International Journal of Scientific Research and Reviews

Molecular Interactions of Imidazole with Ethanol Binary Solution: Ftir and Theoretical Studies

P. Seetha[1*] and S.Sangeetha[1]

[1] Deportment of Physics, Mangayarkarasi college of Arts And Science for Women, Paravai.

ABSTRACT

Two different sample solutions were prepared by dissolving imidazole in ethanol by different weight fractions 20% and 40% respectively. The molecular intraction in the binary solution have been studied by carring out FTIR spectroscopic studies in the frequency range 4000 to 400 cm^{-1}. Based on the analysis of the FTIR spectra, Theoretical calculations have also been made on imidazole monomer, ethanol monomer, dimer, trimer, tetramer and ethanol – Imidazole complex molecules 1:2 (IZ: ETH), 1:3 (IZ: ETH). When the ethanol have a self association through the O-H…O. it is in rich eth solution may consist of eth multimer as a dimer and trimer.

KEY WORDS: FTIR, Imidazole, Ethanol. Blue shifted H-bonds, second order perturbation, energy Interaction energy.

*Corresponding author

Ms. P. SEETHA

Assistant Professor, Deportment of Physics,

Mangayarkarasi college of Arts And Science for Women,

Paravai, Madurai – 625 402.

Tamilnadu, INDIA.

Email: seethapalanivel94@gmail.com

INTRODUCTION

Imidazole (IZ) is an organic compound with the formula $C_3N_2H_4$. Imidazole contains a ring system the positive charge can be located on either of the two nitrogen atoms. Imidazole is a highly polar compound, as evidenced by its electric dipole moment of 3.667 D[1] and imidazole is an excellent electron donor (D). In the manner, the imidazole is reversibly protonated and deprotonated on the interchange of tyrosine redox state[2]. Imidazole can strongly interact with various electron acceptors (A) due to its electron donating capacity. Ethanol (ETH) is a primary alcohol with strong electron acceptor sites in the form of oxygen. A review of literature revealed that the binary mixture of imidazole with ethanol has not been taken for investigation. Therefore in the present work IZ is dissolved in ethanol by varying the weight fractions of IZ separately. The FTIR spectroscopic methods and Density Functional Theory (DFT) calculations have been employed to analyze the molecular interactions taking place between IZ and ETH. Natural Bonding Orbital (NBO) analyses are also done to investigate the hyperconjugation energies corresponding to various interactions in the system.

MATERIALS AND METHODS

Imidazole was purchased from Merck Ltd., Mumbai, India. Ethanol of AR grade with 99.9% was purchased from SD fine Chem. Ltd., Mumbai, India. Both were used as such without further purification. Two different sample solutions were prepared by dissolving imidazole in ethanol by different weight fractions 20% and 40% and they are named solution1 and solution2, respectively in this paper. At room temperature, FTIR spectra of the pure compounds and the solutions1 and 2 were recorded in the region: 4000-400 cm^{-1}, using Perkin Elmer FTIR spectrophotometer (model: spectrum II) with the resolution of 1 cm^{-1}. Quantum chemical calculations were carried out using Gaussian 09W program package[3]. The B3LYP functional[4] with the basis set 6-311++G (d, p) was used for the geometry optimization, frequency calculation and NBO analysis on the complexes of imidazole with ethanol.

RESULTS AND DISCUSSION

FTIR SPECTROSCOPIC STUDIES

The FTIR spectra for pure IZ, ETH and the binary solutions (S1&S2) are presented in Fig.1.

The band assignments for various vibrational modes in the FTIR spectra are listed in table 1. The bands occurring frequencies of pure IZ (Fig. 1a, Table 1) are assigned to $\nu\,(N-H), \nu(C=C), \nu(C=N), \nu(C-N)$ and ring breathing, respectively.[11,12] The $C-H$ stretching modes contribute to two peaks in the spectrum of pure IZ at 3106.41 and 3023.61 cm^{-1} respectively,[5].The average of these two $\nu\,(C-H)$ values is presented in table 1.

