cation and inhibits the hydrogen bonding interaction with indicator and consequently polarity decreases. The thermosolvatochromic study also assists in the prediction of intermolecular solute-solvent interactions in protic ionic liquids. The temperature-independent polarity of protic ionic liquids makes them appropriate media for those processes where constant polarity is required at elevated temperature.

A novel "indicator overlapping method" is employed to measure the Hammett acidity, H_0 of HCOOH, CH_3COOH, and CH_3CH_2COOH in protic ionic liquids, water, and their binary mixtures. This method observes the variation of any physical property upon protonation/deprotonation. The Hammett scale of acidity measurements are used to extend the pH scale on either side. The Hammett acidity of carboxylic acids in protic ionic liquids was different than those of water. The reversal in the order and magnitude of Hammett acidity in these media was independent from their structural and electronic properties as a linear relation was observed between the Hammett acidity of all carboxylic acids in these media. The higher acidic strength of carboxylic acids in protic ionic liquids is decided by the interaction between the protic ionic liquid cation and conjugate anion of acid according to the hard-soft acid-base (HSAB) principle.

Prompted by the similarity between protic ionic liquids and water the Hammett acidity of carboxylic acids is also measured in their binary mixtures. For all carboxylic acids, non-ideality in the Hammett acidity was observed as the composition of binary mixture varied. For HCOOH, a positive deviation was noted in all protic ionic liquids. The extent of deviation lowered as the concentration of acid increased in the binary mixture. For CH_3COOH and CH_3CH_2COOH, in all protic ionic liquids, a positive deviation at lower concentration of acid became negative as the concentration of acid increased. The Hammett acidity measurement in binary mixture clearly indicates the presence of pseudo-solvent and synergetic effect, which varied with the concentration of acid.

The effect of ionic strength and temperature on the Hammett acidity of carboxylic acids is investigated in protic ionic liquid and in highly aqueous solutions of protic ionic liquids. Salts generally affect the solubility of indicator and thus cause variation in the Hammett acidity. However, different behavior of salt ions on the Hammett acidity of carboxylic acid was noted with the increasing concentration of protic ionic liquid in water. This was attributed to the interfering nature of protic ionic liquid ions against salt ions only at lower concentration of protic ionic liquid ($x_{IL} = 0.02$). At higher concentration of protic ionic liquids, *i.e.* $x_{IL} = 0.02$ and 0.05, opposing behavior of protic ionic liquid ions to that of salt ions was vanished. The ability of salt ions in promoting the Hammett acidity was seen different from their rank in the Hofmeister series. The speciation method was employed to measure the concentration of different ionic species in aqueous solution of protic ionic liquids.

The ordering of ions according to the Hofmeister series was established when the relative Hammett acidity was correlated with the "free" ion concentration rather than the total ion concentration of salt. Apart from this, the Hammett acidity using binary salt mixtures in aqueous protic ionic liquid was also measured and the Young's cross square rule (YCSR) was validated.

Thermal effect on the Hammett acidity is because of the higher dissociation of acid and greater availability of indicator. The higher strength of carboxylic acids in protic ionic liquids than those of aprotic counterpart is explained in terms of the thermodynamic parameters, which originates owing to the solute-solvent interactions. Thermodynamic activation parameters (ΔH and ΔS) for the dissociation of carboxylic acids in ionic liquids were obtained by using the van't Hoff equation. Thermodynamic parameters are used as a tool to probe the solute-solvent interaction between ionic liquid and carboxylic acids. The secondary interactions between solute and solvent were noted operative in the dissociation of carboxylic acid. A small difference in thermodynamic parameters for the dissociation of carboxylic acids in protic and aprotic ionic liquids though indicates similar strength of carboxylic acids in these media. However, very large activation energy of proton transfer in aprotic ionic liquids than that of protic ionic liquid points out partial degree of protonation of indicator. This is further supported by analyzing the results by using the polarity parameters of ionic liquids.

