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Empirical Dielectric Constant from Optical Measurements

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Empirical Dielectric Constant from Optical Measurements

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This is certify that the thesis prepared by Matiyos Gebrekidan Yebiyo, entitled: **On Empirical Dielectric Constant From Optical Measurements** and submitted in partial fulfillment of the requirements of the Degree of Master of Science (Physical Chemistry) compiles with regulation of the University and meets the accepted standards with respect to originality and quality.

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Abstract

Solvent effects on the vibrational and electronic absorption band of different compounds were determined. In increasing the polarity of the solvent a shift of the absorption maxima to lower energy was observed in all compounds. The solvation dielectric constant of dioxane was empirically determined from correlation plot of Lippert-Mataga polarity function versus vibrational absorption maxima of picolinamide and other amides (Acrylamide, propylamide etc.). From linear fit the value of solvation dielectric constant of dioxane was goes to infinite ($\varepsilon_{r,solv} = \infty$), which is unrealistic and unphysical. In addition, from correlation plot of Lippert-Mataga polarity function versus electronic absorption maxima of DMABA, BBA and NBA the value of solvation dielectric constant of dioxane was found to be 3.4, 3.8 and 7.7, *respectively. These values were inconsistent and there is no universal solvation dielectric constant from electronic spectroscopy.*

Key word: Lippert-Mataga, polarity function, solvation dielectric constant, picoline amide, 1, 4-Dioxane

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List of symbols and abbreviations

ACN	Acetonitrile
BBA	Bromobenzaldehayde
CCl_4	Carbon tetrachloride
CF	Chloroform
CHX	Cyclohexane
DCE	1, 2-Dichloroethane
DCM	Dichloromethane
DEE	Diethyl ether
Dioxane	1, 4-Dioxane
DMABA	4-(dimethylamino)benzaldehayde
HBO	Hydrogen bonding
HEP	Heptane
NBA	Nitrobenzaldehayde
NLO	Nonlinear optical
THF	Tetrahydrofuran
ε_r	Dipolar dielectric constant
$\varepsilon_{r,solv}$	Solvation dielectric constant
μ_g	Ground state dipole moment
μ_e	Excited state dipole moment
a_0	Onsager cavity radius
Δf	Polarity function
ν_{max}	Wavenumber maximum

List of scheme

1. Introduction

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. This solvent dependence of Electronic/Vibrational bands is known as solvatochromism [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 relative permittivity of the bulk solvent, ε_r, (dielectric constant). The simplest model among these treatments is given by Onsager and Kirkwood [4, 5]. There, the solute molecule is assumed to be a sphere of radius a with a point dipole μ located at the center. The solute dipole interacts with the molecules of the solvent, which in turn create an electric field, the reaction field, E_R [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 (HB) and/or 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].

1, 4-Dioxane (dioxane, for brevity) is assumed to be non-polar solvent with dipolar dielectric constant ($\varepsilon_{r,}$) of 2.25, but experimental results indicate that dioxane shows polar behavior. Many researchers have observed solvatochromic shifts of dipolar chromophores dissolved in dioxane that exceed dielectric continuum theory predictions. This observed phenomenon is often referred to as the “dioxane anomaly” [7].

In a recent molecular dynamics simulation, Geerlings *et. al*. [10] model the dioxane molecule as two separate point dipoles located on the oxygens of the two ether moieties pointing toward the molecular center of mass. Their simulations indicate that a dipole immersed in dioxane has a strong interaction with the closer dipole. Consequently the solute dipole experiences a reaction field that is comparable to that of a solvent having a dielectric constant between 6.4 and 7.7.

From electronic absorption measurement and polarity function Baumann *et.al*. [11] also suggested that the solvation dielectric constant of dioxane is 6 rather than 2.25. The literature shows that there is still difficult to quantify the solvation dielectric constant of those solvents that have quadrupole moment.

The aim of this thesis work is to empirically determine the solvation dielectric constant of dioxane from vibrational spectroscopy measurement using picolinamide as solute compound. The observed vibrational frequencies in different solvents are to be correlated with a Lippert-Mataga polarity function. Furthermore, the empirically determined solvation dielectric constant of dioxane is investigated it can be applied for other compounds. In addition, to investigate the universal applicability of empirically determined solvation dielectric constant of dioxane from electronic absorption measurement.

