Eigen Value Analysis Studies on Hydrogen Bonded Polar Binary Mixtures

S. Sreehari Sastry[a], N. K. S. P. S. Sarma[a], K. Mallika[a], L Tanuj Kumar[a] and Ha Sie Tiong[b]
[a] Department of Physics, Acharya Nagarjuna University, Nagarjunanagar –Guntur, AP-522510
[b]Department of Chemical Science, Faculty of Science, Universiti Tunku Abdul Rahman,
Jalan Universiti, Bandar Barat, 31900 Kampar, Perak., Malaysia

Abstract— ***In this paper intermolecular of two polar molecules for different molar ratios of solution in a non-polar solvent that caused the hydrogen bonded liquid mixtures are investigated. For this purpose Fourier Transform Infrared (FTIR) spectroscopy and considering as maximum eigen value analysis are used. This method is based on the computation of statistical covariance's and Eigen values made on FTIR spectral data. Two polar molecules of the Poly Propylene Glycol (PPG) and Aniline with different molar ratios from (PPG + Aniline: 0.1 + 0.9 to 0.8 + 0.2) are used to obtain the hydrogen bonded liquid complex systems. Intermolecular interactions have resulted in the hydrogen bond formation between the proton donor NH_2 (amino) of Aniline and proton acceptor OH (hydroxyl) of PPG. Molecular interactions involving the various functional groups are studied using FTIR and then the FTIR data explored through the maximum eigen analysis. The results obtained from this method strengthened that the intermolecular hydrogen bond formation is stronger for molar ratio of the liquid complex 0.8 + 0.2 compared to the other systems.***

Keywords-Eigen value analysis; covariances; FTIR spectra; hydrogen bond; intermolecular interactions;

1. INTRODUCTION

Formation of hydrogen bond through intermolecular interactions of molecules is a powerful tool for self assembling molecules to form liquid mixtures with different molecular shapes and structures [1-8]. The self assembling process leads to the formation of new complex systems whose physical properties are differ from origin of compounds. Such physical properties are viscosity, rheological properties, charge transfer, molecular shape, structures etc. Generally, in preparation of new hydrogen boned liquid complex system, the confirmation of hydrogen bond is fundamental task. Hydrogen bonding is studied theoretically and experimentally in different systems by many workers [9-11]. To understand it, many problems would arise especially in the regions of associations which are conditioned by certain configurations and conformation arrangement of functional groups of molecules that forming hydrogen bond.

FTIR spectroscopy becomes a powerful tool for identification of types of functional groups and hydrogen bonds [12-15] present in systems. FTIR spectroscopic data are the composition of data relating to spectral absorbance measured over a range of frequencies or in wave numbers. Collinearity which is a variable typical in spectral absorbance is useful to recognize specific functional groups which undergo self assembling process to form liquid complex systems and for data redundancy. A significant difference in absorption intensity of spectral energy is due to various vibration modes of constituents in the respective regions or groups; and hence, the finger print regions are not discernable with the naked eye. It is uncommon to find overlapping absorption regions of the characteristic bands. In such cases it is fundamental to extract relevant information of characteristic bands from the spectral data of mixtures [16-17]. Therefore, to pull out the significant and non-redundant information contained in the spectra, a statistical process like maximum eigen value analysis is necessitated. Eigen value analysis greatly improves experimental work allowing both quantitative and qualitative analysis. Mathematical concepts such as covariance matrix and eigen values computed from FTIR spectroscopic data are used to determine the molecular distribution involving various functional groups and their frequency of vibration modes [18]. Maximum eigen value analysis has lower computational complexity because of avoiding the eigen value decomposition processing. This process is more crucial one when the liquid mixtures are studied.

In the present work, liquid mixtures are obtained by self organization process of two polar molecules (forming a solution in non polar solvent): PPG and Aniline with different molar ratios (PPG + Aniline: 0.1 + 0.9 to 0.8 + 0.2). Intermolecular interactions with in molecules result in the hydrogen bond formation between proton donor (NH_2) of Aniline and proton acceptor (OH) of PPG. PPG has simple structure of having hydroxyl groups to form hydrogen bonding [19-24]. PPG is extensively used in the lubricant industry, biological systems, dielectrics, and glass industry etc. Aniline plays a vital role in the manufacture of synthetic dyes, drugs and pesticide. Therefore, keeping industrial, scientific interests and their commercial applications in mind, an attempt has been made here to study the hydrogen bond formation between the proton donor NH_2 (amino) of Aniline and proton acceptor OH (hydroxyl) of PPG using FTIR and measure of statistical maximum eigen value analysis.

