ADDIS ABABA UNIVERISTY
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INVESTIGATION OF SOLVATION POWER PARAMETER OF NICOTINAMIDE IN BINARY SOLVENT MIXTURE USING FTIR SPECTROSCOPY

BY
HAILE ABEGAZ

ADVISORS; Dr. MESFIN REDI
Mr. YISAK TSEGAZEAB

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HAILE ABEGAZ

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Advisor: Dr. Mesfin Redi Signature _________ Date __________

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ABSTRACT

The chromic behavior of a compound is due to photochromism, thermochromisim, electrochromism, solvatochromism, Ionochromism, halochromism, tribichromism and Piezochromism. The term solvatochromism is used to describe changes in Infrared vibrational band followed a change in the polarity of the media. Solvent effects on the vibrational absorption band of nicotinamide in different concentration of binary mixture of solvents were determined. In varying the mole fraction of binary mixture of solvents positive and negative solvatochromism were observed according to the solvation energy of the molecule at the ground states and excited states. The wavenumber functionality on mole fraction were obtained from the correlation graph. Solvent dependent solvation dielectric constant was determined from the correlation plots of wavenumber as the function of dielectric constant mixture of binary solvents as solvent polarity parameter.

Key words: Vibrational spectra, Solvent polarity, spectral shifts, Nicotinamide, solvatochromism, dielectric constant.

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List of Abbreviations

ACN –Acetonitrile

C-N –Carbon Nitrogen

DEE-Diethyl Ether

DXN-1,4-DIOANE

CHX- Cyclohexane

FTIR - Fourier Transform Infrared

MIDIR-Mid Infrared

MM –Molecular model

NA-Nicotinamide

UV/VIS-Ultraviolet Visible

ATR-Attenuated Total Reflection

SIFS-Solvent Induce Frequency Shift

ERS-Electron Repulsion Spin

EPD-Electron Pair Donor

EPA-Electron Pair Acceptor

HBD-Hydrogen Bond Donor

HBA-Hydrogen Bond Acceptor

ε_r – dielectric constant

ε_m -dielectric constant of the mixture

1.INTRODUCTION

The chromic behavior of a compound due to photo chromism (light), thermochromisim (heat), electrochromism (electricity), solvatochromism (solvent), Ionochromism(ions), halochromism (pH), tribichromism (friction) and Piezochromism (pressure). The term solvatochromism is used to describe changes in Infrared absorption band followed a change in the polarity of the media. The absorption spectrum for a molecule in solution can exhibit characteristic differences in positions and intensities of the bands than the spectrum of the same molecule in gas phase. Such differences have been known to be strongly dependent on the solvent [1, 2]. Solvation plays a crucial role in various processes taking place in the liquid phase. Therefore, studying the solvation process is important for understanding the solvent effects on spectroscopic measurement [3, 4]. Due to the complexity of intermolecular interactions the development of a generally valid model for solutions is not an easy task. Many models with non-specific solute-solvent interactions like van der Waals have been developed. Several theoretical treatments have been developed to link quantitatively the solvent effects to the bulk properties of solvent, mainly the refractive index, n and dielectric constant of the bulk solvent, ε_r. The simplest model among these treatments is given by Onsager and Kirkwood [4, 5]. The solute molecule is assumed to be a sphere of radius "a "with a point dipole located at the center. The solute dipole interacts with the molecules of the solvent, which in turn create an electric field, the reaction field [6].

Solvatochromism is generally interpreted in the context of dielectric continuum models, which correlate spectroscopic peak shifts with the solvent reaction field. The field results from the response of the dipolar solvent characterized by dielectric constant and refractive index, to the presence of a dipolar solute [7].

Polarity is an important solvent property for explaining solvent effects on many chemical processes. Different polarity parameters have been proposed over the years to account for solute-solvent interactions [3, 4]. Some solvatochromism equations were introduced to measure solvent polarity. But they don't consider specific solute-solvent interaction such as hydrogen bonding, electron pair donor /electron pair accepter and charge transfer. Some of the solvatochromism equation that used for determination of polarity function are Liptay, Lippert-Mataga, McRae and Bakhshieve's. Those solvatochromic equations are based on Onsager's reaction field theory [8, 9]

Commonly, the solvent dependence absorption band shift expressed as the function of dielectric constant. However, it is not reliable and adequate since the dielectric constant regard solvents as a non-structured isotropic continuum, which does not consider other interactions such as quadrupole, hexapole and octupole [10-13] and they do not take into account specific solute-solvent interactions such as hydrogen-bonding and electron pair acceptor /electron pair donor interactions and charge transfer [9] which often play a dominant role in solute-solvent interactions [8]. Thus, instead of changing the solvatochromic equation, the best solution is changing the solvent polarity parameters ε_r ,with solvent dependent dielectric parameter and ignored expression solvent polarity with ε_r to overcome the problem.

The main contribution of this thesis is to propose a better way for approximating the actual solvent dependent polarity parameter ε_{m}, based on the shift, it considers the overall solute-solvent intermolecular interaction over the ranges, which used to redefine and recalculate solvatochromism equation in binary mixture of solvents by applying the FTIR spectroscopy.

2. THEORETICAL ASPECT

2.1. Fundamentals of Spectroscopy

Spectroscopy is basically an experimental area of science and concerned with the studying of electromagnetic radiation and matter (absorption, emission or scattering of electromagnetic radiation by atoms or molecules) interactions. Specially, molecular spectroscopy which is the study of atoms that are bound together in molecules [14]. The electromagnetic radiation carries waves, these energies carry waves strike any particles they produce a change in particles, in which extensively used to obtain information about the identity and structure of substances. Electromagnetic radiation covers a wide range from radio waves to cosmic rays (figure.1) and their different wave length is shined on the molecule and the wave length that gets absorbed most is measured.

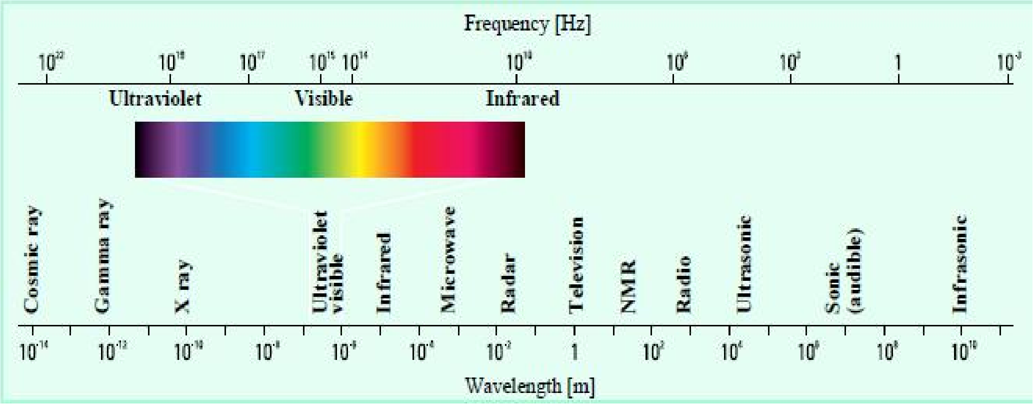

Figure 1:Electromagnetic spectrum ranges with their wave length, frequency and their energy

2.2. Molecular Interactions with Electromagnetic Radiations

Molecules have electromagnetic fields derived from their electrons and nuclei. The electromagnetic radiation interacts with the electromagnetic fields of the electrons to raises their energy levels from one states to other. Thus, absorbed electromagnetic radiation results in transitions between ground and exited states of the molecule. The type of energy states involved in a transition depends on the energy of the radiation absorbed. The specific wave length of the radiation that is absorbed in each region of the electromagnetic spectrum depends on the energy difference between the energy states of a molecule. The absorbed radiation in a spectrum provides information on the energy difference amongst various energy states of the molecule [15]. The specific wavelengths of radiation that are absorbed in each region of the electromagnetic spectrum depend on the energy difference between the energy states of a molecule.

The photon does indeed get turned in to molecular energy, since the molecular energy is quantized, therefore only molecular exited states at certain discrete energy levels. The photon energy has to be equal to the difference energy between some pairs of energy levels of the molecule in order for absorption to occur.

$$\Delta E_{photon} = E_{excite} - E_{ground} \tag{2.1}$$

For any spectroscopic transition between energy states, the changes in energy (ΔE) is given by;

$$\Delta E = h\nu \tag{2.2}$$

Where ΔE is the difference in energy, h is Planck's constant, 6.62606957 × $10^{-34}$$m^2$ kg s, ν is frequency of the electromagnetic radiation absorbed, which is given by

$$\nu = \frac{c}{\lambda} \tag{2.3}$$

Where λ is wave length, C is the speed of light.

The energy gap of a transition is a molecular property and is characteristic of molecular structure which provides structural information of the compound under investigation. According to Born-Oppenheimer (BO) approximation the electronic, vibrational, rotational etc. energies are considered to be independent of each other [16].