The influence of the protic ionic liquids on C-C bond forming reaction was investigated by monitoring the kinetics of Diels-Alder reaction between cyclopentadiene and methylacrylate. The lower rate and stereoselectivity was obtained for the Diels-Alder reaction in protic ionic liquids despite their acidic nature and low viscosity. The rate constant of the Diels-Alder reaction was observed to increase with the decreasing viscosity and increasing acidity. *Albeit* of the higher acidity, a decreasing endo/exo ratio was observed in protic ionic liquids. This unusual behavior of protic ionic liquids was explained by employing the polarity parameters. The hydrogen bond donor acidity of protic ionic liquid cation was reduced by the hydrogen bond acceptor basicity of anion and therefore lower stereoselectivity was seen in these Coulomb media.

Appendix A

NMR Spectra of Ionic Liquids

1. The NMR spectra of pure and dried ionic liquids are recorded before employing them as reaction media are as:

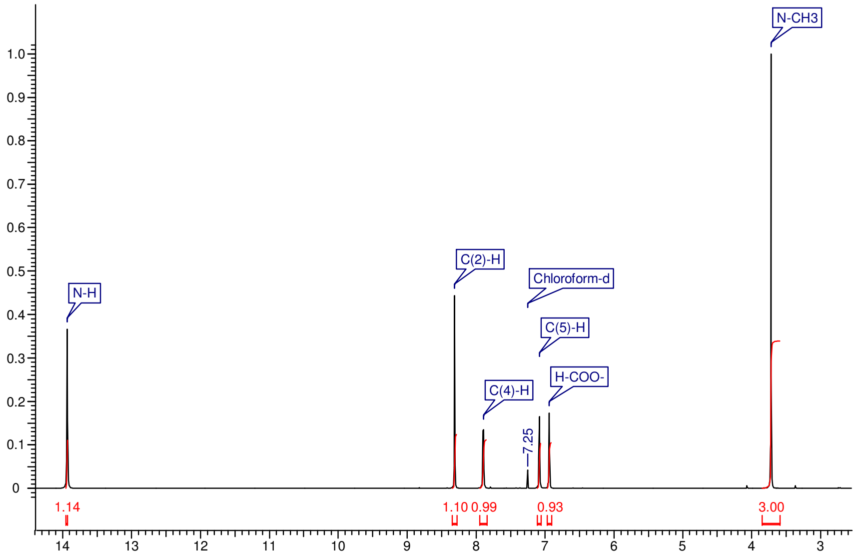


Figure A1. NMR spectra of 1-methylimidazolium formate, [HmIm][HCOO].

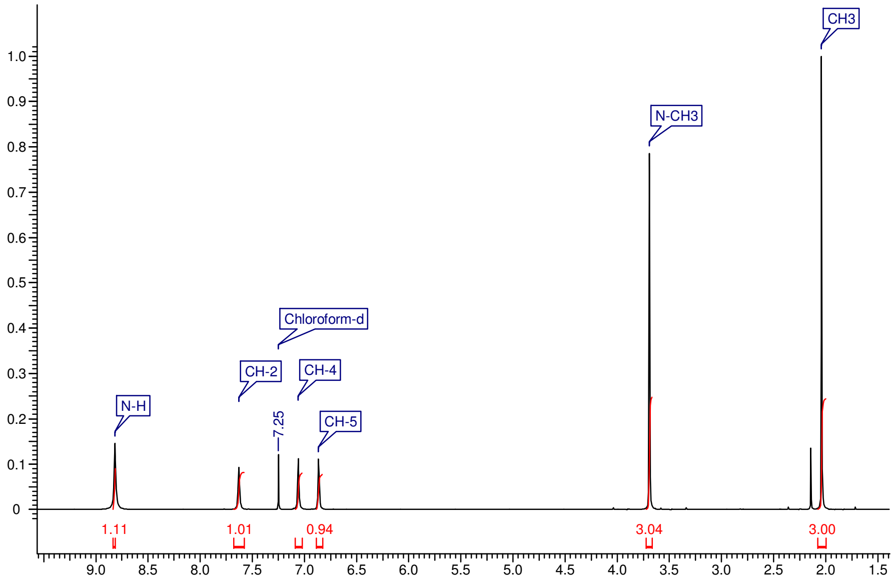


Figure A2. NMR spectra of 1-methylimidazolium acetate, [HmIm][CH_3COO].