II. EXPERIMENTAL DETAILS

The chemicals of Poly Propylene Glycol (PPG) and Aniline of 99% purity were procured from Merck Company, Germany. All liquids used were further purified by standard procedure [25]. The mid fraction of the distillate stored over 4 Å molecular sieves was used for experiments. Firstly, dilute solutions of polar solutes are prepared over a concentration range of 0–1 ml in 10 ml of non-polar solvent benzene.

Infrared (IR) spectra of the compounds were recorded by an Alpha model BRUKER Infrared Spectrometer (BRUKER Corporation, Billerica, MA, USA). Eigen value analysis was carried out on MATLAB platform [26].

III. THEORY: COMPUTATION OF EIGEN VALUES

A statistical measure called covariance matrix and maximum eigen value was used for physical investigation to hydrogen bonded binary liquids. The following are two procedures involved in the computation of eigen values from the FTIR spectroscopic data [27-29]

Eigen value analysis for FTIR Spectra:

Eigen value analysis is applied to two dimensional set of FTIR spectral data to analyze the nature of binary liquids. Two dimensional data matrix of FTIR spectra denotes the variables to signify respective columns indicating the continuous vibrations of transmittance of the samples. This includes the mathematical concepts [30-32]

- Variance: Variance is a measure of variability of the spread in a set of data. Mathematically it is the average square deviation from the mean value of the data.

Let X = {x_1, x_2, x_3…. x_n} be the random vector with *n* data points, Variance of X is given by

$$\text{Variance} \quad V(x,x) = \frac{\sum_{i=1}^{n}(x_i - \bar{X})^2}{n} \qquad (1)$$

where $\bar{X}$ is the mean of random vector *X*.

- Covariance: Covariance is a measure of degree of change together in two random variables. It is usually applied to the two dimensional data. If covariance is zero, the two random variables are not related to each other. If the covariance is positive, two variables are related to each other and move in same direction. If the covariance is negative, two variables are inversely related and hence to move in opposite direction.

Covariance between two random vectors X ={x_1, x_2, x_3…. x_n}, Y= {y_1,y_2,y_3…..y_n}with *n* data points is given by

$$Cov(X,Y) = \frac{\sum_{i=1}^{n}(x_i - \bar{X})(y_i - \bar{Y})}{n-1} \qquad (2)$$

where $\bar{X}, \bar{Y}$ are the mean of two random vectors *X*, *Y.*

Covariance matrix:

Covariance matrix is also known as dispersion matrix or variance covariance matrix. This matrix displays the variance and covariance together. Variance appears along the diagonal position and covariance along the off diagonal position.

$$\text{Covariance matrix } C = \begin{pmatrix} V(x,x) & Cov(x,y) \\ Cov(x,y) & V(y,y) \end{pmatrix} \qquad (3)$$

Eigen values are computed from this covariance matrix using the expression

$$Ca = \lambda a \qquad (4)$$

where a is unknown column of n elements called eigen vector, λ = { λ_1, λ_2 } set of unknown scalar elements called eigen values. From this set obtained the λ_{max} which is useful for our analysis.