The total energy of the molecule is given,

$$E_{total} = E_{electronic} + E_{vibratioal} + E_{rotational} + \cdots \tag{2.4}$$

And consequently, transitions between different energy levels may occur independently. A change in the total energy of a molecule could then be written as

$$\triangle E_{total} = \triangle E_{electronic} + \triangle E_{vibratioal} + \triangle E_{rotational} + \tag{2.5}$$

The approximate orders of magnitude of these changes are

$$_{electronic} \approx 1000x \triangle E_{vibratioal} \approx 1000000x \triangle E_{rotational} . \tag{2.6}$$

While rotational spectra are observed only on molecules that have a permanent dipole moment and vibrational spectra are only observed when the dipole moment of the molecule changes during the vibration, electronic spectra can be obtained from all molecules, since changes in the electron distribution in a molecule are always causing a change in the dipole moment of the molecule. And electron spinning transitions are observed in nuclei having a spin quantum number different from zero.

2.3. Infrared spectroscopy

Infrared spectroscopy is one of the classical methods for structural determination of different molecules, due to its sensitivity to the chemical composition and structure of molecules. The high information content in an infrared spectrum carries over to biochemical system which makes infrared spectroscopy valuable tool for the investigation of amides structures [17] of the molecular mechanism of proteins folding, unfolding and misfolding [18]. The absorption of infrared radiation causes vibrational transition of molecules. The absorption of infrared radiation excites vibrational transitions of molecules. In the mid- and far-infrared spectral regions this is generally the case when the frequencies of light and vibration are equal and when the molecular dipole moment changes during the vibration. Since vibrational frequency and probability of absorption depend on the strength and polarity of the vibrating bonds, they are influenced by intra and Intermolecular effects. The approximate position of an infrared absorption band is determined by the vibrating masses and the type of bond (multiple) and the exact position by electron withdrawing or donating effects of the intra and intermolecular environment and by coupling with other vibrations. The strength of absorption increases with increasing polarity of the vibrating bonds [19].

The energy, $h\nu$,of the absorbed infrared light is equal to an energy difference between a certain energy level of vibration of the molecule (having an energy E_m) and another energy level of vibration of the molecule (having an energy E_n). In the form of an equation,

$$h\nu = E_{m} - E_{n} \tag{2.7}$$

The vibrational absorption wave number can be calculated by using;

$$\tilde{\nu} = \frac{\triangle E}{hc}, = \frac{1}{2}\Pi\sqrt{\frac{k}{\mu}} \tag{2.8}$$

Where k is force constant, μ is effective mass, $\tilde{\nu}$ is wave number, m_1 and m_2 are masses of the two connecting atoms, μ is the reduce mass is given;

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{2.9}$$

Hence the vibrational wave number depends on the force constant and the effective mass. The force constant also depends on the strength of the bond, thus the stronger the bond, the higher is k as well as wave number and the greater the masses of attached atoms the lower the IR frequency at which the bond will absorb.

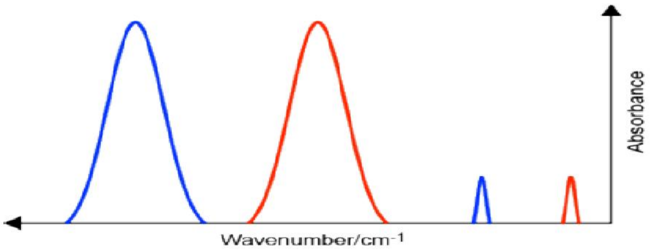

Figure 2:Effect of molecular mass on the vibrational frequency Blue: smaller mass, Red larger mass.

At temperatures above absolute zero, all the atoms in molecules are in continuous vibration with respect to each other. When the frequency of a specific vibration is equal to the frequency of the IR radiation directed on the molecule, the molecule absorbs the radiation. Each atom has three degrees of freedom, corresponding to motions along any of the three Cartesian coordinate axes (x, y, z). A polyatomic molecule of N atoms has 3N total degrees of freedom.

Table 1: Table types of polyatomic molecules the degree of freedom of vibration;

Types of degree of freedom	Linear molecules	Non-linear molecules
Transitional	3	3
Rotational	2	3
Vibrational	3N-5	3N-6
Total	3N	3N

Sometimes a functional group in a molecule can be treated as a whole. Example the –NH_2, and –C=O, of amides represents the whole group. Primary amides show two moderately intense N-H stretching bands corresponding to symmetric and asymmetric N-H stretching vibrations. These bands are found near 3400 and 3500 cm-1, respectively [20] and C=O stretching appears 1650 -1800cm^{-1}. In this thesis it was given high emphasize on the C=O normal mode of vibration in the spectral region of 1650-1720 cm^{-1}.

Absorption of infrared light occurs principally based on a transition between energy levels of molecular vibration. There are transitions which are allowed by a selection rule (i.e., allowed transition) and those which are not allowed by the same rule (i.e., forbidden transition).

In general, transitions with a change in the vibrational quantum number by ±1 are allowed transitions and other transitions are forbidden transitions. Another selection rule with respect to infrared absorption is defined by the symmetry of a molecule. Infrared light is absorbed when the electric dipole moment of a molecule changes as a whole in accordance with a molecular vibration. most molecules are in the ground vibrational state at room temperature, a transition from the state v = 0 to the state v' = 1 (first excited state) is possible. Absorption corresponding to this transition is called the fundamental vibration. Although most bands which are observed in infrared absorption spectra arise from the fundamental vibration, in some cases, we can find bands which correspond to transitions from the state v = 0 to the state v' = 2, 3, 4 (i.e., overtone transitions). However, since overtones are forbidden, overtone bands are very weak [21].

2.4. Solvent Effects on Infrared Spectra or Vibrational Frequency

The vibrational spectrum of a molecule X-Y not only depends on the strength of the bond between X and Y but may also be markedly affected by environmental factor [23]. The intermolecular interactions modify the infrared spectra in a number of ways: the wave number of the normal vibrational modes of a molecule may be shifted to higher or lower values, the intensities can be altered, and the half-width of bands may be greatly increased [24]. Vibrational frequencies and transition dipole moments of normal modes of molecules in solutions are strongly affected by local in homogeneous electric field produced by surrounding solvent molecules. This phenomenon has been recognized as the vibrational solvatochromism. Due to the thermally driven fluctuation of local solvent configuration around a solute, its normal mode frequencies continuously fluctuate in time and solvent bath mode-assisted vibrational energy relaxation occurs [25]. Although the vibrational frequencies are known to be strongly affected by solute-solvent electrostatic interactions in general [26]. Vibrational frequencies undergo either positive solvatochromic shift or negative solvatochromic shift when the solute is dissolved in solvent or solvated by different solvents and such frequency shifting behaviors strongly depend on polarity and hydrogen-bonding ability of solvent molecules as well as on detailed solvation structure around a solute [27].

Both universal (orientation, induction and dispersion) and specific interactions should be taken into account when expressing the frequency shifts by passing the spectrally active molecule between its gaseous and liquid phases [28]. Intermolecular frequency shifts are determined by the normal coordinate dependent parts of the attractive and repulsive interactions between solute and solvent molecules. A number of attempts to develop a quantitatively accurate and physically meaningful explanation of solvent-induced stretching vibration frequency shifts have been presented [29].

There is considerable interest in the study of solvent-induced perturbations on characteristic infrared absorption peaks and linear and nonlinear optical properties of organic compounds. In effect, a number of semi empirical solvatochromic parameters representing “solvent polarity” have been applied to the quantification of medium effects on these properties. It is known that vibrational frequencies for a molecule dissolved in a liquid depend principally on the dielectric nature of medium (solvent polarity-dipolarily) when specific local interactions are absent. It was shown for solute molecules having large permanent dipole moments, that the solvent effect can be explained well by the Onsager reaction field model. This theory provides a means for calculating the energy of equilibrium dielectric solvation of an ideal no polarizable dipole (solute molecule) immersed in a dielectric continuum [29].

The measurement of such solvent-induced IR spectral changes has been extensively used in spectroscopic studies of solute/solvent interactions [23-26], especially hydrogen-bond interactions. When measured in solution, the band maxima of all simple stretching vibrations are displaced to lower wavenumbers whereas those of bending vibrations are shifted to higher wavenumbers. The most solvent-sensitive infrared stretching vibrations are those of X=O bonds (X = C, N, P, S), X-H bonds (X= C, N, O, S, halogens), and C-X bonds (X =halogens).

2.5. Intermolecular Forces

All solvent induced effects in the physical absorption of electromagnetic radiation depends on the intermolecular forces between solute and surrounding solvent molecules. Intermolecular forces include nonspecific forces such as purely electrostatic forces arising from the Coulomb forces between charged ions and dipolar molecules [i.e. ion/ion, ion/dipole, dipole/dipole and polarization forces that arise from dipole moments induced in molecules by nearby ions or dipolar molecules [i.e. ion/nonpolar molecule, dipole/non-dipolar molecule, two nonpolar molecules (dispersion energy)], as well as specific forces such as hydrogen-bonding between HBD and HBA ions or molecules, and electron-pair donor /electron-pair acceptor forces. Intermolecular solute/solvent interactions are highly complicated in nature and difficult to determine quantitatively.

Intermolecular interactions are essential in the chemical transformations and are responsible for organizing the structure of biological molecules. The intermolecular forces not only permit the interactions between solutes and solvents to be explained but also determine the properties of gases, liquids and solids. The main and commonly encountered intermolecular forces are categorized into the following [30] and [31].