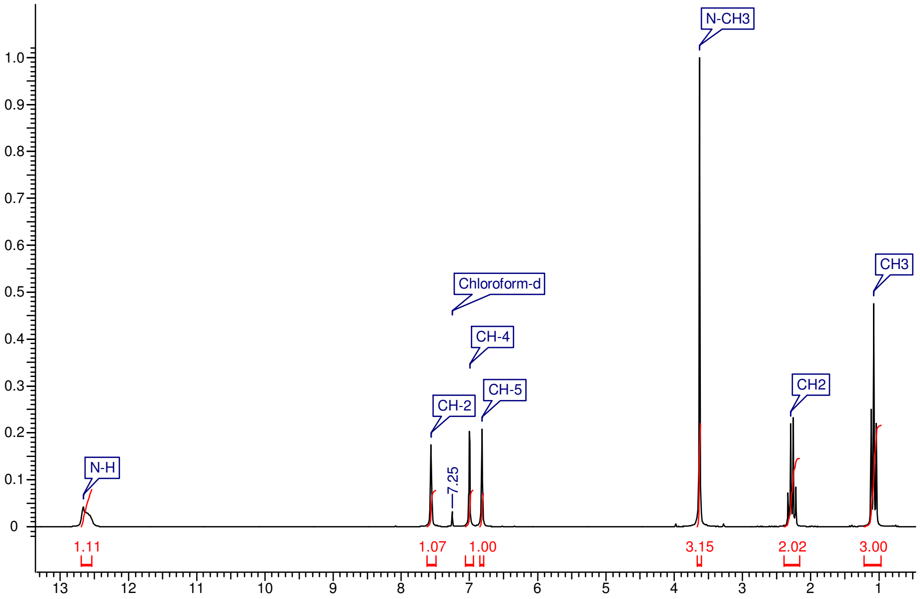


Figure A3. NMR spectra of 1-methylimidazolium propionate, [HmIm][CH_3CH_2COO].

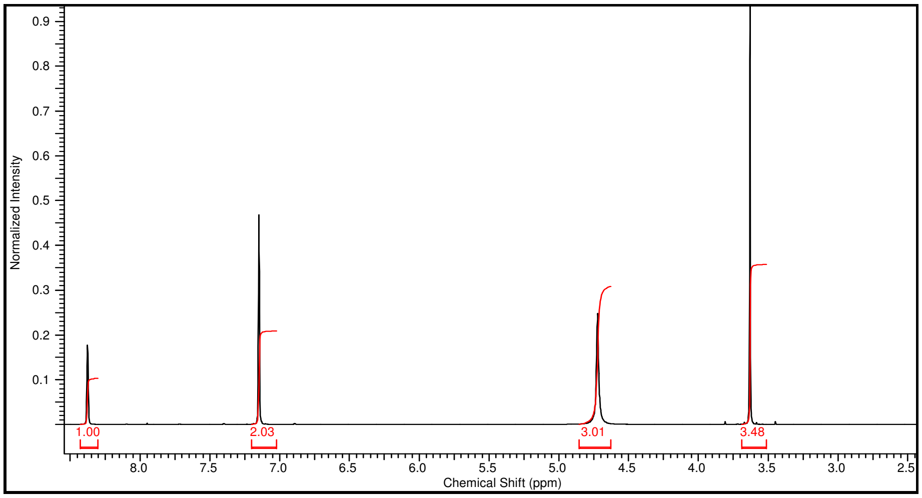


Figure A4. NMR spectra of 1-methylimidazolium bisulphate, [HmIm][HSO_4].