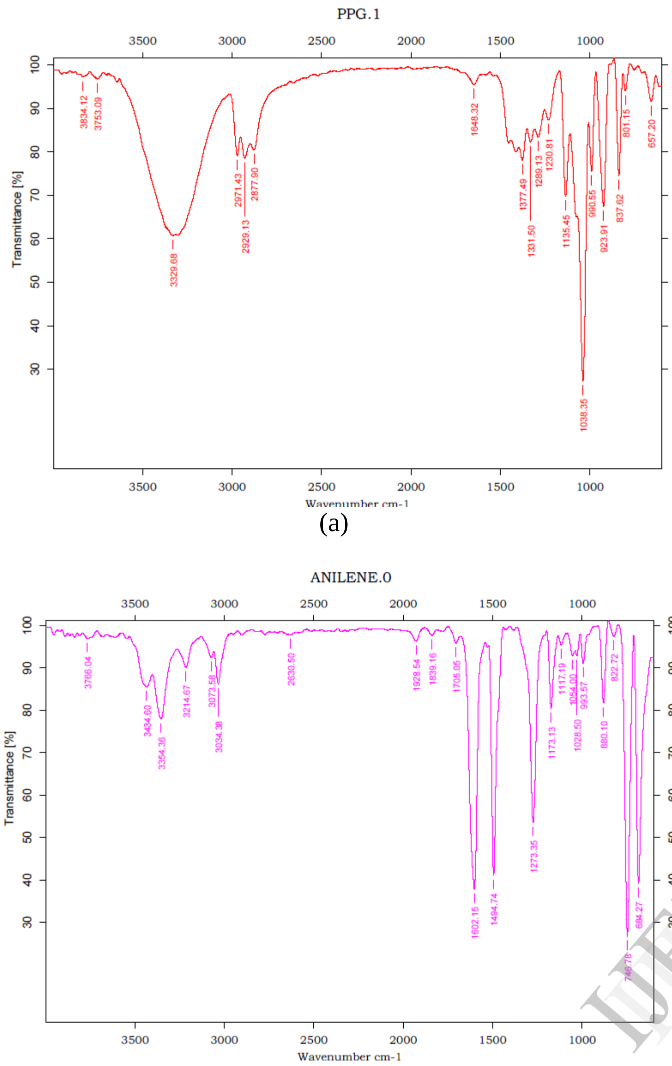
IV. RESULTS AND DISCUSSION

Intermolecular interactions involved in the newly prepared liquid mixtures: (PPG + Aniline) with different molar ratios characterized by FTIR, maximum eigen value analysis are explained in the preceding sections.

A. Fourier Transform Infrared spectroscopy (FTIR):

Infrared spectroscopy is an important and powerful technique for structural elucidation of organic molecules which involve both intra and inter molecular hydrogen interactions. Due to excitation by both molecular vibrations and rotations, the absorption of electromagnetic radiation leaves bands in the IR spectra which are useful to explain the bonding interaction of the molecules. The changes on the following in bands shifts as observed in the spectra bring the information regarding the bonding in liquid mixtures [33-35].

The IR spectrum of PPG shows the absorption bands at frequency of 2971.43cm^{-1} for (C-H), 332943cm^{-1} (OH) stretching mode and different bending vibrations in the finger print region. Aniline shows the absorption bands at frequencies of 3434.6 cm^{-1}, 3354.36 cm^{-1} for NH_2 stretching modes (primary amine), C-N stretching mode at 1273.35 cm^{-1}, bending vibration of NH at 1602.15 cm^{-1} and NH wags in the finger print region at 880.1 cm^{-1}. FTIR spectra of PPG and Aniline are shown in Figure 1.

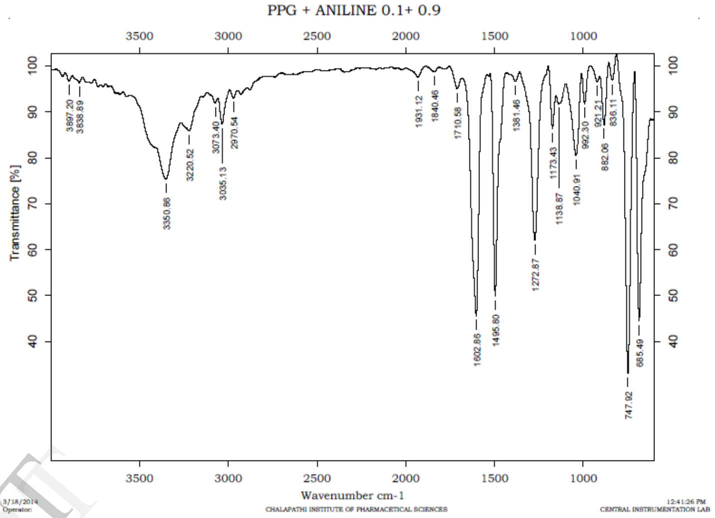


(a)

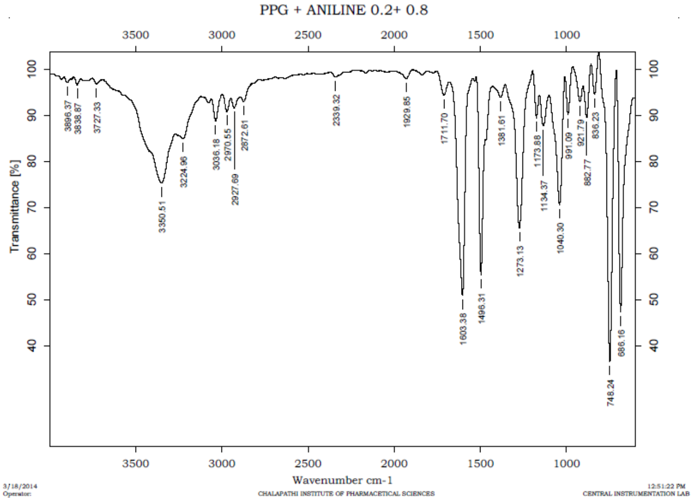
(b)