2.5.1. Electrostatic (Ion-Dipole Forces)

Electrically neutral molecules with an unsymmetrical charge distribution possess a permanent dipole moment μ. If the magnitude of the two equal and opposite charges of this molecular dipole is denoted by q, and the distance of separation l, the dipole moment is given by $\mu = q.l$. When placed in the electric field resulting from an ion, the dipole will orient itself so that the attractive end (the end with charge opposite to that of the ion) will be directed toward the ions and the other repulsive end directed away. The potential energy of an ion-dipole interaction is given by

$$u_{ion-dipole} = -\frac{1}{4\Pi\varepsilon_{\circ}}.\frac{z.e.\mu.\cos\theta}{r^2} \tag{2.10}$$

Where $\varepsilon_{\circ}$ is the permittivity of a vacuum, z. e the charge on the ion, r the distance from the ion to the center of the dipole, and θ the dipole angle relative to the line joining the ion and the center of the dipole. Cos θ = 1 for θ = 0^0, i.e. in this case the dipole is positioned next to the ion in such a way that the ion and the separated charges of the dipole are linearly arranged Equation (2.10) gives the free energy for the interaction of an ionic charge z. e and a so-called ‘point-dipole’ (for which l = 0) in vacuum.

2.5.2. Dipole-Dipole Forces

Directional forces depend on the electrostatic interaction between molecules possessing a permanent dipole moment μ due to their unsymmetrical charge distribution. When two dipolar molecules are optimally oriented with respect to one another at a distance r then the force of attraction is proportional $1/r^3$ in fig .4a. An alternative arrangement is the antiparallel arrangement of the two dipoles as shown in Fig. 4b. Unless the dipole molecules are very voluminous, the second arrangement is the more stable one. The two situations exist only when the attractive energy is larger than the thermal energy. Therefore, the thermal energy will normally prevent the dipoles from optimal orientation. If all possible orientations were equally probable, that is, the dipoles correspond to freely rotating molecules, then attraction and repulsion would compensate each other. The fact that dipole orientations leading to attraction are statistically favored leads to a net attraction, which is strongly temperature dependent, according to (k_B = Boltzmann constant, T = absolute temperature).

$$u_{dipole-dipole} = \frac{1}{(4\Pi\varepsilon_{\circ})^2} \cdot \frac{2\Pi_1\mu_2^{2}}{3k_BTr^6} \tag{2.11}$$

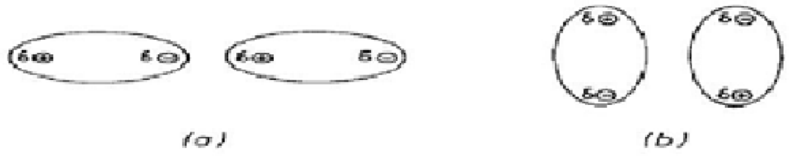

Figure 4: (a) ‘‘Head-to-tail’’ arrangement of two dipole molecules; (b) Antiparallel arrangement of two dipole molecules.

2.5.3. Dipole-Induced Dipole Forces (Polarization)

If we dissolve a polar substance in a non-polar solvent, the molecular dipoles of the solute are capable of distorting the electronic clouds of the solvent molecules inducing the appearance in these of new dipoles. The dipoles of solute and those induced will line up and will be attracted and the energy of this interaction (also called interaction of polarization or induction) is:

$$u_{dipole-inducedipole} = \frac{a_j\mu_j^2}{(4\Pi\varepsilon_{\circ})^2 r^6} \tag{2.12}$$

a_j is polarizability, μ is dipole moment and r intermolecular distance.

2.5.4. Instantaneous Dipole-Induced Dipole Forces (Dispersion)

Even when solvent and solute are constituted by non-polar molecules, there is interaction between them. It was F. London [31], who was first to face up to this problem, for which reason these forces are known as London’s forces, but also as dispersion forces, charge fluctuations forces or electro dynamic forces. Their origin is as follows: when we say that a substance is non-polar we are indicating that the distribution of the charges of its molecules is symmetrical throughout a wide average time span. But, without doubt, in an interval of time sufficiently restricted the molecular movements generate displacements of their charges which break that symmetry giving birth to instantaneous dipoles. Since the orientation of the dipolar moment vector is varying constantly due to the molecular movement, the average dipolar moment is zero, which does not prevent the existence of these interactions between momentary dipoles. Starting with two instantaneous dipoles, these will be oriented to reach a dispersion which will favor them energetically. The energy of this dispersion interaction can be given, to a first approximation, by:

$$u_{dispersion} = -\frac{1}{(4\Pi\varepsilon_{o})^{2}} . \frac{3a_{1}a_{2}}{2r^{6}} . \frac{I_{1}I_{2}}{I_{1}+I_{2}} \qquad (2.13)$$

Where α_1 and α_2 are the electronic polarizabilities and I_1 and I_2 are the ionization potentials of the two different interacting species [33].

2.5.5. Hydrogen Bonding

Hydrogen bonding has held particular interest in recent years due to the central role it plays with regard to molecular recognition in both biological and artificial systems [33]. The strength of hydrogen bond is at a maximum when the proton donor group and the axis of the lone pair orbital are collinear. The strength of the bond decreases as the distance between proton donor group and proton acceptor group increases. The effect of concentration on intramolecular and intermolecular H- bonding is markedly different. The bands that result from intermolecular bonding generally disappear at low concentrations. Intramolecular H- bonding persists at very low concentrations. IR spectroscopy is the leading method for identification of hydrogen bonds. For instance, the formation of an O-H--O hydrogen bond elongates and weakens the O-H bond. The resulting bathochromic shift (positive solvatochromism) of the O-H bond stretching frequency can be easily detected in the IR spectra and its magnitude indicates the strength of the hydrogen bond [35]. Hydrogen bonds appear in substances where there is hydrogen united covalently to very electronegative atoms (e.g., F, Cl, O and N) [36].

2.6. Solvatochromism

Solvatochromism is a solute-solvent interaction induced phenomenon that is manifested when absorption spectrum of chromophores in a given solution is compared with those in different solvents or in the gas phase [44]. Solvatochromic shifts are commonly exploited as simple univocal indices to classify the environment, but in reality, they reflect extremely complex phenomena involving many different intermolecular forces and being affected by coupled dynamical processes of both the molecular probe and the solvent.

Solvatochromic shifts are a result of physical intermolecular solute–solvent interaction forces (such as ion-dipole, dipole-dipole, dipole-induced dipole, hydrogen bonding, etc.), which above all tend to alter the energy difference between ground and excited state of the absorbing species containing the chromophore [8]. As a result of the spectroscopic excitation, the charge distribution of the molecule changes and thus the interaction will be different in the ground state and in the excited state of the molecule. The direction and size of the respective spectral shift depends directly on the difference in the solvation energy of the molecule in those two states.

The larger solvation energy of the ground state, as compared to that of the excited state, results in the negative solvatochromic shift of the spectral maximum. Alternatively, the stronger solvation of them excited state, as compared to the solvation of the ground state, leads to the decrease of the excitation energy and is reflected by the positive solvatochromic shift in the spectrum of the compound [31]

solvent polarity simply as the overall solvation capability i.e. solvation power of solvents, which in turn depends on the action of all possible nonspecific and specific intermolecular interactions between solute ions or molecules and solvent molecules [6]. Solvent polarity determines the solvent effect and is a commonly used term related to the capacity of a solvent for solvating dissolved charged or neutral, a polar or dipolar species. Attempts to express it quantitatively have mainly involved macroscopic physical solvent properties such as relative permittivity, dipole moment, or refractive index, but these parameters cannot effectively account for the multitude and specific interactions of solute-solvent on the molecular-microscopic level.

2.7 Basic Solvatochromism Equation

In different solvatochromic theories different solvent polarity parameters appear. concept of reaction field theory is useful in relating solvent effects with the change of transition infrared energy and frequency shifts in various spectroscopic applications [7]. The reaction field theory introduced by Onsager approximates a solute as a polarizable point dipole in the center of a spherical cavity immersed in a continuous medium with a dielectric constant. The presence of this solute dipole induces a dipole in the solvent molecules (the medium); this medium is considered as an isotropic homogeneous dielectric continuum, and this induced dipole generates an electric field (reaction field) that will in turn interact with the molecular dipole of solute to lead to net stabilization and thus, the local field at the location of the solute molecule, following Onsager's formalism is

$$\vec{F} = \vec{E_c} + \vec{E_r} = g(\varepsilon)\vec{E} + f(\varepsilon)\frac{\vec{\mu}}{2a^3} \tag{2.14}$$

Here $\overrightarrow{E_c}$ and $\overrightarrow{E_r}$ are the cavity and the reaction field, respectively, a is the spherical solvent cavity dimensions, $\vec{\mu}$ is dipole moment vector, $g(\varepsilon)$ is a function that depends of bulk dielectric constant and $f(\varepsilon)$ is the Onsager dielectric continuum function of the reaction field with dependence in bulk dielectric constant and gives a measurement of the strength of the reaction field. In terms of molecular orbital theory, the electrostatic solute-solvent interaction is considered as an additional term in the Hamiltonian of the isolated molecule H_0 and then, the Hamiltonian for the molecule with the reaction field of the solvent ($\hat{H}_P$) is represented by the standard perturbation statement as

$$\hat{H}_P = \hat{H}_\circ + \hat{\mu}\frac{\mu}{2a^3}f(\varepsilon) \tag{2.15}$$

where, $\hat{\mu}$ is the dipolar operator and $f(\varepsilon)$ is the Onsager reaction field function, however, it can be considered as a general dielectric continuum function in terms of bulk dielectric constant (ε) and/or optical dielectric constant (n^2). In this model, different dielectric continuum functions $f(\varepsilon_r)$ has been used, such as the Liptay, Lippert-Mataga, Mac Rae, Bakhshiev [5,26].