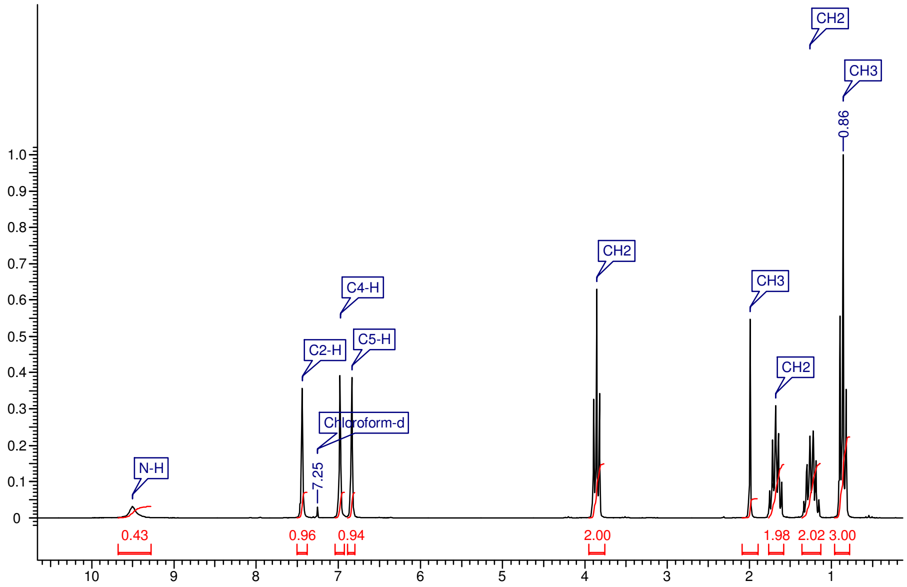


Figure A5. NMR spectra of 1-butylimidazolium acetate, [HbIm][CH_3COO].

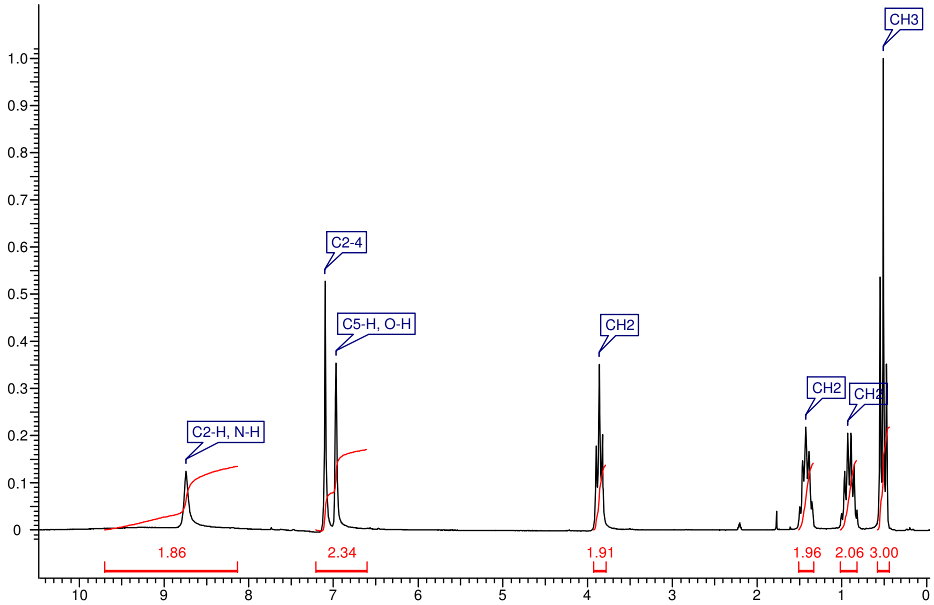


Figure A6. NMR spectra of 1-butylimidazolium bisulphate, [HbIm][HSO_4].