Already certain works are available in literature in which FTIR spectroscopic studies have been carried out on alcohols[6-11] . The ethanol $O-H$ stretching contributes to the broadest peak at 3399.96 cm^{-1} in the FTIR spectrum (Fig. 1b, Table 1). $v_{as}(CH_3), v_s(CH_3), v_{as}(CH_2), v(C-O), v(C-O-C)$ bands of pure ETH appear (Fig. 1b, Table 1). Those assignments have been made based on the earlier reports[14-18] .
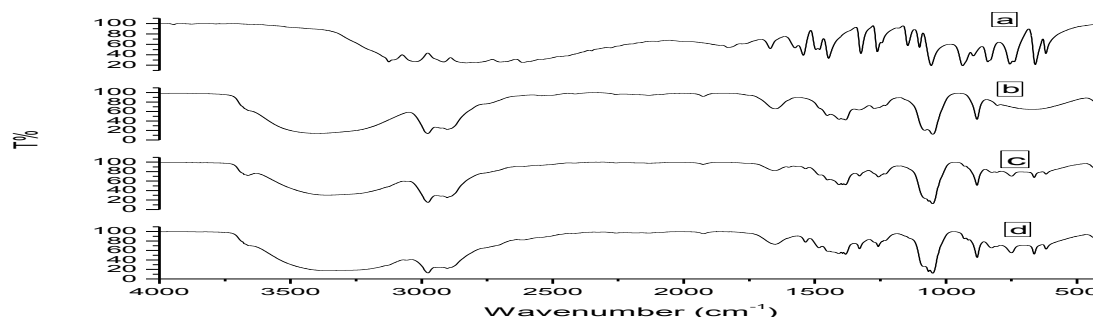

FIGURE1. EXPERIMENTAL FTIR SPECTRUM OF A) NEAT IMIDAZOLE, B) NEAT ETHANOL, C) SOLUTION1 (20% IZ IN ETH), D) SOLUTION2 (40% IZ IN ETH).

Table 1 The experimental FTIR spectral bands of pure compounds and their binary solutions.

Vibrational modes	Wavenumber (cm^{-1})			Vibrational modes	Wavenumber (cm^{-1})		
		Solutions				Solutions	
	Pure compound	S1	S2		Pure compound	S1	S2
Imidazole				**Ethanol**			
v(N-H)	3124.96	-	3121.93	v(O-H)	3399.66	3359.98	3352.64
v(C-H)	3065.30	-	3057.11	v$_{as}$(CH$_3$)	2976.58	2975.60	2975.73
v(C=C)	1543.58	1567.16	1592.83	v$_s$(CH$_3$)	2901.90	2902.09	2902.02
v(C=N)	1475.12	1446.73	1447.88	v$_{as}$(CH$_2$)	2926.77	2926.17	2928.66
v(C-N)	1324.44	1329.77	1329.67	v(C-O)	1080.24	1065.08	1066.06

v - Stretching, s- symmetric, as- anti symmetric.

In the FTIR spectrum of S1 (Fig. 1c) the IZ v(N-H) and $v(C-H)$ bands donot appear. The $v (C = C)$ and ring breathing modes of IZ have undergone blue shifts whereas the $v (C = N)$ band has shifted to lower wave numbers (Fig. 1c, table 1), These shifts may be due to the interactions: (ethanol) $O-H...N=C$ (imidazole) / (ethanol) $methyl\ C-H...N=C$ (imidazole) / (ethanol) $methylene\ C-H...N=C$ (imidazole). Its also possible that ethanol hydrogens may interact with the other imidazole nitrogen as deduced from the blue shift in the v(C-N) mode of IZ in this solution. The red shifts in the hydroxyl/ methyl/ methylene stretching modes of ethanol (Fig. 1c, Table 1) in the solution1 are in favour of these hydrogen bond interactions. . Its not possible to identify the role of imidazole hydrogens in hydrogen bond interaction due to the non availability of the $v(N-$

$H)$ and $\nu(C-H)$ bands in the FTIR spectrum of the solution1. But the $\nu(C-O)$ and $\nu(C-C-O)$ bands of ETH have shifted to lower and higher wavenumber respectively. This could be due to the dissociation of ETH molecules in the solution1.

