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Comparative Study of Anilinium based Ionic liquids

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Abstract

Green chemistry is not an emerging trend but a reality owing to its applications. Green chemistry is a chemical philosophy, encouraging the design of products and processes that reduce or eliminate the use and generation of hazardous substances. Ionic liquids have emerged as possible substitutes for volatile organic solvents and have found many applications in a variety of research area since they are green solvents. Anilium based ionic liquids are prepared and their characteristics like solubility, conductivity and interactions with other substances are measured and used in certain organic synthesis giving higher yield than other traditional solvents.

Keywords - Ionic liquids,solubility,conductance,organic synthesis

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1.Introduction

Most widely used solvents for modern chemical reaction and material synthesis are organics that have potential pollution and toxic implications. Minimizing pollution has become a major concern for chemistry industry. In recent years , ionic liquids have gained a great deal of both academic and industrial attention worldwide as a new class of compounds for a potential effective green replacement of conventional organic solvents for long lasting human society(1).Ionic liquids also referred to “neoteric solvents ”and “designer solvents” which are first introduced in chemical applications in the middle and late 1990’s.(2). An ionic liquid is a liquid that contains only ions .ILs generally consist of bulky, non symmetrical organic cations such as imidazolium, pyrrolidinium,pyridinium, ammonium or phosphonium and numerous different inorganic or organic anions such as tetra fluoroborate and bromide anions(3).The cation and anion present in the ILs are designed so that the resulting salts cannot pack compactly. As a result, Ils do not easily crystallize and remain liquid through a wide range of temperatures.ILs are good solvents for a broad spectrum of inorganic,organic and polymeric materials and are immisible with numerous organic solvents.ILs have ionic interactions (mutual electrostatic or repulsion of charged particles) which makes them very miscible with polar substances.

ILs are generally colorless liquids with relatively high viscosities. They exhibit very low vapour pressure under ambient conditions and thus are non-volatile.The variation of viscosity of pure ionic liquids changes with a variation in the structure of ionic liquids. The effect of cation is smaller as compared to anion effect(4)..The alkyl ammonium based ionic liquids exhibit a higher viscosity than the imidazolium based ILs with the same anion(5).The increase in the vander Waal's interactions due to the presence of a long alkyl chain leads to higher viscosities(6). The decrease in the viscosity depends on the solvent added and the extent of resulting dissociation of ionic liquids into ions.

The commonly used ILs are polar solvents having polarity greater than those of solvents like acetone, dimethyl sulfoxide etc but less than those of water and short chain alcohols(7-9). Most of the ILs are stable at 400oC and above. The thermal decomposition depend on the nature of anion rather than of cation(10).

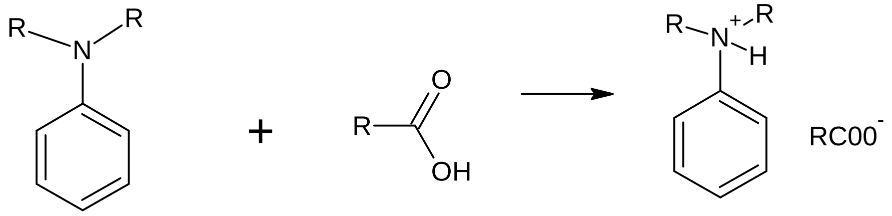
ILs can also be designed to solubilize either polar or non polar molecules. The solubility of ILs in water depends on the nature of the anion, temperature, and the length of the alkyl chain on the organic cations. The hydrophilic/hydrophobic behavior is important for the salvation properties of ILs as it is necessary to dissolve reactants, but it is also relevant for the recovery of products by solvent extraction(11).

ILs act as potential replacements for the conventional volatile, environmentally harmful conventional molecular solvents used in catalytic and organic reactions such as Diels-Aider, Bails-Hillman, Heck reaction, esterification, isomerization and many coupling reactions(12-13).

Material and Methods

2.1 Synthesis

The present study involves the synthesize of Anilinium based ILs using bases like various substituted aniline and acids that include weak and strong acids of both organic and inorganic by taking 1:1 molar ratio in a simple metathesis method.



R-H,CH_3 R-Alkyl, Aryl Anilinium based ILs

2.2 Solubility

The above prepared Anilinium based ILs are tested for selected 24 substrates like urea, thiourea,acetanilide,nitro benzoic acid,benzophenone,diphenyl amine,S-benzylthiouronium chloride,1-naphthol,dextrose,sucrose,naphthalene,2,4 dinitro phenylhydrazene,phthalic anhydride,benzamide,1,4 dichloro benzene,m-dinitro benzene,benzene,cyclohexanone,amyl alcohol,phenyl hydrazine hydrochloride,8-hydroxy quinoline,phenolphthalein,rosaniline hydrochloride,semicarbazide hydrochloride to find out their solubility and showed best solubility report.

Results and Discussion

3.1 Conductance

The conductance of Anilinium based ionic liquids and 10% solutions of various substrates(above mentioned 24 substrates like Urea, Thiourea,Acetanilide,Nitro benzoic acid,Benzophenone,Diphenyl amine etc.) are measured separately using ELICO conductivity meter. The results are shown in tables 1&2.From the results it is noted that Anilinum formate shows the highest conductance when compared to other Anilinium based ILs and it is found that the solutions of various substrates in Anilinum formate shows highest conductance than in other Anilinium based ionic liquids.

Table .1 CONDUCTANCE OF VARIOUS ANILINIUM BASED IONIC LIQUID

S.No	Cation	Anion	Anilinium based Ionic liquids	Conductance (mmho)
1.	Aniline	Formic acid	Anilinium formate	13.10
2	Aniline	Acetic acid	Anilinium acetate	2.03
3.	Aniline	Hydrochloric Acid	Anilinium hydrochlorate	12.45
4.	Aniline	Tri ChloroAcetic acid	Anilinium trichloroacetate	1.30
5.	Aniline	Benzoic Acid	Anilinium benzoate	0.09
6.	N,NDimethyl Aniline	Tri ChloroAcetic acid	N,N dimethyl anilinium trichloro acetate	2.10
7.	N,NDimethyl Aniline	ChloroAcetic acid	N,N dimethyl anilinium chloro acetate	1.40
8.	N,NDimethyl Aniline	Acetic acid	N,N dimethyl anilinium acetate	0.07
9.	N,NDimethyl Aniline	Benzoic Acid	N,N dimethyl anilinium benzoate	0.03
10.	N-Methyl Aniline	Tri ChloroAcetic acid	N- methyl anilinium trichloro acetate	5.20
11	N-Methyl Aniline	ChloroAcetic acid	N- methyl anilinium chloro acetate	3.20
12	N-Methyl Aniline	Acetic acid	N-methyl anilinium acetate	1.48
13.	N-Methyl Aniline	Benzoic Acid	N -methyl anilinium benzoate	0.05

Table.2. Conductance of various substrates in various Anilinium based ionic Liquids