2.7.1 Liptay Equation

For a molecule having a permanent dipole moment $|\mu_g| = \mu_{gz}$ in the vibrational ground state (in the Z-direction) and a permanent dipole moment $|\mu_a| = \mu_{az}$ in the excited state, the solvent dependence of the wave number $\tilde{\nu}_a^{sol}$ of the absorption maximum is given to a good approximation by the following equation.

$$\tilde{\nu}_a^{\ sol} = \tilde{\nu}_a^o - \frac{(\mu_{az} - \mu_{gz})(F_{RM})_z}{hc} - \frac{2(n^2-1)}{a^3(2n^2)}D \tag{2.16}$$

$\tilde{\nu}_a^o$ is the wave number of the absorption maximum in the free molecules gaseous state? The term D describes the solvent dependence of the position of the absorption band due to the dispersion interactions between the dissolved molecule and the surrounding solvent molecules.

The effective electric field F_{RM} in Eq. (2.16) is the mean of the reaction fields of the dissolved molecule in the ground state and in the excited state. i.e. the primary state after the excitation process. The Z-component of F_{RM} is

$$(F_{RM})_z = \frac{1}{a^3}\left[\frac{\varepsilon_r - 1}{2\varepsilon_r + 1}\left(1 - \frac{2a_{gz(\varepsilon_{r-1})}}{a^3(2\varepsilon_r + 1)}\right)2\mu_{gz}\right] + \frac{n^2-1}{2n^2-1}\left[1 - \frac{2a_{gz}(n^2-1)}{a^3 2n^2 - 1}(\mu_{az-}\mu_{gz})\right] \tag{2.17}$$

Where ε_r - Dielectric constant of the solution, n - Refractive index, a_{gz} Z-component of the polarizability tensor, a_g of the molecule in the ground state, transformed to principal axes. The Eq. (2.17) can be represented by a function that depends on the properties of the dissolved molecule ($\mu_{gz}, \mu_{az,} a_{gz}, a, D$) and on the dielectric constant and refractive index of the solvent. At least two parameters that depend on the solvent are necessary for the general description of the solvent-dependence of the absorption bands. A general description involving only one solvent-dependent parameter that has repeatedly been sought, is fundamentally impossible. In the case of a dissolved non-polar molecule, however, FRM disappears, leaving only the term containing the refractive index n in Eq. (2.17), so that the solvent dependence of the wave numbers can now be described by a single parameter (e.g. by n).

For molecule having a large dipole moment in the ground state (μ_{gz}) and a large change in dipole moment ($\mu_{az} - \mu_{gz}$), the solvent-dependence due to the term in n is small, and the effect of the solvent on the wave number approximately depends only on ε_r [38, 23].

2.7.2 Lippert-Mataga Equation

In the description of general solvent effects, the solute is considered to be a dipole in a continuous medium of uniform dielectric constant. This model does not contain any chemical interactions, and hence cannot be used to explain the other interactions which affect the absorption. The other interactions, such as hydrogen bonding or formation of charge transfer states, are sometimes detected as deviations from the general theory. The interactions between the solvent and chromophore affect the energy difference between the ground and excited states. To a first approximation this energy difference (in cm^{-1}) is a property of the refractive index (n) and dielectric constant (ε_r) of the solvent and is described by the Lippert-Mataga equation [24].

A simplification of Liptay equation was first developed by Lippert and Mataga. It is based on Onsager's reaction-field theory, assuming a point dipole situated in the center of the spherical cavity with radius a in homogeneous and isotropic dielectric with relative permittivity ε_r and neglecting the mean solute polarizability α in the states involved in the transition ($\alpha \cong \alpha_e \cong \alpha_g \cong 0$) [24]. Lippert–Mataga equation is as follows:

$$\Delta\tilde{\nu} = \tilde{\nu}_a - \tilde{\nu}_f = \frac{1}{4\Pi\varepsilon_\circ}\cdot\frac{1}{2hca^3}\left(\mu_{e-\mu_g}\right)^2 \Delta f + conts \qquad (2.18)$$

$$\text{With } \Delta f = f(\varepsilon_r) - f(n^2) = \left[\frac{\varepsilon_{r-1}}{2\varepsilon_r + 1} - \frac{1}{2}\left(\frac{n^2 - 1}{2n^2 + 1}\right)\right] \qquad (2.19)$$

Where $\Delta\bar{\nu}$ is the frequency shift (in cm^{-1}) between absorption and emission, Δf is the orientation polarizability, $f(\varepsilon_r)$ describes the total polarization, $f(n^2)$ represents the induction polarization and μ_e and μ_g are the excited-state and ground-state dipole moments, [25, 26].

The refractive index (n) is a high-frequency response and depends on the motion of electrons within the solvent molecules, which is essentially instantaneous and can occur during light absorption. In contrast, the dielectric constant (ε_r) is a static property, which depends on both electronic and molecular motions. The latter being solvent reorganization around the excited state.

An increase in refractive index allows both the ground and excited states to be instantaneously stabilized by movements of electrons within the solvent molecules. This electron redistribution results in a decrease in the energy difference between the ground and excited states. An increase in ε will also result in stabilization of the ground and excited states. However, the energy decrease of the excited state due to the dielectric constant occurs only after reorientation of the solvent dipoles [25].

The first term $(\varepsilon_r-1)/(2\varepsilon_r+1)$ accounts for the spectral shifts due to both the reorientation of the solvent dipoles and to the redistribution of the electrons in the solvent molecules. The second term $(n^2-1)/(2n^2+1)$ accounts for only the redistribution of electrons. The difference of these two terms representing the solvent's orientation polarization, accounts for the spectral shifts due to reorientation of the solvent molecules, and hence the term orientation polarizability [33, 25].

2.7.3 McRae Equation

Here, the molecular polarizability was included and assumes an approximate relationship between solvent cavity size and solute molecular polarizability such as $a = \left(a^3/2\right)$. This approach allows self-consistent feedback between the solvent reaction field and the polarizable solute dipole as in Onsager's model for the dielectric constant of polar liquids [41, 42]

$$\tilde{\nu}_a - \tilde{\nu}_f = \frac{2\left(\mu_e - \mu_g\right)^2}{4\Pi\varepsilon_\circ hca^3}\Delta f \qquad (2.20)$$

The approximation $a = (a^3/2)$ yields $\Delta f = \left[\frac{\varepsilon_{r-1}}{2\varepsilon_r+1} - \frac{1}{2}\left(\frac{n^2-1}{2n^2+1}\right)\right]$ (2.21)

By combining Eq. 2.20 and 2.21

$$\tilde{\nu}_a = \tilde{\nu}_a^o + \frac{2\mu_g\left(\mu_e-\mu_g\right)^2}{4\Pi\varepsilon_\circ hca_\circ^3}\left[\frac{\varepsilon_{r+1}}{\varepsilon_r+2} - \frac{n_{2-1}}{n^2+2}\right]\frac{2n^2+1}{n^2+2} \qquad (2.22)$$

2.7.4 Bakhshive Equation

In order to express the solvent influence on the bands shifts Bakhshive uses the polarity function $f\left(\varepsilon,n\right)$ and $f(n)$.

$$f\left(\varepsilon,n\right) = \frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2} \qquad (2.23)$$

$$f\left(n\right) = \frac{n^2-1}{n^2+2} \qquad (2.24)$$

Usually, one checks multiparameter linear correlations of the type:

$$v^a = v_o^a + c_1^a f\left(\varepsilon,n\right) + c_2^a f\left(n\right) + c_3^a \delta H \qquad (2.25)$$

where the correlation coefficient v_o^a and c_1^a are determined by statistical methods, in such a way that the standard deviations are the smallest. The first term in the relation Eq. (2.25) signifies the wave number at the maximum of the electronic band measured in the gaseous phase of the spectrally active molecule. The middle terms give the spectral shifts induced by the universal interactions. The last term from Eq. (2.25) was added to take into consideration the contribution of the specific interactions to the total spectral shift [43]. In Bakhshiev theory, the correlation coefficients c_1^a from Eq. (2.25) depend on the microscopic electro-optic parameters of the spectrally active molecule. According to the results obtained by Bakhshiev and Perov, c_1^a coefficient have the following expression

$$c_1^a = \frac{2}{a^3}\frac{2n^2+1}{n^2+2}\left(\mu_g\mu_e\cos\theta - \mu_{g^2}\right) \qquad (2.26)$$

But in order to determine the polarity function equation proposed by Bakhshiev the last term in Eq. (2.25), which is the contribution of the specific interactions, excluded and one gets the equation Eq. (2.25) [26].

$$\tilde{\nu}_a = \tilde{\nu}_a^\circ + \frac{2\mu_g\left(\mu_e-\mu_g\right)^2}{4\Pi\varepsilon_\circ hca_\circ^3}\left[\frac{\varepsilon_{r+1}}{\varepsilon_r+2} - \frac{n_{2-1}}{n^2+2}\right]\frac{2n^2+1}{n^2+2} \qquad (2.27)$$

3. OBJECTIVES

3.1 General Objective

The general objective of this study is to investigate solvent-dependent polarity parameter ε_m using FTIR spectroscopy on nicotinamide in binary mixture of solvents.