The FTIR spectrum of solution2 (Fig. 1d) indicates that IZ $\nu(N-H)$, $\nu(C-H)$ and $\nu(C=N)$ bands have undergone red shifts. The $\nu(C-N)$ mode of IZ has shifted to higher wavenumber. These shifts maybe due to the following interactions: (imidazole) $N-H\dots O$ (ethanol) / (imidazole) $C-H\dots O$ (ethanol) and /or (ethanol methyl) $C-H\dots N$ (imidazole), (ethanol methylene) $C-H\dots N$ (imidazole) and (ethanol) $O-H\dots N$ (imidazole). The possibilities can be further confirmed by the red and blue shifts in the asymmetric stretching modes of CH_3 and CH_2 group of ethanol. Moreover the $\nu(O-H)$ mode of ethanol has suffered red shift, which is also in favour of the interaction (ethanol) $O-H\dots N$ (imidazole). In IZ $\nu(C=C)$ and ring breathing modes suffer blue shifts. The blue shift in ring breathing mode of imidazole in both the solutions indicates that (ethanol) $C-H\dots\pi$ (imidazole) contacts are also possible.

THEORETICAL STUDIES

On the basis of the experimental results, DFT calculations have been carried out on imidazole monomer, ethanol (monomer, dimer, trimer and tetramer) and 1:2 (IZ: ETH), 1:3 (IZ: ETH) complexes of imidazole with ethanol in Fig.2. The shifts in the theoretical frequencies corresponding to the IZ vibrational modes except the $\nu(N-H)$ in the complexes 1:2 and 1:3 are found to agree very well with experimental frequency shifts. The theoretical frequencies (unscaled) of 1:2 and 1:3 complexes are compared with the pure imidazole (monomer), pure ethanol (monomer, dimer, trimer and tetramer) frequencies. As far as ethanol is concerned, most of the vibrational modes except the $\nu(C-O)$ of 1:2 and 1:3 complexes display shifts in agreement with the experimental results when ethanol dimer and trimer frequencies are compared. Therefore only the optimized geometries of Imidazole, ethanol (dimer and trimer) and the complexes of imidazole with ethanol are presented in the Fig. 2. The theoretical vibrational spectra for these structures are depicted in Fig. 3.
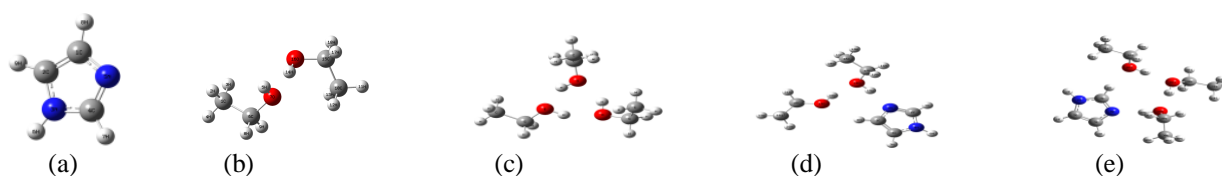

(a)	(b)	(c)	(d)	(e)

Figure.2 Optimized Structure Of (A) Pure Imidazole B) Ethanol Dimer C) Ethanol Trimer D) 1:2 (Iz : Eth) Complex E) 1:3 (Iz : Eth) Complex.

Comparison of the interaction energies of complex molecules with pure ethanol dimer and trimer (table 2) predicts that 1:3 complex is more stable than the 1:2 complexes and other ethanol dimer and trimer. This describes that in the binary solutions of imidazole with ethanol, there are

more chances for dissociation of ethanol dimer and trimer molecules and complex molecules are formed with more stability.

Table 2 Theoretical vibrational bands (cm^{-1}) of pure IZ, pure ETH and complex molecules with interaction energies (kJ/mol).