SUBSTRATE		OBSERVED CONDUCTANCE (mmho)													
		AF	AA	AHC	ATCA	AB	DMTCA	DMACA	DMAA	DMAB	MATCA	MACA	MAA	MAB	H_2O
01	Urea	7.98	1.30	6.45	1.09	0.02	1.90	1.01	-	-	3.31	2.22	1.04	-	0.15
02	Thiourea	7.76	1.21	5.60	0.90	0.01	1.65	0.90	-	-	2.70	1.23	0.81	-	0.22
03	Acetanilide	5.26	1.01	3.20	0.20	0.01	1.38	0.75	-	-	1.82	1.98	0.21	-	0.05
04	Nitro benzoic acid	5.52	1.07	3.65	0.30	0.02	1.50	0.02	-	-	1.90	1.02	0.41	-	0.04
05	Benzophenone	5.87	1.12	3.90	1.00	0.07	1.45	0.03	-	-	1.45	1.10	0.98	-	0.03
06	Diphenyl amine	5.38	1.09	2.70	0.10	0.03	0.09	0.02	-	-	1.25	1.33	0.11	-	0.07
07	S- Benzylthiouronium chloride	4.27	0.80	2.60	0.97	0.02	0.40	-	-	-	1.31	1.96	0.77	-	0.16
08	1-Naphthol	3.52	0.78	2.30	0.23	-	1.20	0.02	-	-	0.95	0.01	0.32	-	0.07
09	Dextrose	2.79	0.81	1.10	0.10	-	1.30	-	-	-	0.75	0.02	0.21	-	0.03
10	Sucrose	4.29	1.20	2.70	0.50	-	0.70	-	-	-	2.32	0.045	0.40	-	0.32
11	Naphthalene	3.30	0.79	1.40	0.655	0.01	0.40	0.01	-	-	1.21	0.23	0.71	-	0.04
12	2,4 dinitro phenylhydrazene	3.94	0.87	1.20	0.35	-	1.10	-	-	-	1.03	0.38	0.41	-	0.18
13	Phthalic anhydride	5.50	1.23	2.40	0.75	-	1.16	0.75	-	-	1.98	0.52	0.81	-	0.04
14	Benzamide	4.04	1.04	2.10	0.28	0.05	0.98	0.50	-	-	2.01	0.26	0.31	-	0.03
15	1,4 dichloro benzene	3.88	1.01	1.50	0.33	-	0.78	0.70	-	-	1.09	0.31	0.37	-	0.12
16	m-dinitro benzene	3.82	0.66	1.80	0.30	0.03	0.45	0.90	-	-	1.54	0.09	0.31	-	0.09
17	Benzene	8.12	4.60	7.20	1.02	-	1.80	0.01	-	-	3.87	1.31	1.02	-	0.06
18	Cyclohexanone	8.27	4.30	6.90	1.04	-	1.45	0.01	-	-	3.43	1.45	1.09	-	0.05
19	Amyl alcohol	3.58	1.34	1.30	0.40	0.03	0.09	0.03	-	-	0.09	0.21	0.31	-	0.03
20	Phenyl hydrazine hydrochloride	5.67	1.79	4.20	0.97	0.01	1.11	-	-	-	1.63	0.32	0.77	-	4.69
21	8-hydroxy quinoline	4.49	1.12	3.20	0.80	0.05	1.01	-	-	-	1.07	0.96	0.91	-	0.06
22	Phenolphthalein	4.34	1.10	3.60	0.34	-	0.55	0.01	-	-	1.72	0.02	0.41	-	0.04
23	Rosaniline hydrochloride	4.77	1.65	3.30	0.78	0.03	0.80	0.02	-	-	1.87	1.02	0.69	-	3.72
24	Semicarbazide hydrochloride	6.94	2.13	5.20	0.98	0.06	1.75	-	-	-	2.76	1.21	1.09	-	5.73

AF-Anilinium formate

AA-Anilinium acetate

AHC-Anilinium hydrochlorate

ATCA-Anilinium trichloroacetate

AB-Anilinium benzoate

DMACA-N,N dimethyl anilinium chloro acetate

DMATCA-N,N dimethyl anilinium trichloro acetate

DMAA - N,N dimethyl anilinium acetate

DMAB - N,N dimethyl anilinium benzoate

MATCA - N- methyl anilinium trichloro acetate

MACA - N- methyl anilinium chloro acetate

MAA - N-methyl anilinium acetate

MAB -N -methyl anilinium benzoate

Spectroscopic Studies

3.2 Electronic Spectra

The UV Visible spectra is exclusively recorded for the ionic liquid AF using the Jasco (V-530) Ultra violet/visible spectrophotometer and also for various compounds in various solvents and in Anilinium formate (IL). The values are given in table 3 and the spectra are presented in figure 1-10.

While proceeding, it is found that the substance which is present in ILs exhibit absorption enormously increases comparing to other solvents. This difference or sudden hike in absorption may be due to the Vander Waal's interaction of the long alkyl chain present in the ILs.

Table.3 **UV-VISIBLE ANALYSIS OF COMPOUNDS IN VARIOUS SOLVENTS AND IN AF(IL)**

COMPOUND	Λmax (nm)	
	Various Solvents	AF(IL)
Benzophenone	252 (Ethanol)	500,637,739,880
2,4 dinitro benzene	297 (Heptane)	444
Acetanilide	240 (Ethanol)	502,742,877
Amyl alcohol	217 (Petrolium ether)	445,499,739
Diphenylamine	218 (Heptane)	507
Urea	270 (Ethanol)	501,741
Semicarbazide hydro chloride	210 (Heptane)	465
Phenolphthalein	310 (Petrolium ether)	505
S-benzylthio uranium chloride	230 (Petrolium ether)	454
Citric acid	219 (Heptane)	452