3.2 Specific Objectives

The Specific Objectives of this Study are to;

- Observe the effect of binary mixture of solvents on the vibrational frequency C=0 stretching of the Nicotinamide.
- Correlate the wave number functionality on mole fraction of vibrational frequency of C=O of nicotinamide in binary mixture of solvents.
- Assess solvent polarity parameter from the linear regression of wave number on dielectric constant of the mixture.
- Suggest solvent dependence polarity parameter ε_m to recalculate and redefine solvatochromic equation.

4. EXPERIMENTAL DETAILS

4.1. Materials and chemicals, Methods and Procedures

Nicotinamide was procured from Sigma Aldrich with 99% purity was used for this thesis. The amide was studied without further purifications, Acetonitrile (99.9%, Sigma-Aldrich, Switzerland), Diethyl ether (99.8% Carlo Erba reagents group), 1,4–Dioxane (99% Scharlaw, Spain) and Cyclohexane (Spectroscopic grade, Riedel de Haen, Germany) solvents were used for the investigation for studying solvation power. Distilled water and acetone (laboratory reagent grade) were used for cleaning purpose all the times. Micro balance was used for measuring weight of the solvents and PerkinElmer Spectrum 65 FT-IR spectrometer to record the spectra.

4.2. Methods and Procedures

The dilute solution of Nicotinamide was prepared in binary mixture of solvents (1,4-dioxane-cyclohexane and diethyl ether -acetonitrile and acetonitrile -dioxane) by varying the mole fraction of solvents and the size and concentration of nicotinamide is kept constant. After binary mixture of the solvents were prepared.

IR spectra of the amides solutions were measured using FT-IR spectrophotometer (PerkinElmer Spectrum 65 FT-IR spectrometer). The infrared spectra of the solution were recorded in a spectral range 1720 cm^{-1}- 1650 cm^{-1}. A cell ZnSe surface for the reflection were employed since nicotinamide is well soluble enough in the binary mixture. All the measurements were performed under room temperature and pressure. Before measuring the spectra of the sample base line correction were done. to makes binary solution which used to study the solvent effects on Nicotinamide.

5. RESULT AND DISCUSSION

The infrared absorption spectra of Nicotinamide were recorded with solvents of various composition. The solvents used are mixture of 1,4- dioxane - cyclohexane, mixture of acetonitrile – diethyl ether and acetonitrile-Dioxane was prepared in varying the mole fraction with fixed composition of Nicotinamide in order to see the solvent dependence absorption bands shift, to correlate the wave number with the mole fraction and wave number as the function of mixture of the dielectric constant which are solvent dependent.

5.1 Spectral Shift of Nicotinamide in Binary Mixture of DXN–CHX.

The binary mixture of 1,4-dioxane and cyclohexane were prepared in varying the mole fraction with fixed composition of Nicotinamide in order to absorbs the trend in solvent influence on the band shift and to find out the wave number functionality on mole fraction. For this purpose, $\nu_{C=O}$ was selected due to the presence of observable and well identified spectral shift in the given binary mixture of solvents. The important frequency of Nicotinamide is associated with the $\nu_{C=O}$ stretching vibration which falls in the ranges of 1650-1720 cm^{-1}. The observed infrared spectra of nicotinamide in the mixture are presented in figure 3a, b, c and the maxima wave number as mole fraction in table 2.and wave number as the function of mixture of dielectric constant were summarized in Table 3.

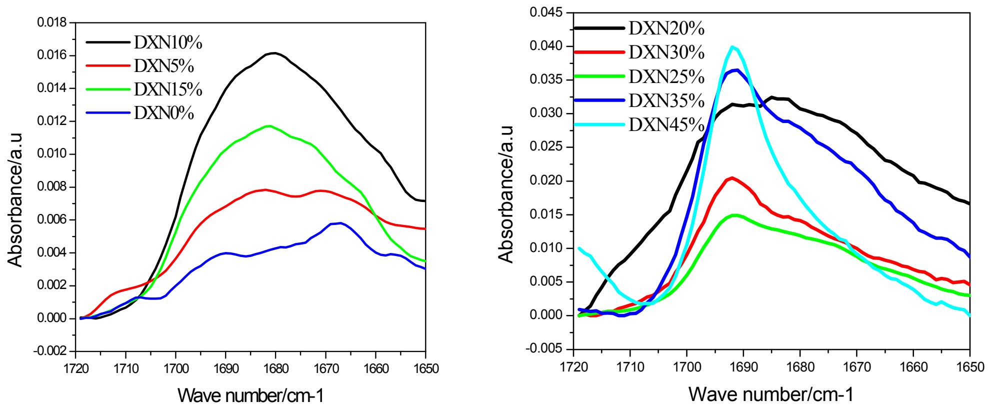

Figure 3 a and b: Peak position of $V_{C=O}$ absorption band of Nicotinamide in binary mixture of 1,4- dioxane –cyclohexane.

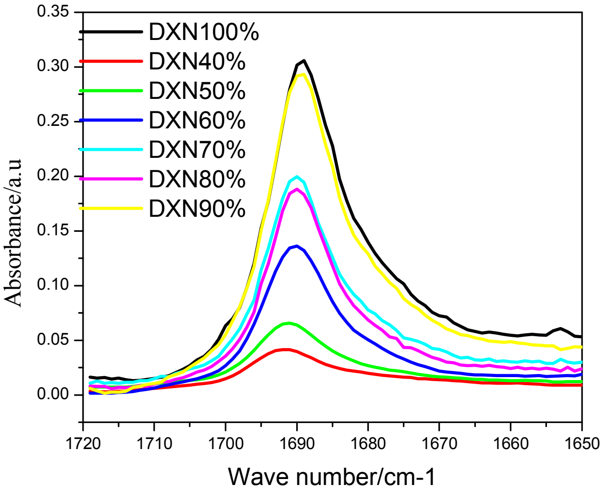

Figure 3c: Peak position of $\nu_{C=O}$ absorption band of Nicotinamide in binary mixture.

Figure 3a, and b we have observed that it is the mole fraction of DXN increases (0-20%) the trend of $\nu_{C=O}$ stretch vibration has the frequency follow the normal trend but the spectra are broad and show convolution which indicates the presence of two structure at the equilibrium by the delocalization. And also, one can clearly have observed that as the mole fraction increases (25-45%)the broadness of the peak changes to somehow sharp and finally become sharp due to one of the structure dominate.

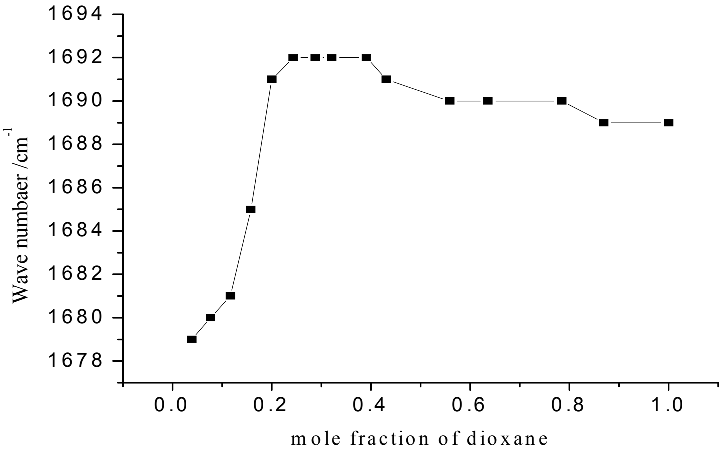

Figure 4:The trend of peak position of nicotinamide spectra in varying mole fraction of dioxane.

From figure 4. varying the concentration of the solvents in the mixture the solvent dependent band shifts were clearly observed. As the mole fraction of dioxane is increased (0.00-0.2434) the Infrared absorption of nicotinamide in the binary mixture shifts to the higher energy or to the longer wave number. That the dipole moment the nicotinamide in the ground state is larger than the excited states $\mu_g > \mu_e$). From this one can conclude that the binary mixture better stabilizes the ground state than the excited state which results negative solvatochromism [31] in this case the separation between the two states increases, then the excitation energy increased. This is due to the higher energy in the given range [6].

No spectral shift observed in the mole fraction (0.2434-0.431) which indicates preferentially solvation takes places.

At higher mole fraction of the dioxane (0.43-1.00) the absorption spectra in the binary mixture decreased in small extent revealed that the dipole moment of the excited state of nicotinamide is larger than the ground states. This show that the binary mixture better stabilizes the excited states results positive solvatochromism [31]. then the separation of the two state decreases which have lower solvation energy. That is the reason why the spectra shift to lower energy.