Figure 1: FTIR Spectra of (a) PPG; (b) Aniline

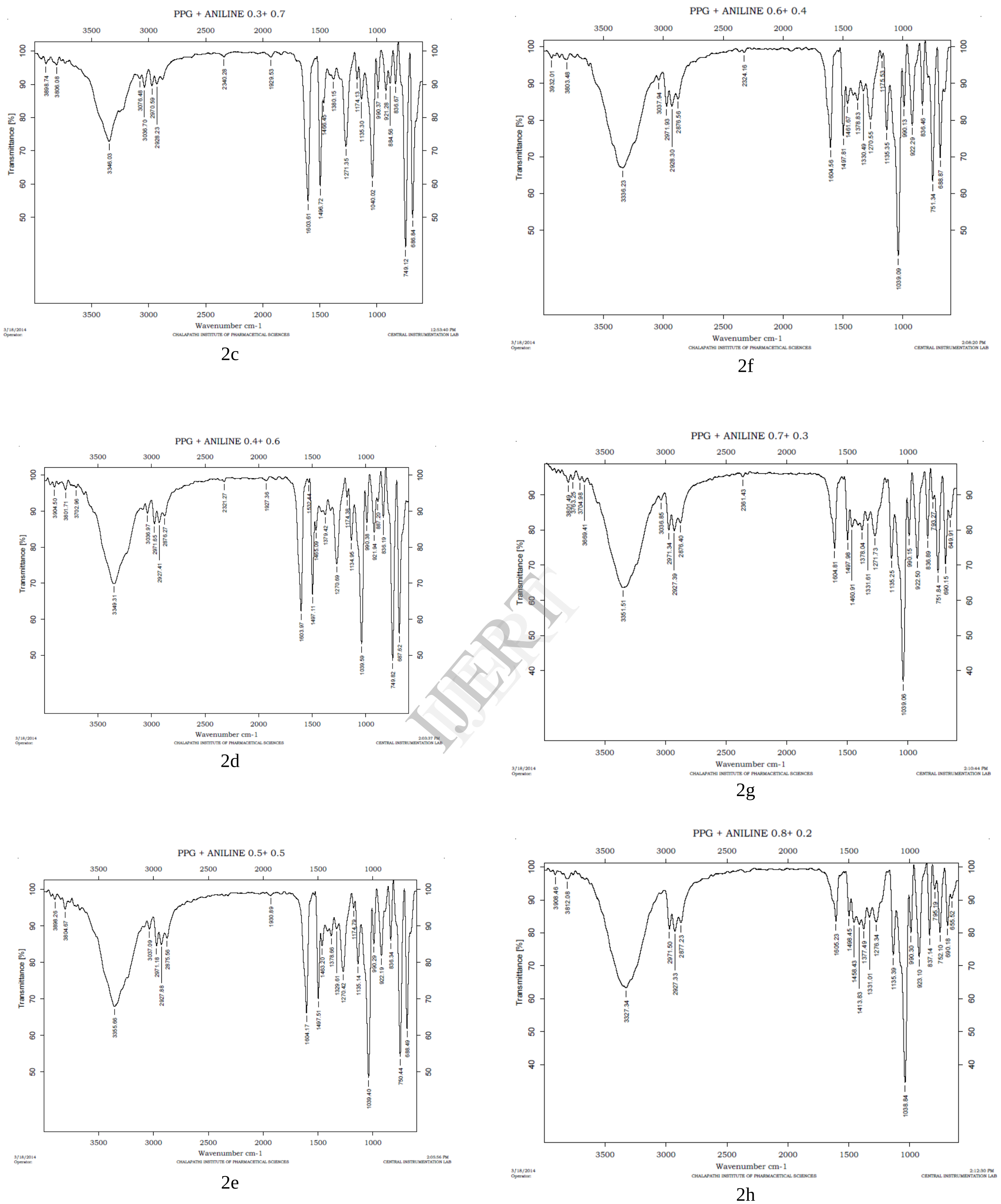
FTIR spectra of PPG + Aniline mixtures with molar ratios 0.1+0.9 to 0.8+0.2 are shown in Figure 2. The stretching, bending and vibrations involving proton donating groups (NH_2) and proton acceptor groups (O-H) has shown shifts in their absorption frequencies that confirming the formation of hydrogen bonding in liquid mixtures Aniline with proton accepting substituent's O-H and the intra molecular H-bond in aniline have disturbed the symmetry of the amino group. Therefore, the formation of intermolecular H-bond with acceptor substituent is formed by the free N-H group. Stability of the hydrogen bonding is observed by IR peak shift in the O-H stretching mode. The C-H stretching mode has shifted to a higher frequency side as where O-H stretching mode shifting to lower frequency side. This is observed specifically in case of molar ratio PPG+Aniline: 0.8+0.2 compared to remaining liquid mixtures (PPG+Aniline: 0.1+0.9 to 0.8+0.2). The frequencies of them are shown in Table 1. Therefore, the formation of hydrogen bonding is strong in the case of mixture with molar ratio PPG+Aniline: 0.8+0.2 when compared to the remaining mixtures. This is due to the increase in accepting power proton with the increasing molar ratio of PPG. As a result the intermolecular hydrogen bond becomes stronger when the frequency differences of characteristic functional groups change their sign. This is observed in Table 1 and also shown in Figure 3. The IR spectral data along with the underlying functional groups have exhibited by the PPG, Aniline and liquid mixtures with different molar ratios (PPG+Aniline: 0.1+0.9 to 0.8+0.2) as given in Table 2. The frequency vibrations of O-H stretching modes with different molar ratios are shown in Figure 4.