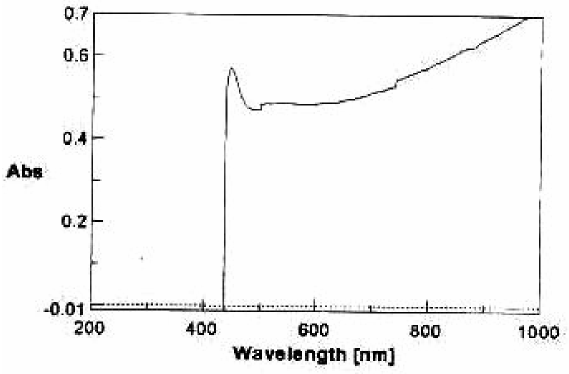


Fig 1UV–Visible spectrum of Amyl alcohol in AF

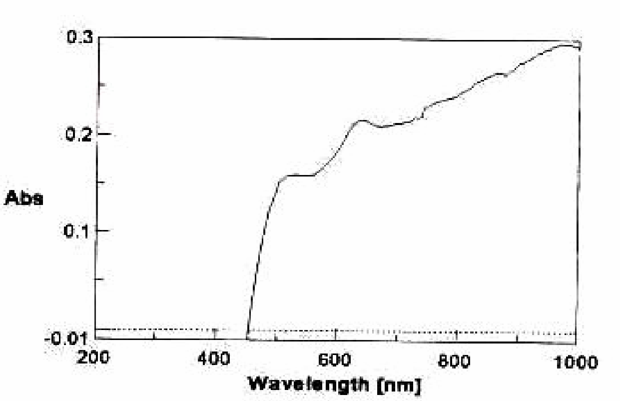


Fig 2 UV–Visible spectrum of Benzophenone in AF

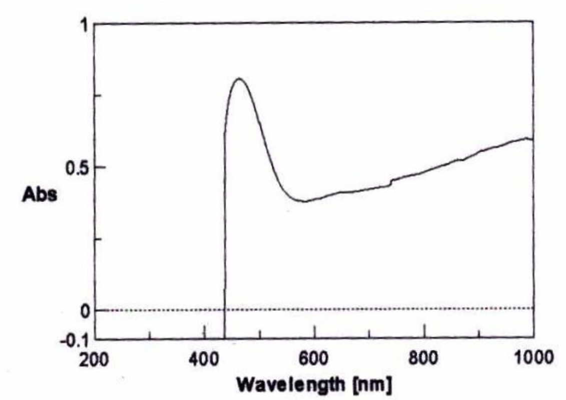


Fig .31 UV – Visible spectrum of Semicarbazide hydrochloride in AF

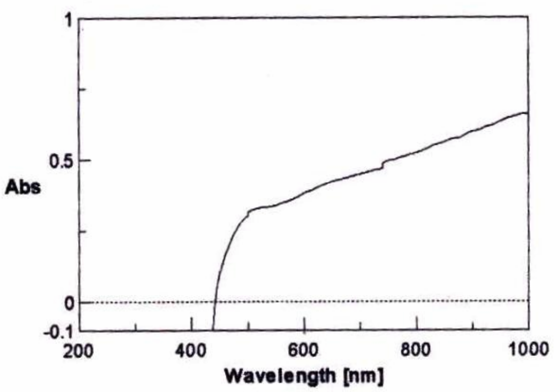


Fig . 4 UV – Visible spectrum of Urea in AF

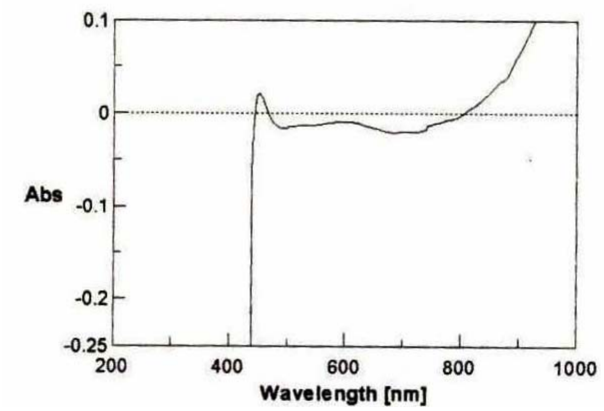


Fig . 5 UV – Visible spectrum of Citric acid in AF

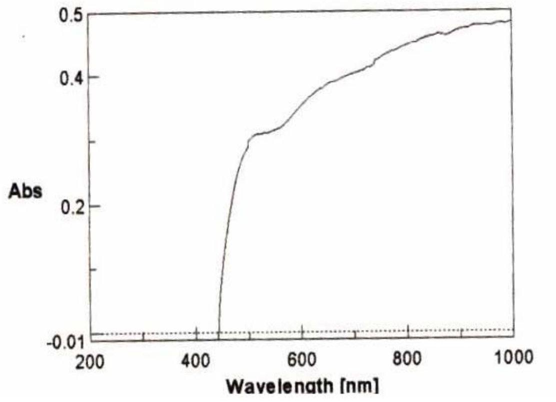
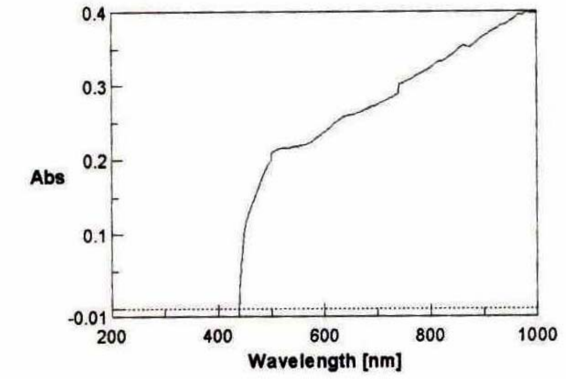


Fig . 6 UV – Visible spectrum of Diphenalamine in AF



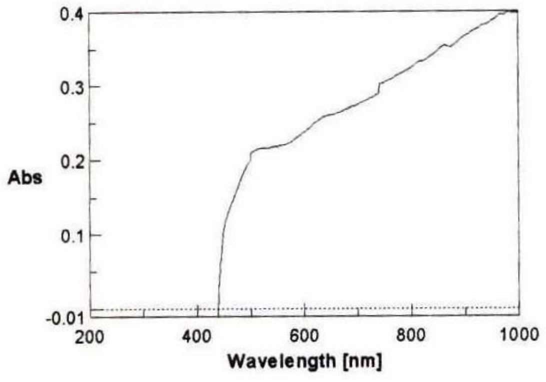


Fig . 7 UV – Visible spectrum of Phenolphthalein in AF Fig. 8 UV – Visible spectrum of S-benzyl thiouronium chloride in AF

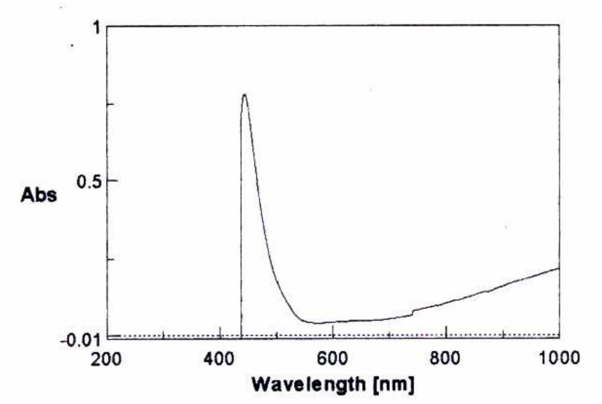


Fig . 9 UV – Visible spectrum of 2,4 Dinitrobenzene in AF

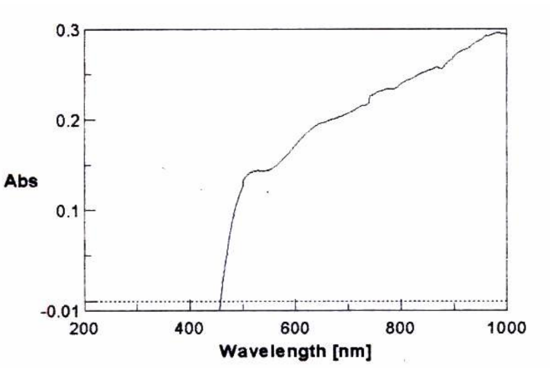


Fig . 10 UV – Visible spectrum of Acetanilide in AF

3.3. FT-IR Spectra

The spectra are exclusively recorded for anilinium formate using the Jasco (FT-IR 460) and also for the solutions of various compounds in Anilinum Formate based ionic liquids.

The recorded FT-IR spectrum are presented in figure 11-23.

The strong absorption at 3297cm^{-1}&1596 cm^{-1} in the FT-IR spectrum of Anilinium formate (Fig.11) confirms the presence of $NH3^+$ &COO^- ions.This clearly shows that the prepared ionic liquid is well formed. Furthermore, in all other cases the absorption of functional group of various compounds in AF are in well agreement with the literature values and also there is a strong absorption around 3290 cm^{-1} & 1590 cm^{-1}.This confirms that in all the solutions AF is present in an ionic form and does not form any new compound.