Table 2 :The mole fraction of 1,4-dioxane and the IR spectra shift of Nicotinamide.

$X_{dioxane}$	0.00	0.039	0.077	0.117	0.158	0.200	0.243	0.288	0.321	0.391	0.431	0.559	0.636	0.788	0.869	1
$\nu_{C=O}$	1667	1671	1680	1681	1685	1691	1692	1692	1692	1692	1691	1690	1690	1690	1689	1689

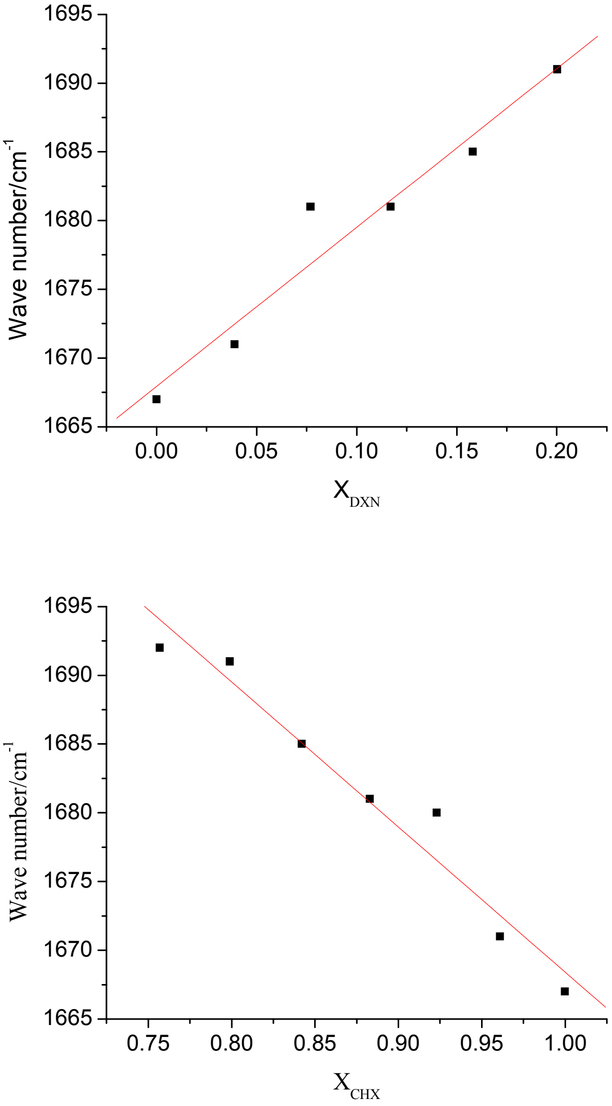

Figure 5 a, b: The wave number as the function of mole fraction of each component of the mixture.

The above figure 5a and b. the fit of the graphs of the wavenumber versus mole fraction results in better linear relationship with a correlation factor of $R = 0.972$ and $R= 0.979$ on the whole range. Therefore, the wave number functionality on the mole fraction, for which the equation (3.1) is given below, may be used as a better way for approximating the actual solvent dependent polarity parameter ε_m based on the shift that can be obtained in a specific solvent.

$$\bar{v}(x_2) = slope.x_2 + \bar{v}(x_2 = 0) \qquad (3.1)$$

where $\bar{v}(x_2)and\bar{v}(x_2 = 0)$ represent the wave number at any mole fraction value x_2 and $x_2 = 0$, respectively.

Commonly, polarity is expressed in terms of the relative permittivity (dielectric constant) ε_r, which is a ratio of capacitance in solution to capacitance in vacuum. As a result, ε_r only accounts for the dipolar interactions between the solvent and the solute molecules but not all the rest of interactions like quadrupole, hexapole, octupole, dispersive, etc. Therefore, it generally leads to unavoidable discrepancies in theoretical interpretation of solvatochromic shifts observed experimentally.

The dielectric constant of the binary mixture is determined from the mole fraction and dielectric constant of the component of each solvent by

$$\varepsilon_m = \varepsilon_{r1} x_1 + \varepsilon_{r2} x_2 \qquad (3.2)$$

Where $\varepsilon_{r(1,2)}$ or ε_m theoretical calculated dielectric constant of the mixture, $\varepsilon_{r1}, \varepsilon_{r_2}$ X_1 and X_2 are dielectric constant and mole fraction of solvent 1 and solvent 2 respectively. With this regard, the stronger solvatochromic shift commonly observed than expected, from the dipolarity determined dielectric constant ε_r= 2.209 can serve as appropriate example. This “anomalous” solvatochromic behavior 1,4-dioxane lead to Baumann et al. to suggest a solvent (44) corrected dielectric constant ε_r= 6.0. this value is employed in this thesis.

Table 3:The maximum wave number and the dielectric constant of the binary mixture.

$\varepsilon_{r(1,2)}$	2.02	2.18	2.33	2.49	2.65	2.82	2.99	3.17	3.30	3.58	3.74	4.25	4.99	4.99	5.48	6
$\nu_{C=O}$	1667	1671	1680	1681	1685	1691	1692	1692	1692	1692	1691	1690	1690	1690	1689	1689

As seen from the table above, the dielectric constant of the mixture fails between the dielectric constant of each components. The functionality of the wave number as the function of dielectric constant and correlation factors of binary solvent mixture is given figure 7.

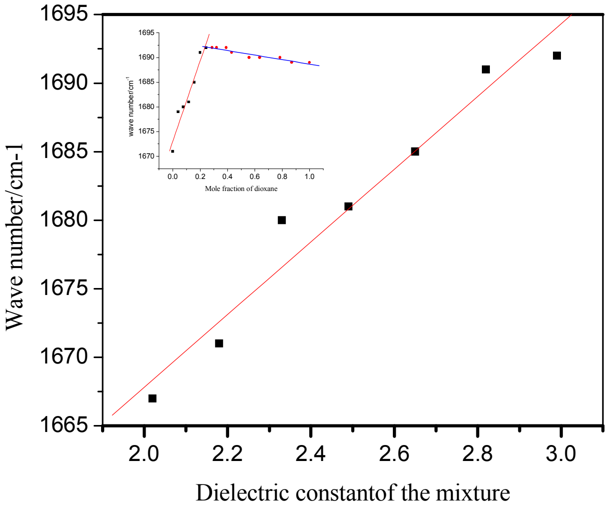

Figure 6: curve fit of wave number as the function of dielectric constant

As one can see from the figure vibrational wave number has the functionality to the dielectric constant of the mixture with range 2.02-2.99 observed, however the dielectric constant of mixture 3.17-6 were not seen since the presence of preferential solvation with one solvent spectral shift were not occurred.

The fit of the graph of the wavenumber versus dielectric constant of the mixture ε_m, results in excellent linear relationship with a correlation factor of $R = 0.978$. The wave number functionality on the dielectric constant of the mixture equation (3.2), suggest that it should possible to develop and recalculate the solvent dependent dielectric constant as the solvent polarity parameter from solvents of binary mixture which used to redefine and recalculate the solvatochromic equation to overcome the problem associated with dielectric constant.

$$\bar{v}(\varepsilon_{m2}) = m\varepsilon_{m2} + \bar{v}(\varepsilon_{m2} = 0) \qquad (3.2)$$

where m is the slope $\bar{v}(\varepsilon_{m2}) and \bar{v}(\varepsilon_{m2} = 0)$ represent the wave number at any $\varepsilon_{m_1} and \varepsilon_{m_2} = 0$ value respectively.

Then it should important to recalculate and modify solvatochromic equation by the solvent dependent dielectric constant using composition of binary solvent mixture to express the solvent dependence band shift (to expresses the solute -solvent interaction) instead of expressing in dielectric constant. The former accounts all the solute / solvent interaction in the given mole fraction range to overcome the drawback of the dielectric constant.

The precise dielectric constant data of the binary mixture are necessary for understanding the nature of intermolecular interaction and structural rearrangement [45].

5.2. Spectral Shift of Nicotinamide in Binary Mixture of DEE - ACN

Infrared spectra of nicotinamide were recorded in binary mixture of solvents to formulate the functionality of the wave number as the function of composition of the solvent and dielectric constant of mixture the observed infrared spectra shift of nicotinamide in the mixture is presented in fig 7.

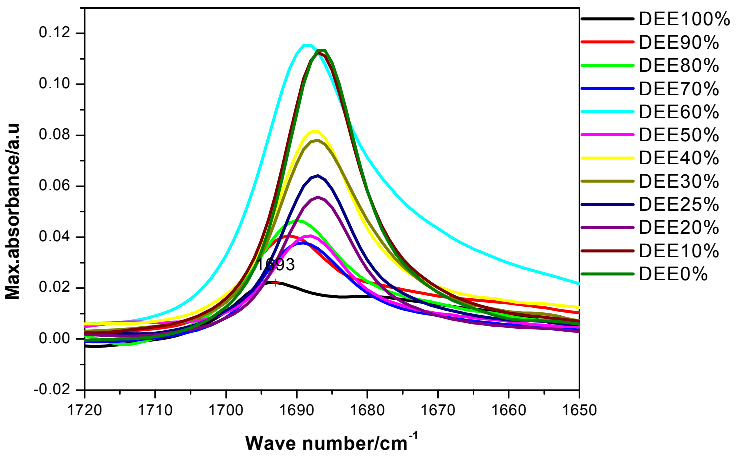

Figure 7 :IR spectra of Nicotinamide in varying mole fraction of DEE in mixture of DEE-ACN.