2a



2b



2c 2f

2d 2g

2e 2h

Figure 2(a) to 2(h): FTIR spectra of PPG + Aniline mixtures with molar ratios from 0.1 +0.9 to 0.8+0.2

Table 1: FTIR spectra data of PPG, PPG+Aniline with molar ratios (0.1+0.9 to 0.8+0.2).

PPG+Aniline Molar ratios	0+1.0	0.1+0.9	0.2+0.8	0.3+0.4	0.4+0.6
N-H Stretch O-H stretch	3434.6 3354.36#	3350.86#	3350.51*	3346.03*	3349.31#
N-H bending	1602.15	1602.86	1602.38	1603.61	1603.97
C-N stretch	1273.35	1272.87	1273.13	1271.35	1270.69
C-H stretch	3034.38	3035.13	3035.50	3035.70	3036.97
PPG+Aniline Molar ratios	0.5+0.5	0.6+0.4	0.7+0.3	0.8+0.2	1.0+0
N-H Stretch O-H stretch	3355.36#	3336.23*	3339.51*	3327.34	3330.68
N-H bending	1604.17	1604.56	1604.81	1605.23	
C-N stretch	1270.42	1270.55	1271.73	1276.34	
C-H stretch	3037.09	3037.14	3036.15	3037.95	

*With weak shoulder band, # with shoulder band

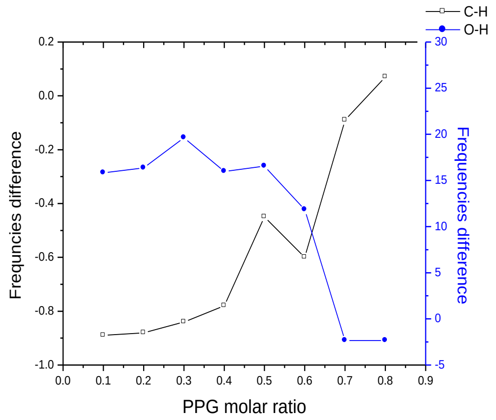


Figure 3: frequency differences of characteristic functional groups of PPG

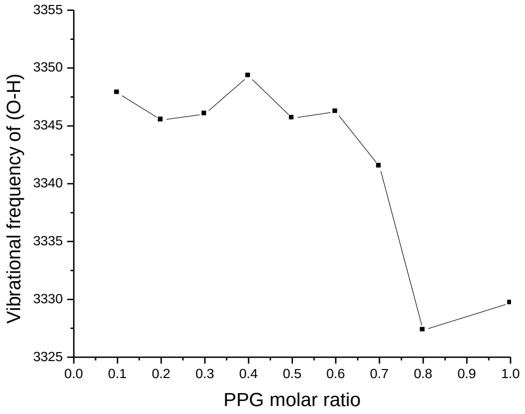


Figure 4: Frequency vibrations of O-H stretching modes with different molar ratios

B. Eigen value analysis of FTIR spectra

Eigen values computed from the FTIR data are used for the investigation of hydrogen bond in liquid mixtures: PPG and Aniline with different molar ratios (PPG + Aniline: 0.1 + 0.9 to 0.8 + 0.2). FTIR data contain two columns of matrix indicating the continuous molecular vibrations of frequencies with their transmittance. Analysis is applied to the band for peak positions, since FTIR spectra contain a large amount of data with overlapping contributes of main functional groups. Maximum eigen value analysis has lower computational complexity for avoiding the eigen value decomposition processing. From eqs (1) - (4), covariance matrix and its eigen values for PPG and Aniline with different molar ratios (PPG + Aniline: 0.1 + 0.9 to 0.8 + 0.2) are computed using MATLAB software [26] and the values are given in Tables 2 and 3. Covariance matrix contains the vector of variance in diagonal position and covariance along off diagonal position. The first diagonal element of covariance matrix represents the variance of frequencies and second diagonal element represent in the variance of transmittance of the samples. Off diagonal elements of the matrix are representing the variance between frequencies and transmittance of the spectral data of the samples. It is a measure of strength of correlation between two columns of variables.