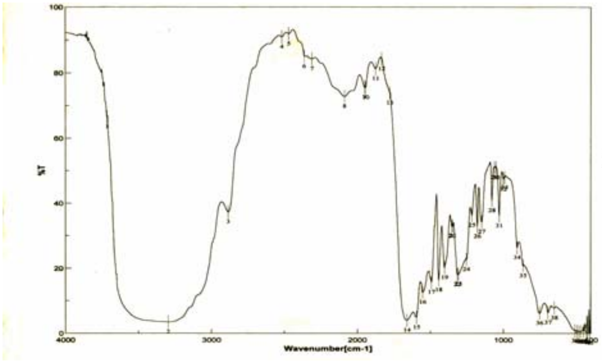


Fig. 11 FT-IR Spectrum of Anilinium formate (IL)

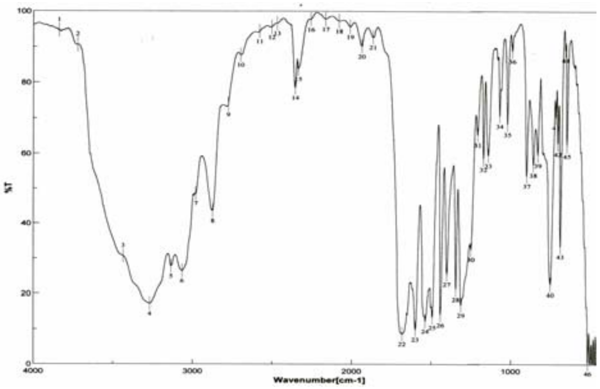
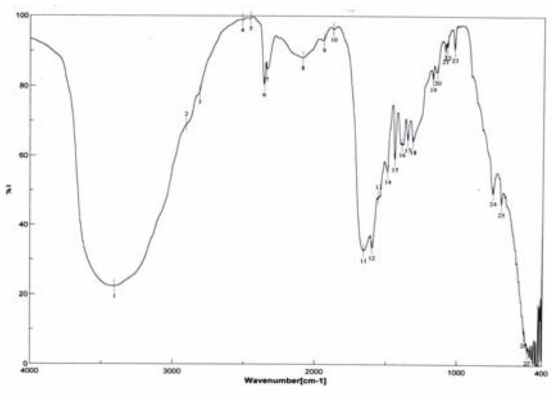


Fig. 12 FT-IR Spectrum of 2,4 dinitro benzene in AF



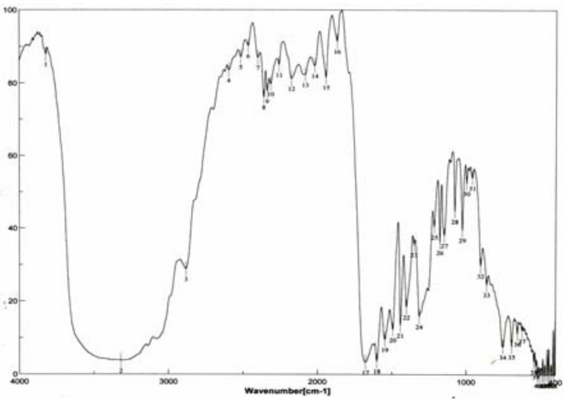
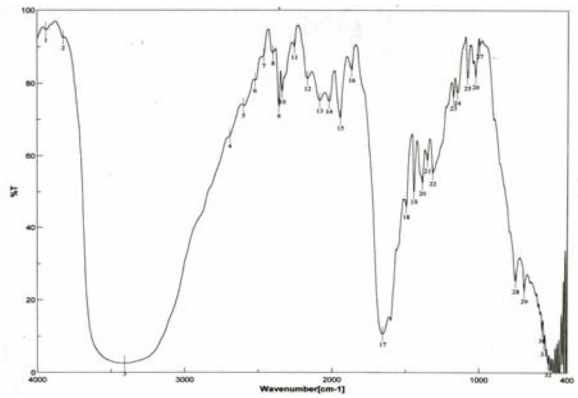


Fig. 13 FT-IR Spectrum of 8-hydroxy quinoline in AF

Fig. 14 FT-IR Spectrumof Acetanilide in AF



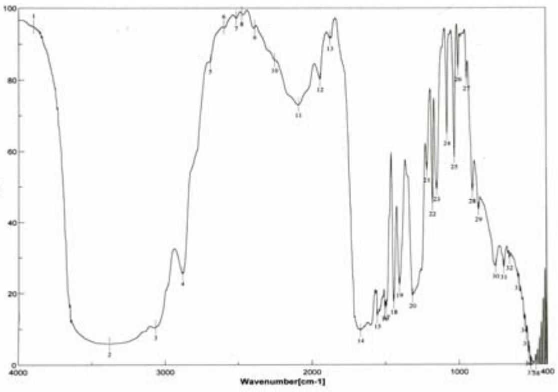
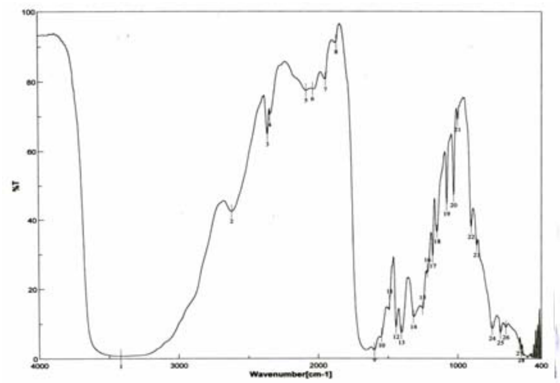


Fig. 15 FT-IR Spectrum of 1-Naphthol in AF

Fig. 16 FT-IR Spectrum of Benzophenone in AF



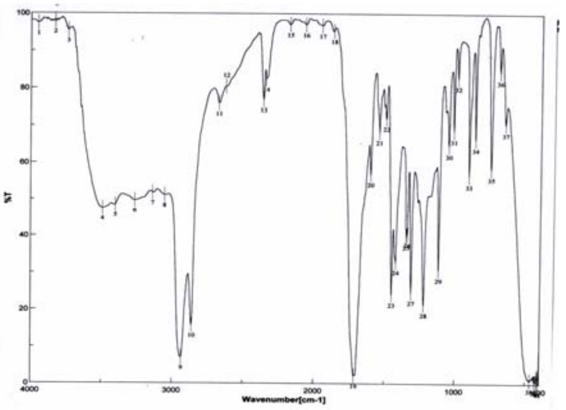
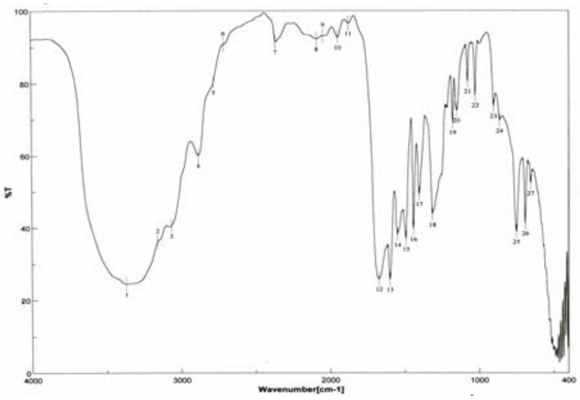