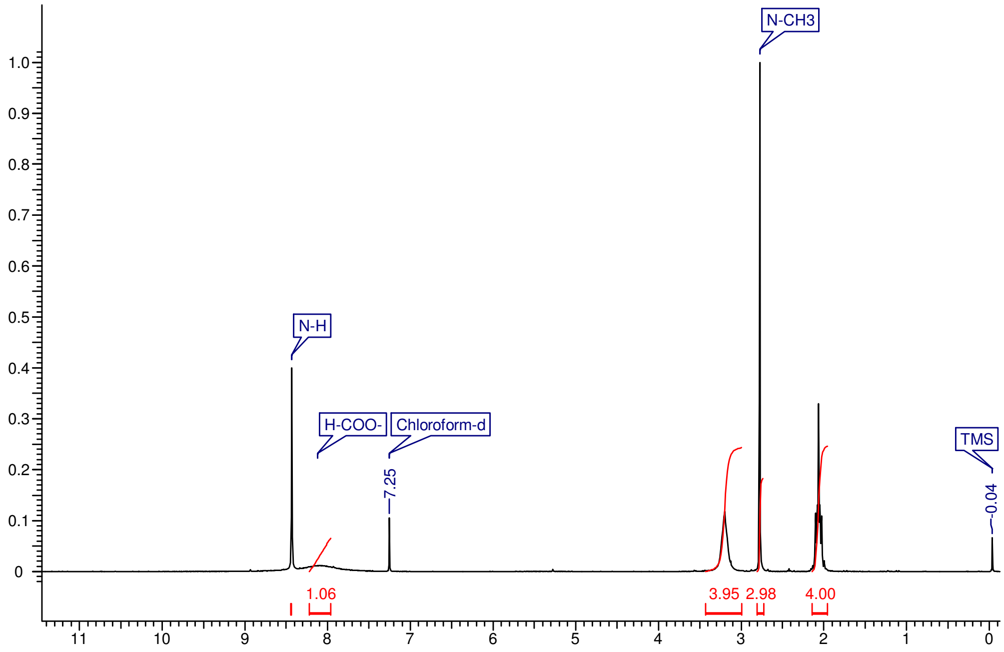


Figure A7. NMR spectra of 1-methylpyrrolidinium formate, [HPyrr][HCOO].

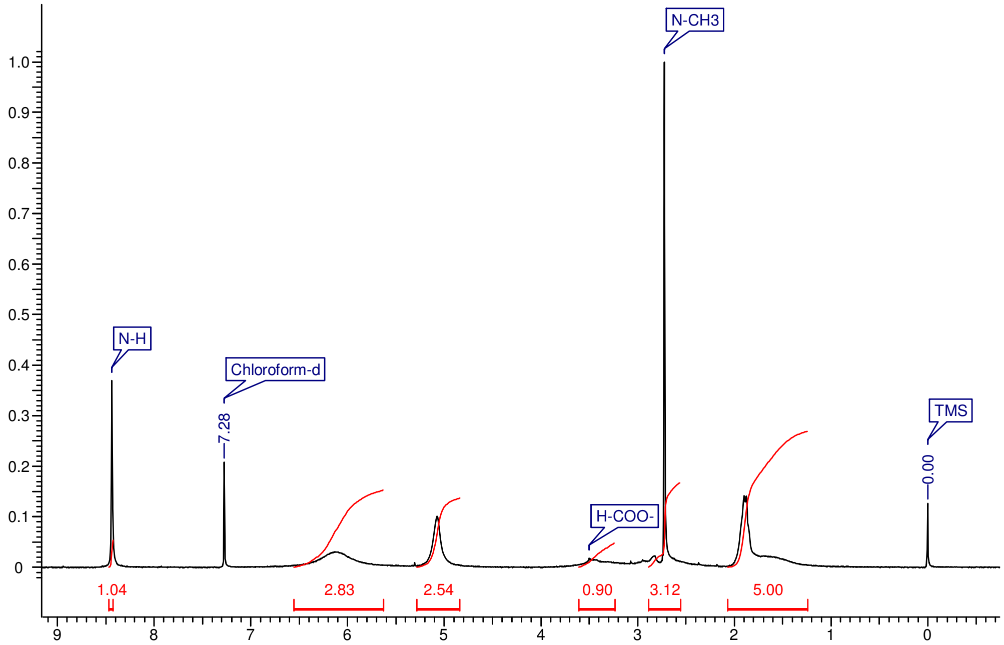


Figure A8. NMR spectra of 1-methylpiperidinium formate, [HPyrd][HCOO].