Table 2: Covariance matrices of PPG, Aniline and PPG+ Aniline with molar ratios 0.1 +0.9 to 0.8 + 0.2

Molar Ratio PPG+Aniline	Covariance matrix: 1.0e+006*	
0.0+1.0	1.1928	0.0002
	0.0002	0.0652
0.1+0.9	1.2128	0.0002
	0.0002	0.0551
0.2+0.8	1.2125	0.0001
	0.0001	0.0448
0.3+0.7	1.2107	0.0001
	0.0001	0.0391
0.4+0.6	1.2123	0.0001
	0.0001	0.0282
0.5+0.5	1.2145	0.0001
	0.0001	0.0208
0.6+0.4	1.2060	0.0001
	0.0001	0.0143
0.7+0.3	1.2112	0.0001
	0.0001	0.0120
0.8+0.2	1.2000	0.0001
	0.0001	0.0652
1.0+0.0	1.2183	0.0000
	0.0000	0.0351

Table 3: Maximum Eigen values of Covariance matrices of PPG, Aniline and PPG+Aniline with molar ratios 0.1 + 0.9 to 0.8 + 0.2

Molar Ratio PPG+Aniline	Eigen values 1.0e*+006*
0.0+1.0	1.1928
0.1+0.9	1.2128
0.2+0.8	1.2125
0.3+0.7	1.2107
0.4+0.6	1.2123
0.5+0.5	1.2145
0.6+0.4	1.2060
0.7+0.3	1.2112
0.8+0.2	1.2000
1.0+0.0	1.2183

It is observed from Table 3, that the covariances between transmittance and wave numbers of PPG and Aniline are zero indicating that the two variables of transmittance and wave numbers are not related to each other. For PPG +

Aniline with different molar ratios: 0.1 + 0.9 to 0.8 + 0.2, the values of covariances are positive, indicating that the two variables are covary in a positive way. The transmittance variances of the liquid mixtures (PPG+Aniline : 0.1+0.9 to 0.8+0.2) are low when compared to the individual compounds. Various functional groups involved in the formation of the liquid mixtures through hydrogen bonding have undergone self assembling process in the liquid mixtures with lowering intensity. This is clearly observed in case of molar ratio PPG+Aniline: 0.8+0.2 compared to remaining liquid mixtures (PPG+Aniline: 0.1+0.9 to 0.8+0.2) as shown in covariance matrices of mixtures in Table 3. Upon this complex process the characteristic bands have show new broad and narrow peaks with the significant intensity variations which are shown in Figure 1 and 2.

Inter molecular hydrogen bonding of liquid mixtures are also explored by the Eigen value analysis [18]. The idea is to relate the frequency variances or wave number variances of the function groups of the samples (PPG, Aniline) involved in the self assembling process to form liquid mixtures (PPG+Aniline). Eigen value measures the amount of data variance, and the maximum variance of data set is indicated by the largest Eigen value. Table 4 presents the maximum Eigen values of PPG, Aniline and liquid mixtures (PPG+Aniline: 0.1+0.9 to 0.8+0.2). From Table 4, the difference in the magnitude of maximum eigen values of pure compounds and mixtures is shown very small indicating that the mixtures have maintained the same functional groups like pure compounds and shifted in the characteristic vibration frequencies which are responsible for the hydrogen bond formation. Therefore, magnitude of the Eigen values are directly related to the vibrational frequencies of the molecular functional groups and the magnitude of eigen value has increased in proportion with the shift of vibrational frequencies. In case of liquid mixture with molar ratio (PPG+ Aniline:0.8+0.2), the magnitude of the maximum eigen value is small that indicates the shift in the vibrational frequencies of the characteristic bands towards lower frequency side of the spectrum compared to the other mixtures. The significant vibrational modes of this complex are not correlated with the remaining mixtures. This is observed from the Tables 1 and 2. The special behavior of the liquid mixture shows that, the formation of hydrogen bonding is strong in case of mixture with molar ratio PPG+Aniline: 0.8+0.2 than that of compared to the remaining mixtures. Hence, it strengthens the argument that is very week interactions taking place in the mixtures of PPG and Aniline.

V. CONCLUSIONS

An attempt of modeling the FTIR spectral data of liquid mixtures using variance, covariance, covariance matrix and its eigen values is made. The difference in the magnitude of maximum eigen values for the pure compounds and liquid mixtures has indicated the mixtures maintaining the shifts in the characteristic vibrations that confirmed the hydrogen bond formation. The magnitude of the eigen value of liquid mixture with molar ratio 0.8+0.2 has indicated the shift in the vibrational frequencies of the characteristic bands towards lower frequency side of the spectrum and confirmed that the formation of hydrogen bonding is strong in the mixture compared to the remaining. The mixtures where the molar volume of aniline is relatively less to PPG have indicated that aniline is a highly self associated liquid when compared to PPG.