Fig. 17 FT-IR Spectrum of Citric acid in AF

Fig. 18 FT-IR Spectrum of Cyclohexanone in AF



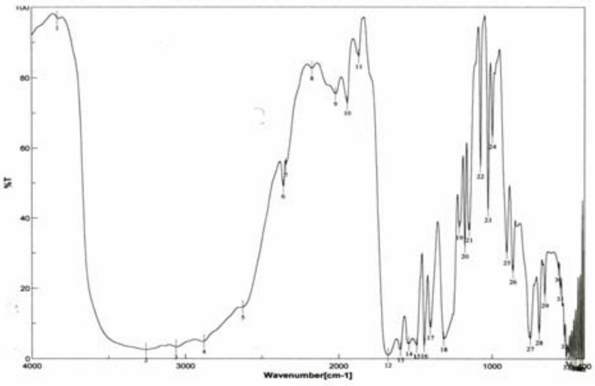
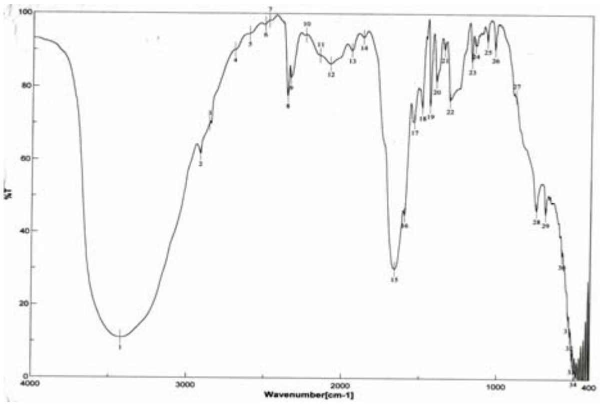


Fig. 19 FT-IR Spectrum of Diphenylamine in AF Fig. 20 FT-IR Spectrum of Hydroxylamine hydrochloride in AF



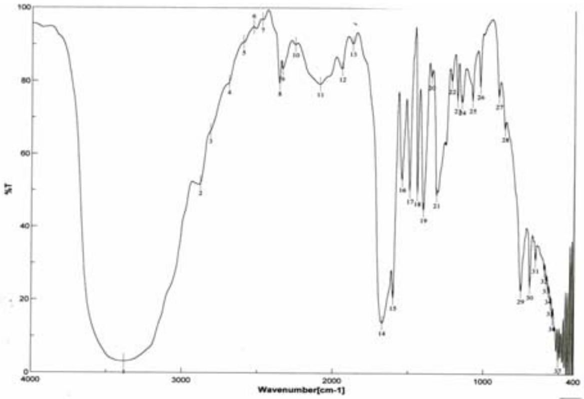


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Fig. 21 FT-IR Spectrum of Phenolphthalein in AF Fig. 22 FT-IR Spectrum of Thio urea in AF

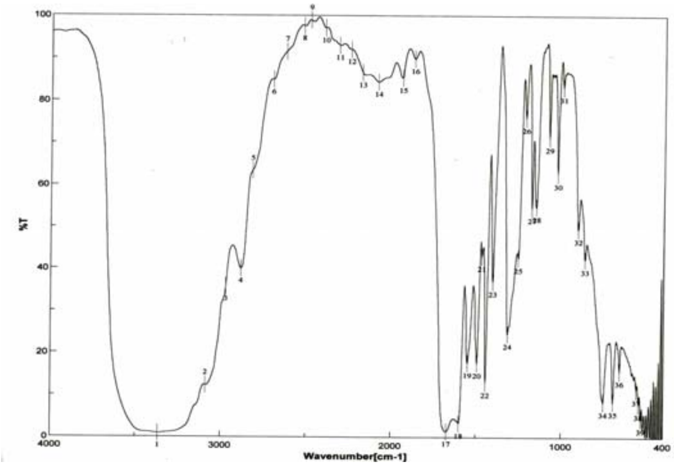

Fig. 23 FT-IR Spectrum of Urea in AF (IL)

3.4. Nuclear Magnetic Spectra

To confirm the structure of the prepared Anilinum formate,The proton nuclear magnetic resonance spectra for the ionic liquid (AF) is recorded in a Bruker 300 MHZ NMR Spectrometer using $CDCl_3$ as solvent, and shown in fig 24.

A Chemical shift value at 6.6-7.8ppm equivalent to five aromatic protons indicates the mono substituted benzene ring and the Chemical shift value at 4.259 ppm equivalent to three protons indicates the $NH3^+$group.But H of NH_2 group in aniline appear at 3.20 ppm.A Chemical shift value at 8.209 ppm indicates the formate group. The data confirms the formation of AF(IL)

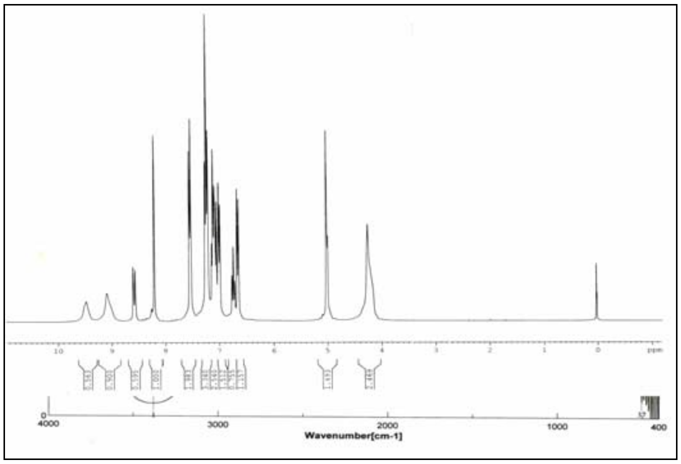

Fig. 24 NMR Spectrum of Anilinium formate (IL)

3.5 Computational Method

Through docking using HEX software the interaction energies of receptor (Anilinium formate) with various substrates are calculated and are listed in table 5 and are shown in fig 25-38.A low (negative) energy indicates a stable system and thus a likely binding interaction.The scoring value for formate (Ligand) in Anilinium (Receptor) is –37.48.The negative value of energy observed gives an indication of interaction between AF and other substances.

The order of interaction is, Rosaniline hydrochloride > Citric acid >2,4 dinitro phenylhydrazine > m-dinitro benzene > Glucose > Benzophenone > Diphenylamine>8-hydroxy quinoline> Acetanilide > Phthalic anhydride > Naphthalene >1-NaphtholBenzamide > Phenyl hydrazine hydrochloride >1,4 dichloro benzene > Amyl alcohol > Oxalic acid > Cyclohexanone > Semicarbazide hydrochloride >Urea >Benzene >Thiourea

Table: 4 Docking energies (scoring values) for different substrates (ligand) in Anilinium formate (Receptor)

S.No	Compound	E_{total}	H-bond
1	Urea	-45.98	0
2	Thiourea	-45.12	0
3	Acetanilide	-70.44	0
4	Benzophenone	-76.81	0
5	Diphenylamine	-76.30	0
6	S-Benzyl thiouronium chloride	-80.92	0
7	1-Naphthol	-64.93	0
8	Glucose	-82.60	0
9	Naphthalene	-65.80	0
10	2,4 dinitro phenylhydrazine	-83.97	0
11	Phthalic anhydride	-69.42	0
12	Benzamide	-64.50	0
13	1,4 dichloro benzene	-60.87	0
14	m-dinitro benzene	-82.73	0
15	Benzene	-45.41	0
16	Cyclohexanone	-55.45	0
17	Amyl alcohol	-57.79	0
18	Phenyl hydrazine hydrochloride	-64.03	0
19	8-hydroxy quinoline	-71.04	0
21	Rosaniline hydrochloride	-94.52	0
22	Semicarbazide hydrochloride	-52.64	0
23	Citric acid	-91.51	0
24	Oxalic acid	-56.04	0