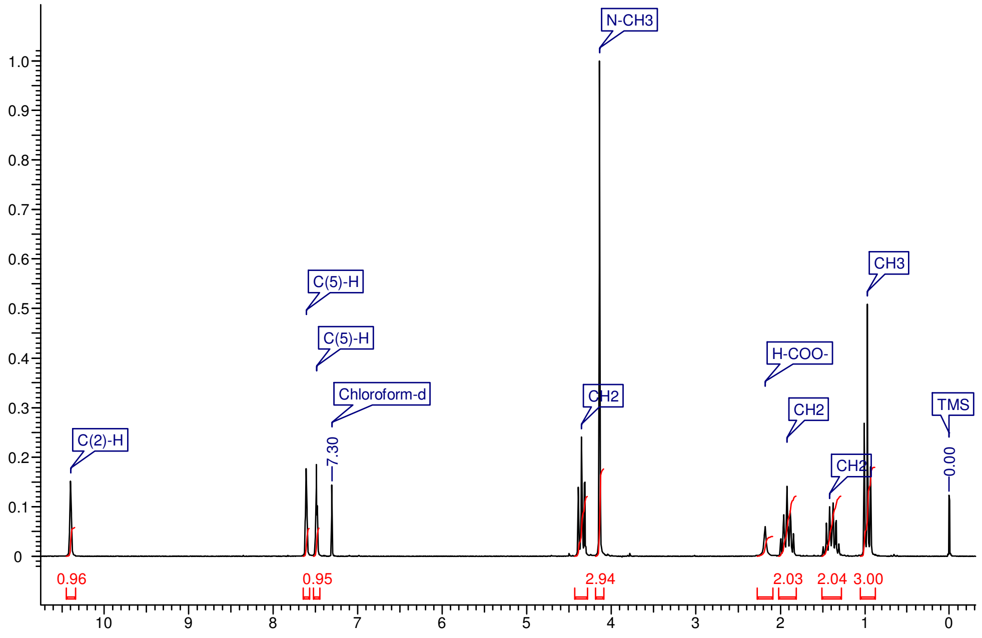


Figure A9. NMR spectra of 1-butyl-3-methylimidazolium formate, [BMIm][HCOO].

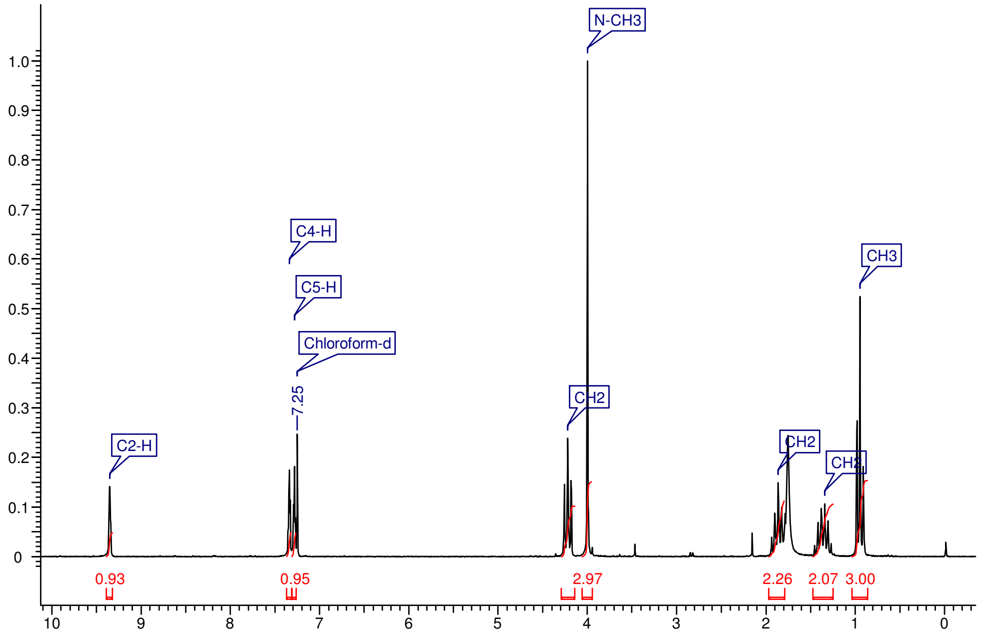


Figure A10. NMR spectra of 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIm][BF_4].