Vibrational bands	Pure molecules			Complex molecule	
	Imidazole	Ethanol			
	monomer	dimer	trimer	1:2	1:3
ν(N-H)	3652.94			3656.46	3656.26
ν(C-H)	3254.16			3252.45	3237.28
ν(C=C)	1555.36			1568.24	1565.97
ν(C=N)	1496.01			1412.56	1437.99
ν(C-N)	1396.01			1438.53	1438.93
Ring breathing	1160.03			1164.12	1171.50
ν(O-H)					
ν_{as}(CH$_3$)		3749.66	3599.05	3483.77	3398.84
ν_s(CH$_3$)		3086.49	3095.03	3094.59	3092.32
ν_{as}(CH$_2$)		3019.18	3024.89	3027.1	3022.65
ν(C-O)		3056.26	3049.57	3095.76	3057.24
ν(C-C-O)		1088.27	1108.59	1115.34	1115.55
		1057.65	1061.00	1062.33	1060.32
Intreraction energy		-18.4014	-54.579	-55.5087	-97.9266

S1- scheme1 1:2, S2 – scheme2 1:2, S3 – scheme1 1:3, S4 – scheme2 1:4

Table 3 details of interaction type and hyperconjugation energy (HE), the second order perturbation energy (kJ/mol) for dimer, trimer and the complex (1:2 and 1:3) molecules.

The second order perturbation energy profile for ethanol dimer and trimer, 1:2 and 1:3 complexes have been given in the table 3. On examining the Hyper conjugation Energy (HE) profile of ethanol dimer and trimer, it is clean that the self association of ethanol is only through the $O - H \ldots O$ contacts.

Dimer		Trimer	
Interaction type	HE	Interaction type	HE
$\eta_{O7LP(1)} \longrightarrow \sigma *_{H14-O16}$	54.182	$\eta_{O8LP(1)} \longrightarrow \sigma *_{O13-H15}$	22.343
$\eta_{O7LP(2)} \longrightarrow \sigma *_{H14-O16}$	68.366	$\eta_{O8LP(2)} \longrightarrow \sigma *_{O13-H15}$	1368.21
$\sigma_{H14BD(1)} \longrightarrow \sigma *_{H5-O7}$	8.158	$\sigma_{O13BD(1)} \longrightarrow \sigma *_{O13-H27}$	17.866
$\eta_{O16LP(1)} \longrightarrow \sigma *_{H5-07}$	14.393	$\sigma_{O19BD(1)} \longrightarrow \sigma *_{O8-H9}$	30.962
$\eta_{O16LP(2)} \longrightarrow \sigma *_{H5-07}$	101.839	$\eta_{O19LP(1)} \longrightarrow \sigma *_{O8-H9}$	16.778

		$\eta_{O19LP(2)} \longrightarrow \sigma *_{O8-H9}$	362.878		
		$\eta_{O19LP(3)} \longrightarrow \sigma *_{O8-H9}$	1063.531		

1:2 Complex		1:3 Complex	
Interaction type	**HE**	**Interaction type**	**HE**
$\eta_{N5LP(1)} \longrightarrow \sigma *_{H12-C17}$	0.2928	$\eta_{N5LP(1)} \longrightarrow \sigma *_{C10-H13}$	792.993
$\eta_{O18LP(1)} \longrightarrow \sigma *_{O19-H20}$	6.903	$\eta_{O19LP(1)} \longrightarrow \sigma *_{O12-H18}$	13.221
$\eta_{O18LP(2)} \longrightarrow \sigma *_{O19-H20}$	25.104	$\eta_{O19LP(2)} \longrightarrow \sigma *_{O12-H18}$	1101.689
$\sigma_{O19BD(1)} \longrightarrow \sigma *_{C3-H8}$	0.25104	$\eta_{O28LP(1)} \longrightarrow \sigma *_{O19-H22}$	22.133
		$\eta_{O28LP(2)} \longrightarrow \sigma *_{O19-H22}$	1136.5

LP – lone pair; BD – bond orbital

The involvement of methyl / methylene hydrogen of ethanol in self association may not be possible in these structures. The (ethanol) $O - H \dots O$ (ethanol) contacts may be retained in the 1:2 complex irrespective of the presence of weak heterointeractions (ethanol methylene) $C - H \dots N$ (ethanol) and (imidazole) $C - H \dots O$ (ethanol).