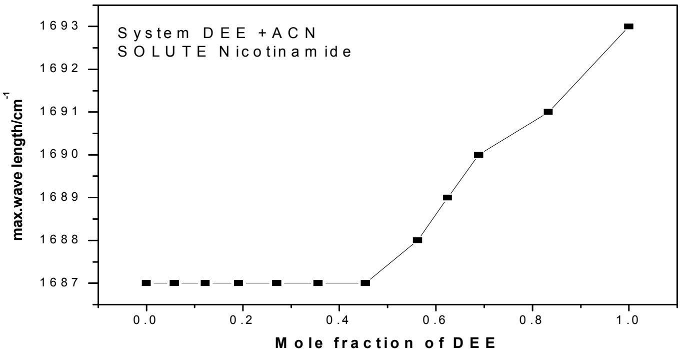

Figure 8:Maximum wave number versus mole fraction of DEE-CAN

Form figure 8, the mole fraction of diethyl ether increases (0.0-0.454) there is no spectra shift and the vibrational wave number shift to the higher wave number when the mole fraction DEE increased (0.454-1.00)

It is suggested the nicotinamide preferentially solvation takes places, results in no spectral shift have been seen. The mixture of solvents serves as to stabilized the ground states than the excited states (better stabilization the molecule in the ground state by solvation), in this case the separation between the two states are increased and the solvation energy is large. This is the reason for the spectra shift to the higher wave number /energy / at the more mole fraction of diethyl ether increases. That dipole moment in the ground state is larger than the dipole moment of the excited state results negative solvatochromism [31].

The vibrational spectral shift as the function mole fraction were summarized in the following table 4 and figure 10.

Table 4:Spectral shift trends of $\nu_{C=O}$ in varying mole fraction of DEE in the mixture

X_{DEE}	0	0.058	0.122	0.191	0.270	0.356	0.454	0.562	0.624	0.689	0.833	1
$V_{C=O}$	1687	1687	1687	1687	1687	1687	1687	1688	1689	1690	1691	1693

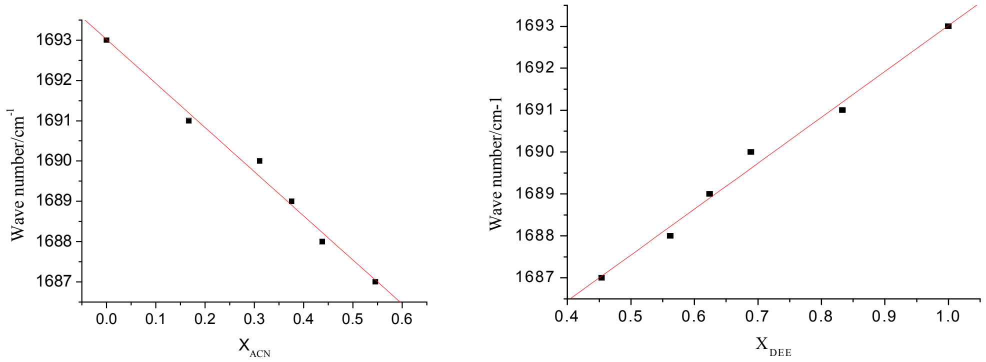

Figure 9:Maximum wave number versus mole fraction of DEE and ACN.

Form the graph all mole ranges are covered and the wave number functionality have been seen.

An excellent linear relationship with a correlation factor of $R = 0.994$ and R= 0.995 over the whole range of the solution have been see from the fit of the graph of the wavenumber versus mole fraction. Therefore, the wave number functionality on the mole fraction, for which the equation is given (3.3) may be used as a better way for approximating the actual solvent dependent polarity parameter ε_m based on the shift that can be obtained in a specific solvent.

$$\bar{v}(x_2) = mX_2 + \bar{v}(x_2 = 0) \qquad (3.3)$$

where represent the wav $\bar{v}(x_2) and \bar{v}(x_2 = 0)$ number at any mole fraction value x_2 and $x_2 = 0$, respectively.

Then polarity of solvent would be better expressed in terms of the solvent dependent dielectric parameter ε_m, rather than dielectric constant ε_r ,which only accounts for the dipolar interactions between the solvent and the solute molecules, but not all the rest of interactions like quadrupole, octa pole, dispersive, etc. interactions. Therefore, it generally leads to avoidable discrepancies in theoretical interpretation of solvatochromic shifts observed experimentally.

The dielectric constant of the mixed solvent is the average of the solvent dielectric constant weighing the mole fraction of each solvent as given [46]

$$\varepsilon_m = \sum \varepsilon_{ri} x_i \qquad (3.4)$$

the theoretical dielectric constant of the mixture is determined from the mole fraction of each solvent and the dielectric constant of the solvents by

$$\varepsilon_m = \varepsilon_{r1} x_1 + \varepsilon_{r2} x_2 \qquad (3.5)$$

Where $\varepsilon_{r(1,2)}$ or ε_m theoretical calculated dielectric constant of the mixture, $\varepsilon_{r1}, \varepsilon_{r_2}$ X_1 and X_2 are dielectric constant and mole fraction of solvent 1 and solvent 2 respectively. ($\varepsilon_{r(ACN)} = 37.5$ & $\varepsilon_{r(DEE)}$ = 4.33) [45] and the result is presented in the table.

Table 5:Spectral shift trends of Nicotinamide in varying mole fraction of in DEE +CAN.

$\varepsilon_{r(m)}$	37.5	35.6	33.5	31.2	28.5	25.69	22.44	18.86	16.80	14.65	9.87	4.33
$V_{C=O}$	1687	1687	1687	1687	1687	1687	1687	1688	1689	1690	1691	1693

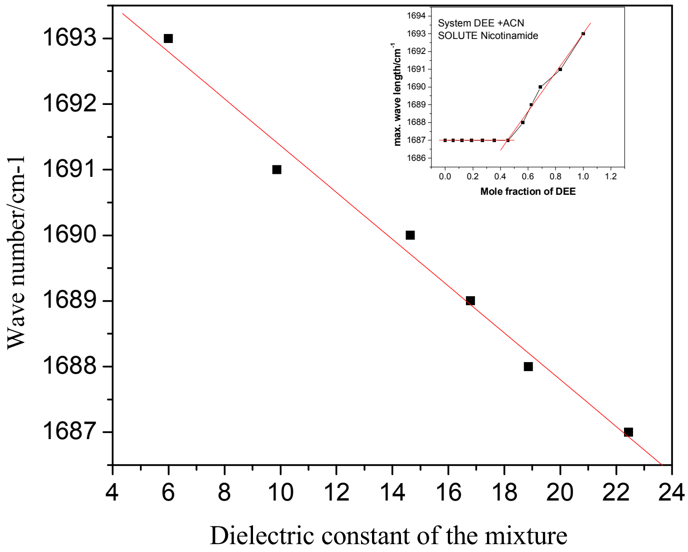

Figure 10:The graph of wave function as the function of dielectric constant of the mixture.

The linear fit from figure 10 we can clearly have observed that the wavenumber versus dielectric constant of the mixture results in an excellent linear relationship with a correlation factor of $R = 0.996$. Therefore, the wave number functionality on the dielectric constant of the mixture is given below equation (3.4). Which revealed that there is good relationship between the wave number and ε_m hence one is dependable on the other from this it should possible to determine the solvent dependent dielectric constant which used to redefine recalculate the solvatochromism equation instead of using dielectric constant to express the solvent polarity quantitatively which account all the intermolecular interactions.

$$\bar{\nu}(\varepsilon_{m_2}) = m\varepsilon_{m_2} + \bar{\nu}(\varepsilon_{m_2} = 0) \tag{3.6}$$

Here the whole range of dielectric constant are not seen in the wave number versus dielectric constant of the mixture. From this point of view, it should possible to recalculate and redefine solvent polarity parameter as solvent dependent dielectric constant which account the all solute solvent interaction.

The same result and conclusion have been achieved from the binary mixture of acetonitrile and 1,4-dioxane on the nicotinamide recorded. the graph table give at the appendices.

6.CONCLUSION

In this work, the effect of binary mixture of solvent in different mole fraction on the vibrational absorption spectra of nicotinamide were studied. Up on varying mole fraction of solvents the vibrational spectra bands shifted to higher energy when non-polar character dominates.

The wave number functionality on the mole fraction and ε_m expresses solvent polarity which is used as a better way for approximating the actual solvent dependent polarity parameter based on the shift that can be obtained in a specific solvent.

From the correlation of vibrational wave number on the solvent dependent dielectric constant ε_m gives information to modify and recalculate the solvent dependent dielectric constant which consider the overall solute solvent interaction which is meaning full and physical. Since solvent polarity is expressed in terms of the relative permittivity (dielectric constant) ε_r, only accounts for the dipolar interactions between the solvent and the solute molecules, but not all the rest of interactions like quadrupole, octa pole, dispersive, etc. interactions. Therefore, it generally leads to unavoidable discrepancies in theoretical interpretation of solvatochromic shifts observed experimentally, then to overcome the problem the best solution is expressing solvent polarity in actual solvent dependent ε_m as polarity parameter, which account all the solute -solvent interactions. hence solvatochromic equation must be recalculated and refined based on the ε_m rather than ε_r to overcome the problem.