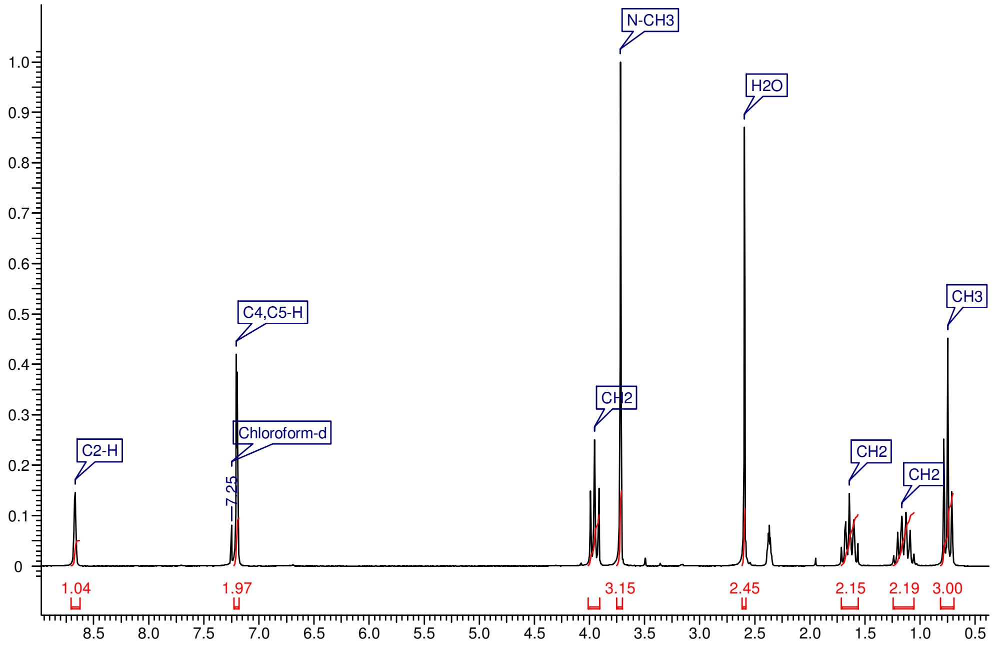


Figure A11. NMR spectra of 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIm][PF_6].

Appendix B

Gas Chromatography Parameters

B.1] GC Parameters for Kinetic Analysis of Diels-Alder Reactions:

The following parameters were set for a typical kinetic analysis:

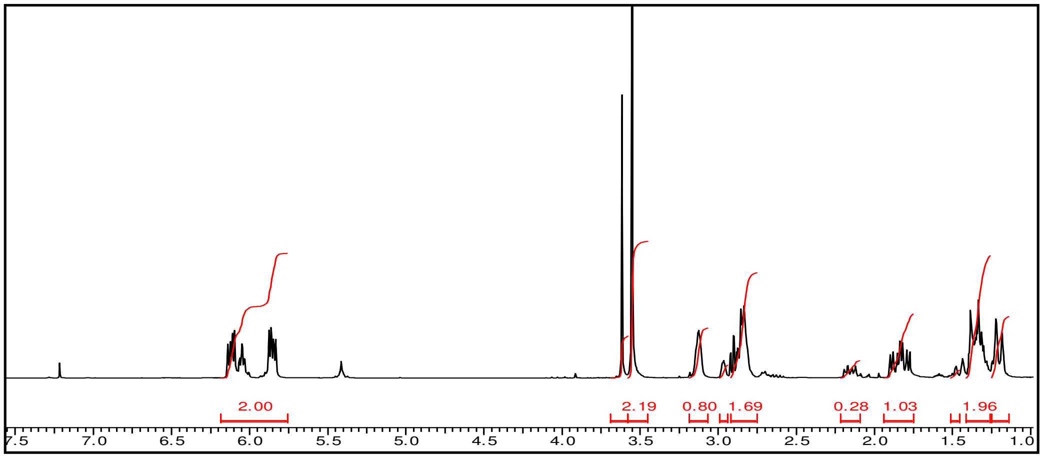
Column make	CP SIL 5CB
Column length	15m
Internal diameter	0.25 mm
Film thickness	0.25-micron
Flow rate	0.9 ml/min of nitrogen
Injector temperature	200^{o}C
Detector temperature	250^{o}C
Total run time	20.66 min (Hold at 70^{o}C for 5 min, ramp at 79^{0}C and then maintain at 180^{o}Cfor 5 min.)
Internal Standard (IS)	Chlorobenzene