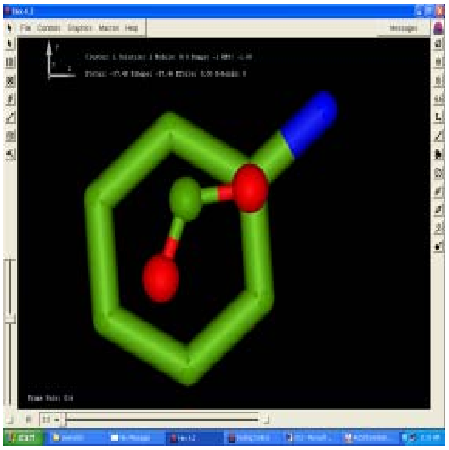

Fig: 27 Anilinium ion + Formate ion

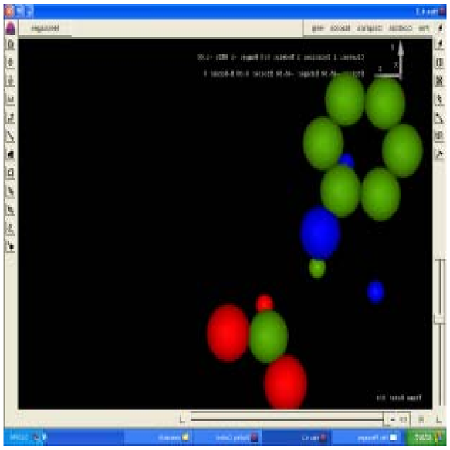

Fig : 28 Af(Receptor) +Urea (Ligand)

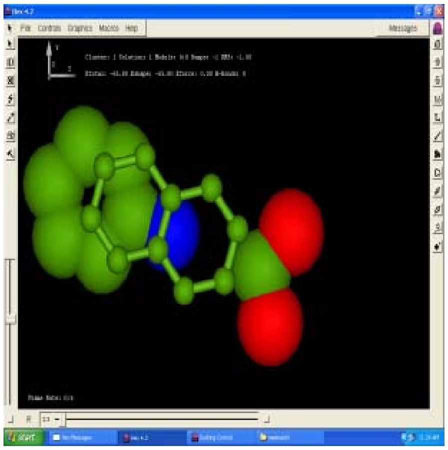

Fig : 30 AF(Receptor) +Naphthalene (Ligand)

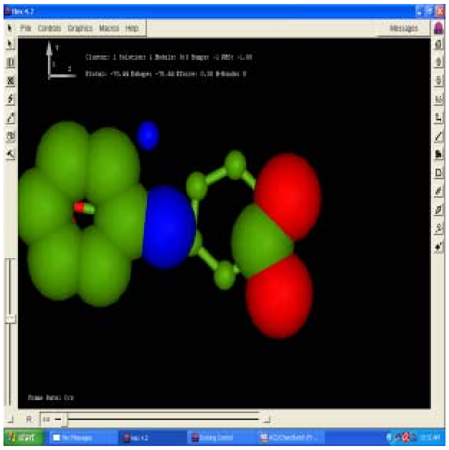

Fig : 31 AF(Receptor) +Acetanilide (Ligand)

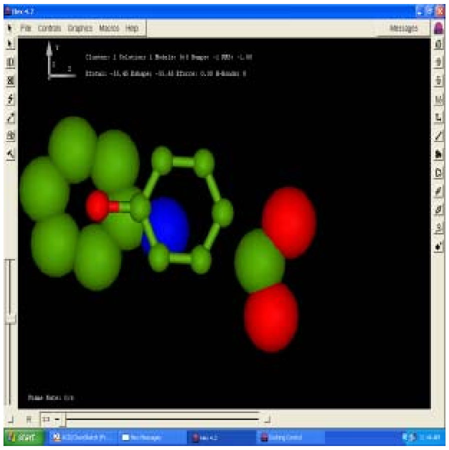

Fig : 32 AF(Receptor) +Cyclohexanone (Ligand)

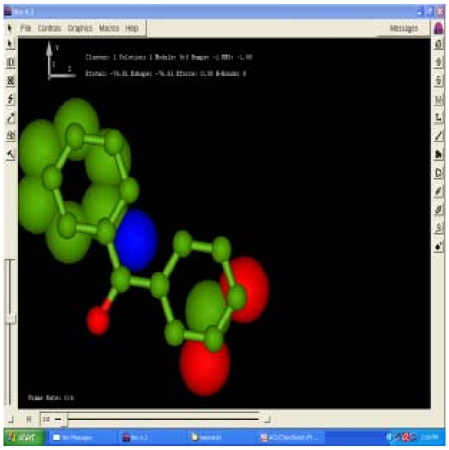

Fig : 33 AF(Receptor) +Benzophenone (Ligand)

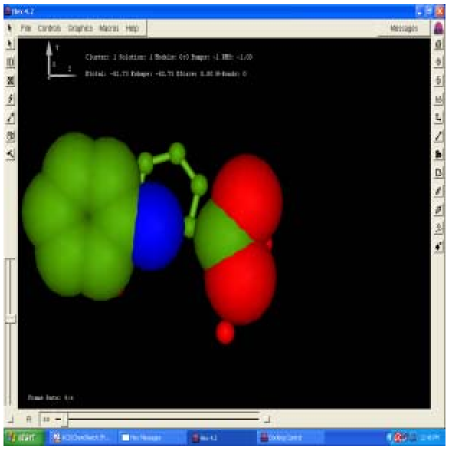

Fig : 34 AF(Receptor) +2,4 Dinitrobenzene (Ligand)

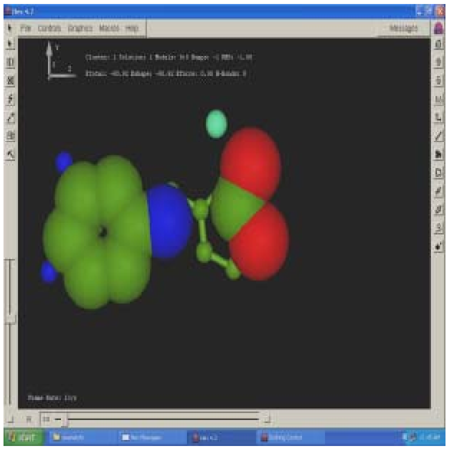

Fig : 35 AF(Receptor) +S-Benzylthiouronium Chloride(Ligand)

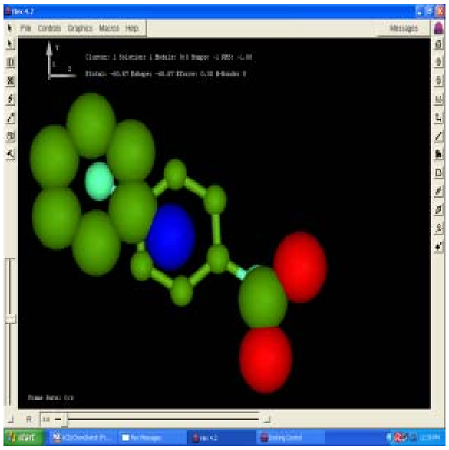

Fig : 36 AF(Receptor) +1,4 Dichlorobenzene (Ligand)