VI. ACKNOWLEDGEMENTS

The authors gratefully acknowledge University Grants Commission - Departmental Research Scheme at Level III program No. F.530/1/DRS/2009 (SAP-1), dated 9 February 2009, and Department of Science and Technology - Fund for Improving Science and Technology program No. DST/FIST/ PSI–002/2011 dated 20-12-201, New Delhi, to the department of Physics, Acharya Nagarjuna University for providing financial assistance.

REFERENCES

[1] U. Kaatze, “Dielectric spectra of glycerol-ethanol mixtures”Chem. Phys. vol.403 pp.74–80, 2012.

[2] Y.S. Joshi, A.C. Kumbharkhane, “Study of dielectric relaxation and hydrogen bonding in water + 2-butoxyehanol mixtures using TDR technique” Fluid Phase Equilib.vol.317pp.96–101,2012.

[3] A.N.Prajapathi,V.A.Rana,A.D.Vyas, “Dielectric dispersion studies of mixtures of aniline and benzonitrile in benzene solutions” J. Mol. Liq. vol.144 pp.1-4, 2009.

[4] Y. Yomogida, R. Nozaki, “Dielectric study of acetophenone and its Derivatives” J. Mol. Liq. Vol. 149 pp 1-4, 2009

[5] T. Vijaya Krishna, T. Madhu Mohan, “Study of molecular interactions in the polar binary mixtures of N-methyl aniline and alcohols, using excess dielectric and thermodynamic parameters” J. Chem. Thermodyn. Vol.47 pp.267-275, 2012.

[6] T. Vishwam, V.R..K. Murthy, “ Microwave dielectric relaxation studies of Hydrogen bonded polar binary mixtures of isobutanol and aninline”, J. Mol. Struct. vol.1035 pp.46-53, 2013.

[7] S.S. Kadam, P.G. Hudge, D.B. Suryawanshi, A.C. Kumbharkhane , Dielectric relaxation study of 2 and 3 –chloroaniine and 2 and 3 –methoxy-aniline with 1,4 –dioxane mixture using time domain technique” J. Mol. Liq. Vol.177 pp. 426-431, 2013

[8] M. T. Hosamani, N. H. Ayachit, D. K. Deshpandey, Activation energy ([DELTA]G*), enthalpy ([DELTA]H*), and entropy ([DELTA]S*) of some indoles and certain of their binary mixtures”J. Therm. Anal. Calorim. vol.107 pp.1301-1306, 2012.

[9] A. Chaudhari, H. Chaudhari, S. Mehrotra, “Dielectric properties for the binary mixture of di methylacetamide with 2- nitrotoluene at micro wave frequencies” Fluid Phase Equilib. Vol.201 pp107-111, 2002.

[10] C . Gabriel, S. Gabriel, E.H. Grant, B.S.J. Halstead, D.M.P. Mingos, “Dielectric parameters relevant to microwave dielectric heating" Chem. Soc. Rev.27 P213–223, 1998.

[11] A . Loupy, Microwaves in Organic Synthesis, Wiley–VCH Verlag GmbH & Co.,Weinheim, 2006

[12] T. Vijaya Krishna, T. Madhumohan, “Study of molecular interactions in the polar binary mixtures of N-methyl aniline and alcohols using excess dielectric and thermodynamic parameter” J. Chem. Thermodyn. Vol.47 pp. 267–275,2012

[13] T. Vishwam, M. Chitra, V. Subramanian, V.R.K. Murthy, ”Conformational and dielectric analysis of hydrogen bonded polar binary mixtures of propan-1-ol with propionaldehyde” Mol. Phys. vol.105 pp.2411–2417, 2007.

[14] R.J. Senowa, S. sanihla, A.J. Macromol., “Dielectric dispersion study of poly(vinyl pyrrodone)-polar solvent solutions in the frqeuncy range 20Hz-1MHz” Sci. –Part B: Phys. Vol. 46 pp 717-747, 2007.

[15] M.T. Hosamani, N.H. Ayachit, D.K. Deshpande, “Activation energy (DEL TA)G*, enthaly([DEL TA]H*) and entropy ([DEL TA]S*) of some Indoles and certain of their binary mixtures” J. Therm. Anal. Calorim. Vol.107 pp. 1301-1306, 2012.