Typical Retention Times of the compounds analyzed:

Compound	**Retention time (min)**
Chlorobenzene **(IS)**	1.824
3(a)	7.869
3(b)	8.123

Note: The GC method was calibrated with respect to the product concentrations using pure samples of the products. The amount of product formed as a function of time gave the extent of the reaction.

B.2] NMR spectra of the product cyclopentadiene and methylacrylate: methyl bicyclo[2.2.1]hept-5-ene-2-carboxylate:



Appendix C

List of Publications

1. Shashi Kant Shukla, Nageshwar D. Khupse, Anil Kumar
Do Anions Influence the Polarity of Protic Ionic Liquids?
Phys. Chem. Chem. Phys. **2012**, *14*, 2754-2761.

2. Shashi Kant Shukla, Anil Kumar
Probing the Acidity of Carboxylic Acids in Protic Ionic Liquids, Water, and Their Binary Mixtures: Activation Energy of Proton Transfer.
J. Phys. Chem. B **2013**, 117, 2456-2465.

3. Shashi Kant Shukla, Anil Kumar
Do Protic Ionic Liquids and Water Display Analogous Behavior in Terms of Hammett Acidity Function?
Chem. Phys. Lett. **2013**, *566*, 12-16**.**

4. Shashi Kant Shukla, Anil Kumar
Polarity Issues in Room Temperature Ionic Liquids.
Clean Techn Environ Policy, **2015**, *17*, 1111-1116.

5. Shashi Kant Shukla, Anil Kumar
Dissociation of Equimolar Mixtures of Aqueous Carboxylic Acids in Ionic Liquids: Role of Specific Interactions
J. Phys. Chem. B **2015**, *119*, 5537-5545.

6. Shashi Kant Shukla, Anil Kumar
How Does Speciation Assist in Revalidating the Hofmeister Series?
Manuscript under preparation

7. Shashi Kant Shukla, Anil Kumar
Kinetics of Diels-Alder Reaction in Protic Ionic Liquids: Dominance of Viscosity Effects over Catalytic Effects.
Manuscript under preparation

8. Vijay Beniwal, **Shashi Kant Shukla**, Anil Kumar

Solvent Polarity: How to Convert Non-ideality to Ideality in the Liquid Mixtures using a Pseudo-solvent Methodology?

Manuscript under preparation

Appendix D

Posters and Oral Presentations

1. Poster presented at “13th CRSI National symposium in chemistry and 5th CRSI-RSC Joint symposium in chemistry” held at NISER Bhubaneswar (2011)

2. Poster presented at “1st CRSI Zonal meeting (2011)” held at NCL Pune

3. Poster presented at “15th CRSI National symposium in chemistry and 7th CRSI-RSC Joint symposium in chemistry” held at BHU Varanasi (2013)

4. Poster presented at “16th CRSI National symposium in chemistry and 8th CRSI-RSC Joint symposium in chemistry” held at IIT Mumbai (2014)

5. Poster presented at “National Science Day”, NCL Pune (2011, 2012, 2013, 2014)

6. Oral presentation at “2nd International Workshop on, “*Ionic Liquids: Alternative Benign Materials for Renewable Energy and Its Applications*” between 16-17th January, 2013 held at CSIR-NCL, Pune 411008.”

Erratum

Erratum

Erratum