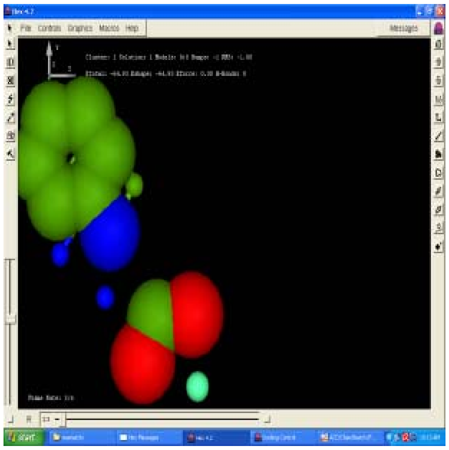

Fig : 37 AF(Receptor) +Phenylhydrazine Hydrochloride (Ligand)

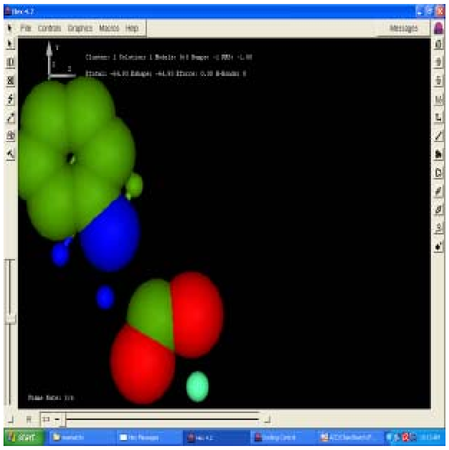

Fig : 38 AF(Receptor) +1-Naphthol (Ligand)

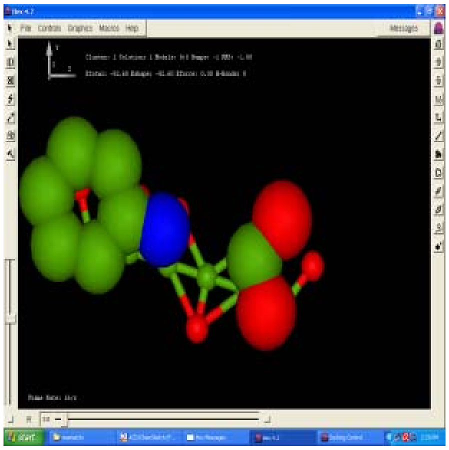

Fig : 39 AF(Receptor) +Glucose (Ligand)

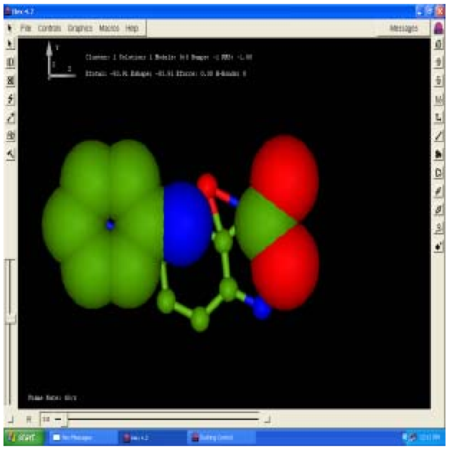

Fig : 40 AF(Receptor) +2,4 Dinitrophenylhydrazine (Ligand)

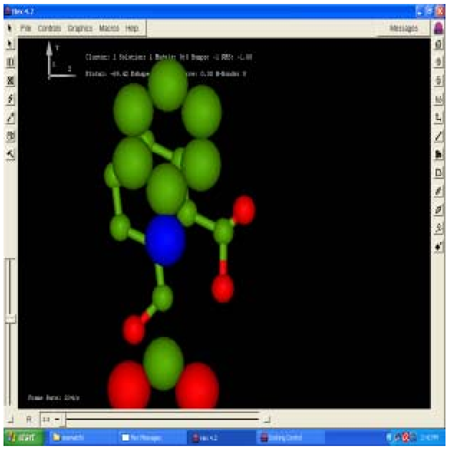

Fig : 41 AF(Receptor) +Phthalicanhydride (Ligand)

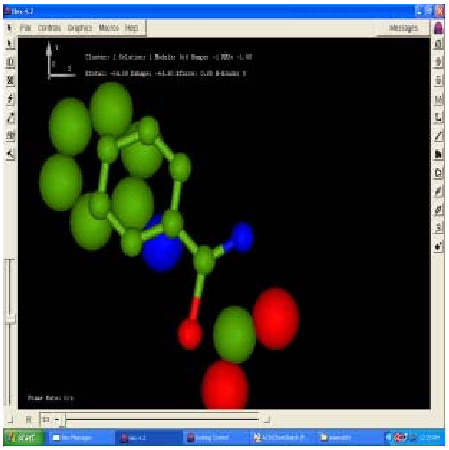

Fig : 42 AF(Receptor) +Benzamide (Ligand)

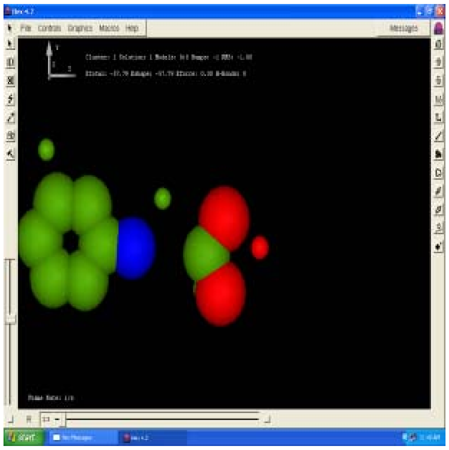

Fig : 43 AF(Receptor) +Amylalcohol (Ligand)

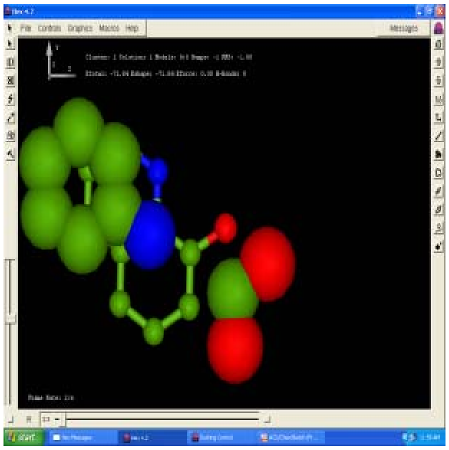

Fig : 44 AF(Receptor) +8-Hydroxyquinoline (Ligand)

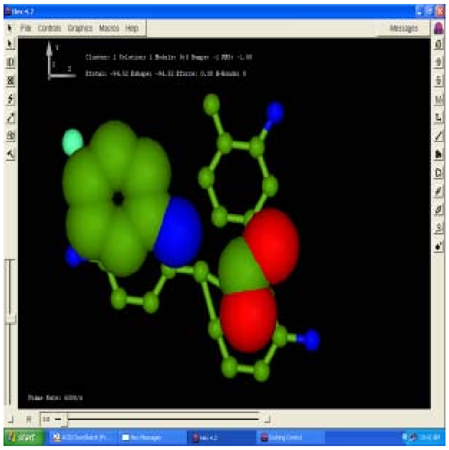

Fig : 45 AF(Receptor)+Rosanilinehydrochloride (Ligand)