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Appendances

Appendance A

Figure 1.the spectral shift of nicotinamide in binary mixture of DXN and CHX.

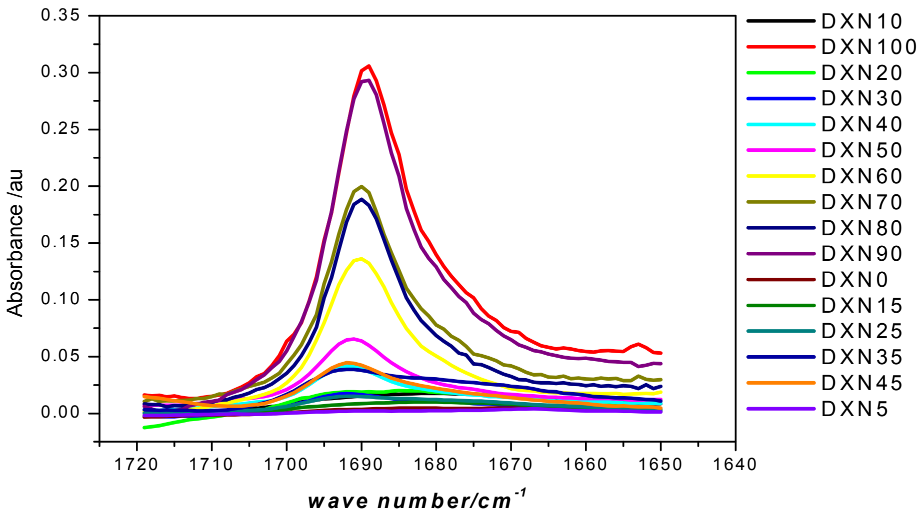


Table 1: Frequency shift of absorption bands of Nicotinamide in dioxane-cyclohexane mixture.

% of DXN	Mass of DXN	Mole of DXN	%of CHX	Mass of CHX	Mole of CHX	X $_{DXN}$	X CHX	$\nu_{C=O}$ in cm^{-1}
0	0g	0	100	10g	0.12	0	1.0	1671
5	0.5g	0.0045	95	9.5g	0.112	0.039	0.961	1679
10	1g	0.0089	90	9g	0.107	0.077	0.923	1680
15	1.5g	0.0134	85	8.5g	0.101	0.117	0.883	1681
20	2.0g	0.0179	80	8g	0.095	0.158	0.842	1685
25	2.5g	0.0223	75	7.5g	0.089	0.2003	0.799	1691
30	3.0g	0.0268	70	7g	0.083	0.2434	0.757	1692
35	3.5g	0.03125	65	6.5g	0.077	0.288	0.712	1692

40	4.0g	0.0357	60	6g	0.0714	0.321	0.679	1692
45	4.5g	0.0417	55	5.5g	0.065	0.391	0.609	1692
50	5.0g	0.0446	50	5g	0.05	0.431	0.569	1691
60	6.0g	0.054	40	4g	0.0426	0.559	0.441	1690
70	7.0g	0.0625	30	3g	0.0312	0.636	0.364	1690
80	8.0g	0.0714	20	2g	0.024	0.748	0.252	1690
90	9.0g	.0803	10	1g	0.012	0.869	0.13	1689
100	10g	0.0893	0	0g	0	1.0	0	1689

Appendence B

Table 3: the mole fraction of each solvent with dielectric constant of the binary mixture

X_{DXN}	1	0.874	0.767	0.523	0.354	0.309	0.276	0.2	0.13	0.08	0.04	0
X_{ACN}	0.0	0.126	0.233	0.477	0.646	0.691	0.724	0.80	0.87	0.92	0.87	1
$\varepsilon_r(m)$	1.105	3.21	4.99	9.04	11.89	12.64	13.19	14.46	15.63	16.5	17.1	17.8

$\varepsilon_{r(m)}$	37.5	35.58	33.45	31.16	28.54	25.69	22.44	18.86	16.80	14.65	9.87	4.33
X_{ACN}	1	0.942	0.878	0.809	0.730	0.644	0.546	0.438	0.376	0.311	0.167	0
X_{DEE}	0	0.058	0.122	0.191	0.270	0.356	0.454	0.562	0.624	0.689	0.833	1
$V_{C=O}$	1687	1687	1687	1687	1687	1687	1687	1688	1689	1690	1691	1693

Appendices C

Graph absorbance versus wave number of Nicotinamide in binary mixture of ACN and DXN.

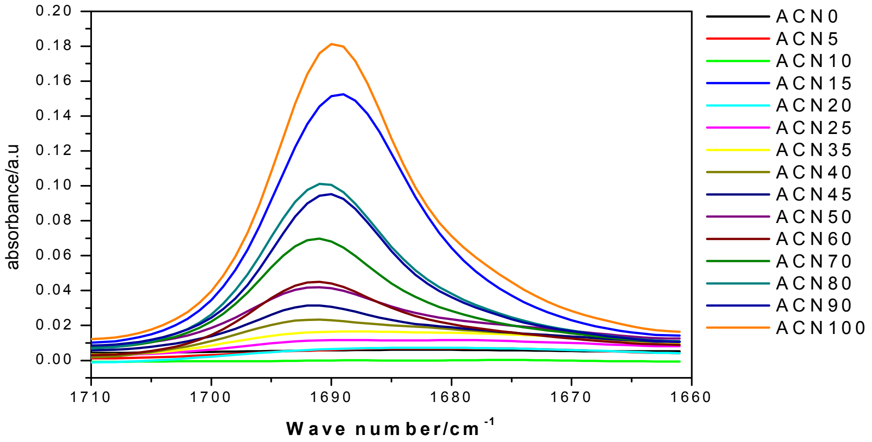
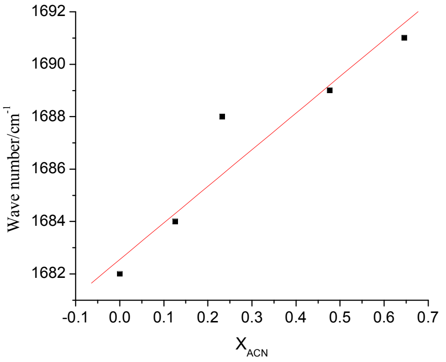
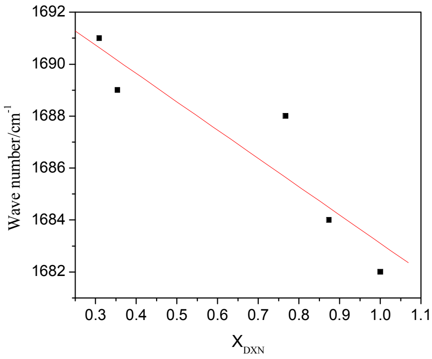


Table 6: Mole fraction of ACN and DXN max. absorbance of VC=O

X_{DXN}	X_{ACN}	$V_{C=O}$
1	0.0	1682
0.874	0.126	1684
0.767	0.233	1688
0.523	0.477	1689
0.354	0.646	1691
0.309	0.691	1691
0.276	0.724	1691
0.20	0.80	1691
0.13	0.87	1691
0.08	0.92	1691
0.04	0.96	1690
0	1.0	1690





Appendices D

Trends of spectral shit in varying mole fraction of ACN

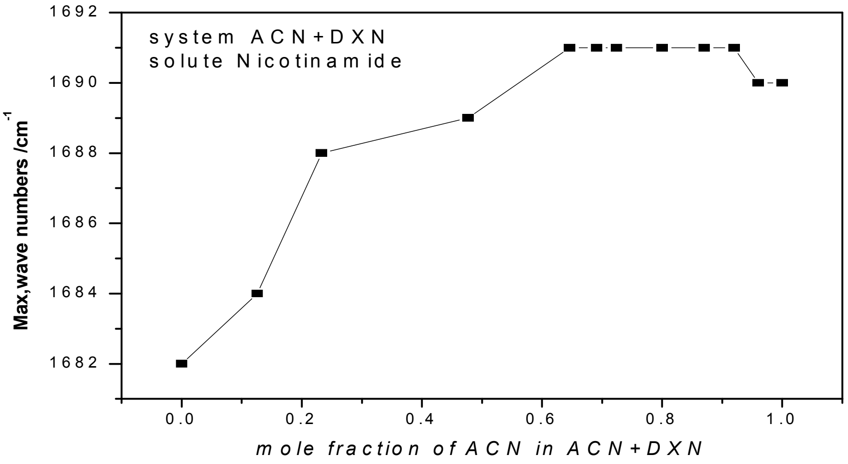


Table: the dielectric constant of the mixture and their wave length.

$\varepsilon_r(m)$	6.00	10.00	13.34	18.03	26.35	27.77	28.81	31.20	33.41	34.98	36.24	37.5
$V_{C=O}$	1682	1684	1688	1689	1691	1691	1691	1691	1691	1691	1690	1690