[16] V. Madhurima, B. Viswanathan, V.R.K. Murthy, "Effect of steric hindrance of ketones in the dielectric relaxation of methanol + ketone systems". Phys. Chem. Liq.vol. 44 pp.563–569,2006

[17] M. Chitra, B. Subramanyam, V.R.K. Murthy, "Conformational and dielectric analysis of hydrogen bonded polar binary mixtures of methyl benzoate with N-methylaniline"Mol. Phys. 99 (2001) 1569–1573.
[18] S. Sreehari Sastry. K. Lakshmi Sarada K. Mallika, C. Nageswara Rao, S. Lakhminarayana3 and Ha Sie Tiong, "Eigen value analysis studies on hydrogen bonded mesogens". Liq Cryst. In press. 2014, DOI:10.1080/ 02678292.2014.927539
[19] E.L.Janssen , I.E.Salazar ,S.R. Friday ,K.N. Wiegel , "Supramolecular main-chain liquid crystalline polymers and networks with competitive hydrogen bonding: flexible biscinnamic acids as hydrogen bond donors in thermoreversible networks and polymers" Liq Cryst.vol.39 pp.857-863,2012
[20] D.D.Fredrickson ,B.A. Hilberg , K.K.Lasure ,J.D. Tessner, A.E. Waner, M.D. Zenner ,K.N. Wiegel. "Supramolecular main-chain liquid crystalline polymers and networks with competitive hydrogen bonding: a study of rigid networking agents in supramolecular systems", Liq Cryst. vol.39,pp.1243-1251,2012
[21] A.Martinez-Felipe , Lu Z, P.AHenderson , S.J.Picken , B.Norder, C.T.Imrie, "Ribes- Greus Synthesis and characterisation of side chain liquid crystal copolymers containing sulfonic acid groups" Polymer, vol.53pp.2604-2612. 2012
[22] A.Martinez-Felipe, C.T.Imrie, A.Ribes-Greus "Study of Structure Formation in Side- chain Liquid Crystal Copolymers by Variable Temperature Fourier Transform" Infrared Spectroscopy. Industrial & Engineering Chemistry Research. vol.52,pp.8714-8721. 2013
[23] V.N.Vijayakumar, M.L.N.Madhu Mohan, "Double Hydrogen Bonded Liquid Crystals:A study of Light Modulation and Field Induced Transition (FiT)" Mol. Cryst Liq cryst.vol. 517 pp.113-126. 2010
[24] D.Demus A.R., Knetz ,F.K. Von Willison. Non emissive electro optic displays. Plenum Press : New York, (1976).
[25] D.D. Perrin, W.L.F. Armarego, Purification of Lab Chem, third ed., Pergamon Press, Oxford, 1980.
[26] Gonzalez R C, Woods R E, Eddins S L, Digital Image processing Using MATLAB, (Dorling Kindersley (India) Pvt. Ltd., Delhi, 2004
[27] Vijayakumar V N, Madhu Mohan M L N, Experimental evidence of an optical shutter in cholesteric phase of a double hydrogen bonded liquid crystal. Brazilian J Phys, vol. 39 pp. 677-683. 2009;
[28] Janssen EL, Salazar IE, Friday SR, Wiegel KN. "Supra molecular main-chain liquid crystalline polymers and networks with competitive hydrogen bonding: flexible bis-cinnamic acids as hydrogen bond donors in thermoreversible networks and polymers". Liq Cryst. vol. 39 pp.857-863 2012.
[29] Fredrickson DD, Hilberg BA, Lasure KK, Tessner JD, Waner AE, Zenner MD, Wiegel KN. Supramolecular main-chain liquid crystalline polymers and networks with competitive hydrogen bonding: a study of rigid networking agents in supramolecular systems. Liq Cryst. Vol. 39pp.1243-1251. 2012;
[30] Cook AG, Martinez-Felipe A, Brooks NJ, Seddon JM, Imrie CT. New insights into the transitional behaviour of methyl-6-O-(n-dodecanoyl)-alpha-D-glucopyranoside using variable temperature FTIR spectroscopy and X-ray diffraction. Liq Cryst.vol. 40 pp.1817-1827. 2013
[31] Dankers P Y W , E W Meijer, Supramolecular biomaterials – A modulator approach towards tissue engineering. Bull Chem Soc.Japan. vol.80 pp. 2047–2073, 2007;
[32] Chunhui Zhao, Furong Gao, Tao Liu, Fuli Wang. An improved statistical modeling strategy by spectroscopy for online monitoring and diagnosis of batch processes. Proc. of the 7th Asian Control Conference, Hong Kong, China, 27-29 August, 2009; pp.893-898.
[33] Yarwood. J, Chapter 4: Spectroscopic studies of intermolecular forces in dense phases, Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.1979; 76:99-130.
[34] Silverstein, R M, Webster. F X, Spectroscopic identification of organic compounds.John Wiley and Sons : New York; 2004.
[35] Sherman Hsu C P. Chapter 15: Infrared Spectroscopy. [Internet] [Cited 2014 April 8].Available from: http://www.prenhall.com/settle/chapters/ch15.pdf