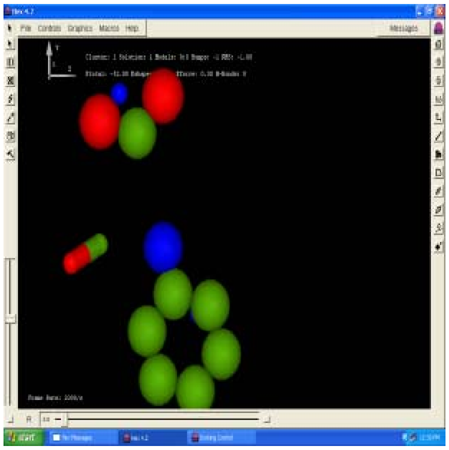

Fig : 46 AF(Receptor) +SemicarbazideHydroChloride (Ligand)

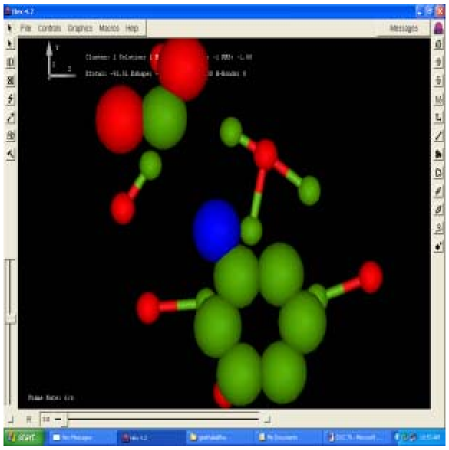

Fig : 47 AF(Receptor) +Citricacid (Ligand)

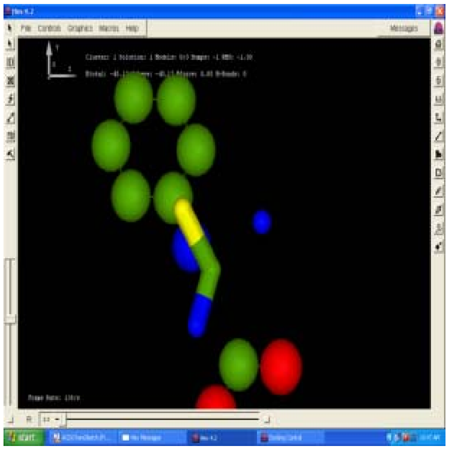

Fig : 48 AF(Receptor) +Thiourea (Ligand)

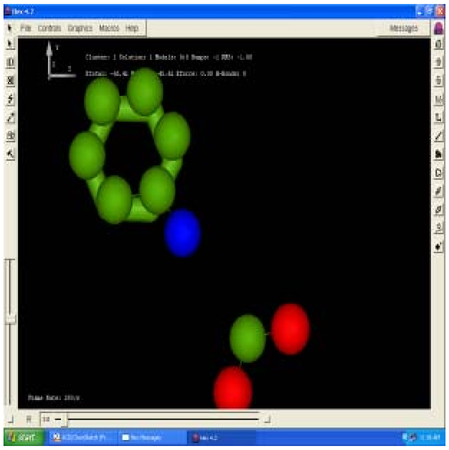

Fig : 49 AF(Receptor) +Benzene (Ligand)

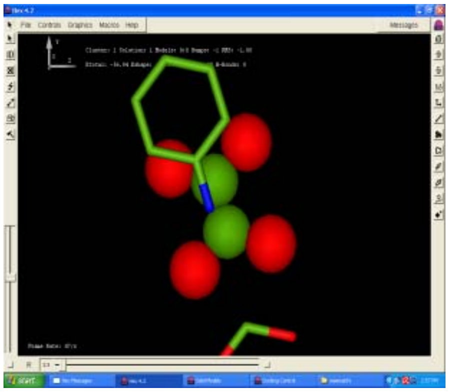

Fig : 50 AF(Receptor) +Oxalicacid (Ligand)

3.7 Organic preparation

The prepared ionic liquid AF is not only a good solvent but also functions as a good medium in preparing various organic compounds. To prove the above one can prepare p-bromoacetanilide using AF and some of the other Anilinium based ILs.

The yield of the product (p-bromo acetanilide) using AF as reaction medium is found to be 91% but in conventional method the yield is found to be only 84%. Thus the yield of the prepared p-bromo acetanilide is higher in AF than in other Anilinium based ILs and in the conventional medium.This shows that AF act as a good reaction medium and solvent. The formation of the product (p-bromo acetanilide) is confirmed by the FT-IR Spectral studies and also this is shown in following figure 51.

Table:5 Preparation of p-bromo acetanilide in Various Anilium based ionic Liquids

S.No	Ionic Liquids	Yield(%)
1.	Anilinium Formate	91
2.	Anilinium Acetate	48
3.	Anilinium Hydrochlorate	62
4.	Anilinium Benzoate	32
5.	N Methyl Anilinium TriChloro acetate	52
6.	N Methyl Anilinium Chloro acetate	54

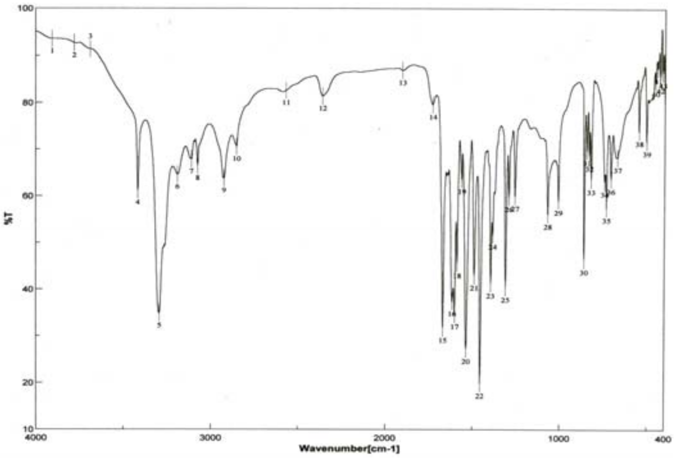

Fig 51. FT-IR Spectra of P-bromo acetanilide in AF

CONCLUSION

Anilinium based ILs are prepared by mixing equimolar proportions of aniline and substituted aniline with various carboxylic acids and inorganic acids. Of all these Anilinium based ILs,Anilinium formate is formed in good manner and shows high conductance. The ability of AF to dissolve various compounds is tested and it is found that around 26 Compounds dissolved in AF. Many compounds which are insoluble in water found to be soluble in AF. The higher values of conductance for the solutions of the substrates in ionic liquid (AF) than in water which obviously proves that AF is a better solvent . FT-IR spectra of solutions of various substrates in AF are recorded. The absorption peaks of FT-IR spectra confirms the interactions between AF and various other substrates in solution. These interactions are also proved by UV-Visible spectral studies. To establish the ability of AF to act as a reaction medium, bromination reaction is being carried out in AF and other Anilinium based ILs. It is noted that, the product is obtained with a yield greater in AF than observed in conventional procedures and in other Anilinium based ILs. The extended calculations of docking process are done to find out the energy values and H-bonding. The interactions are quantified with Hex docking results.

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