The HE profile of 1:3 complexes describes that the methylene hydrogens of ethanol may prefer to form hydrogen bonds with ethanol oxygens in the presence of a imidazole molecule. This homomolecular interaction was not evident even in the pure trimer network of ethanol. The homointeractions (ethanol methylene) $C - H \dots O$ (ethanol) and (ethanol) $O - H \dots O$ (ethanol) are stronger than the heterointeractions (ethanol methyl) $C - H \dots N$ (imidazole) in this 1:3 complex. These strong interactions may be responsible for the increased stability of this 1:3 complexes.
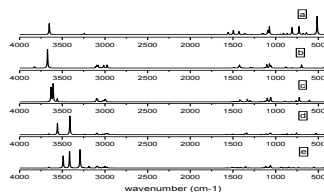

Figure. 3 Theoretical Vibrational Spectrum Of A) Imidazole B) Ethanol Dimer C) Ethanol Trimer D) 1:2 Complex E) 1:3 Complex

CONCLUSIONS

The imidazole-ethanol binary solutions at various weight fractions of imidazole in ethanol are 20% and 40% have been investigated by FTIR spectroscopic studies. The theoretical work has also been done on 1:2 (imidazole: ethanol) and 1:3 (imidazole: ethanol) complexes.

THE FOLLOWING CONCLUSIONS CAN BE ARRIVED FROM THE PRESENT WORK:

1. (ethanol) $O - H \ldots N$ (Imidazole), (ethanol methyl) $C - H \ldots N$ (imidazole), (ethanol methylene) $C - H \ldots N$, (imidazole) $C - H \ldots O$ (ethanol) and (imidazole) $N - H \ldots O$ (ethanol) interactions are possible, as deduced from FTIR spectral studies.

2. The ethanol molecules exist as dimer and trimeric entities in the environment of imidazole.

3. In both the 1:2 and 1:3 complexes (ethanol) $O - H \ldots O$ (ethanol) interactions are preserved.

4. In 1:3 complexes, the ethanol methylene hydrogens tend to form hydrogen bond with the ethanol oxygens, a possibility which is not even found in the pure ethanol dimer /trimer.

5. The 1:3 complexes are more stable than pure imidazole and ethanol (dimer and trimer) and the 1:2 complexes.

REFERENCES

1. D. Christen, J.H. Griffiths, J. Sheridan, Z. Naturforsch. 1982; 37: 1381.

2. G.T. Babcock, B.A. Barry, R.J. Debus, C.W. Hoganson, M. Atamin, L. Mcintosh, I. Sithole, C.F. Yocum, Bio Chem. 1989; 28: 9557.

3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G., R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, and D. J. Fox, Gaussian 09, Revision D.01, Inc., Wallingford CT, 2013. D. Becke, J. Chem. Phys. 1993; 98: 5648.

4. K. Lai, T. Kobayashi, Ultrason. 2016; 28: 41.

5. R. Ramasamy, Armen. J. Phys. 2015; 8: 54.

6. G. S. S. Saini, S.Kaur, S.K. Tripathi, S.D. Dogra, J.M. Abbas, C.G. Mahajan, Vib.Spectrosc. 2011; 56: 72.

7. D.L. Jadhav, N.K. Karthick, P.P. Kannan, R. Shanmugam, A. Elangovan, G. Arivazhagan, J. Mol. Struct. 2017; 1130: 498.

8. R. A. Provencal, J. B. Paul, K. Roth, C. Chapo, R. N. Casaes, R. J. Saykally, G. S. Tschumper, H. F. Schaefer, J. Mol. Struct. 1998; 110: 4258.

9. Y. Zhou, Y.Z. Zheng, H.Y. Sun, G. Deng, Z.W. Yu, J. Mol. Struct. 2014; 110

10. E.K. Plyer, J. Res. Natl. Bur. Stand. 1952; 48: 284.

11. Elangovan R. Shanmugam, G. Arivazhagan, A. Mahendraprabu, N.K. Karthick, Chem. Phys. Lett. 2015; 639:162.