2. Theoretical Background

2.1. Interaction of electromagnetic radiation with molecular system

All macroscopic aspects of the statics and dynamics of the electromagnetic field in the presence of material media are described by Maxwell's equations [12].

$$\nabla \cdot \mathbf{D}(r,t) = \rho(r,t) \qquad \text{Gauss's Law} \qquad (1)$$

$$\nabla \cdot \mathbf{B}(r,t) = 0 \qquad (2)$$

$$\nabla \times \mathbf{E}(r,t) = -\frac{\partial}{\partial t}\mathbf{B}(r,t) \qquad \text{Faraday's Law} \qquad (3)$$

$$\nabla \times \mathbf{H}(r,t) = \frac{\partial}{\partial t}\mathbf{D}(r,t) + \mathbf{J}(r,t) \qquad \text{Ampere's Law} \qquad (4)$$

For a given position vector **r** (m) and a time t (s) the Maxwell's equations couple the dielectric displacement vector **D** (C m^{-2}), the charge density ρ (C m^{-3}), the magnetic induction vector **B** (T:T= s m^{-2}), the electric field strength **E** (V m^{-1}), the magnitude field strength **H** (A m^{-1}) and the total current density **J** (A m^{-2}).

The response of the medium to the electric and magnetic fields may be expressed by the so called constructive or material equations:

$$\mathbf{D}(\mathbf{r},t) = \varepsilon_0 \mathbf{E}(\mathbf{r},t) + \mathbf{P}(\mathbf{r},t) \qquad (5)$$

$$\mathbf{B}(\mathbf{r},t) = \mu_0 \mathbf{H}(\mathbf{r},t) + \mu_0 \mathbf{M}(\mathbf{r},t) \qquad (6)$$

P is the dielectric polarization vector (C m^{-2}) induced by the electric field, **M** is the magnetization vector (A m^{-1}) induced by the magnetic field, ε_0 is the vacuum permittivity (ε_0 = 8.8542.10^{-12} $CV^{-1}m^{-1}$) and μ_0 is the vacuum permeability ($\mu_0 = 4\pi.10^{-7}$ $Vs^2C^{-1}m^{-1}$). Assume the media do not contain macroscopic charge and current density, hence $\rho = 0$ and $J = 0$, and they magnetized, so that $\mathbf{M} = 0$. Then Maxwell's equations and constitutive relations may be combined to yield the following coupled partial differential equations between electric field E and the dielectric polarization, $\mathbf{P}$.

$$\nabla \times \nabla \times \mathbf{E}(\mathbf{r},t) = -\mu_0 \frac{\partial^2}{\partial t^2}\{\varepsilon_0 \mathbf{E}(\mathbf{r},t) + \mathbf{P}(\mathbf{r},t)\} \qquad (7)$$

The solution of the above equation for the case of linear optics where constitutive relation defines $\mathbf{P}$ as a linear function of the electric field. Optically linear medium are characterized by linear response of the medium to the electric field. Considering an alternating electric field at position r which varies sinusoidally with time $\mathbf{E}(t)$ i.e. $\left[\mathbf{E}(t) = \mathbf{E}_0 \cos(\omega t)\right]$. In the electric dipole approximation, the dielectric polarization $\mathbf{P}(t)$ is created by local response in the medium [13].

$$\mathbf{P}(t) = \varepsilon_0 \chi^{(1)} . \mathbf{E}_0 \cos(\omega t) \tag{8}$$

Where the linear susceptibility, $\chi^{(1)}$, is a tensor quantity characteristic of the first order (linear) response of the medium and is frequency-dependent. The argument parenthesis describes the nature of this dependence. Two waves interact with each other through the medium. The frequency of the resulting wave is stated first, then the frequency of the incident wave(s). in general, $\chi^{(1)}$ is a second-rank tensor, that is, a 3 x 3 matrix. For optically linear medium $\nabla . \mathbf{E} = 0$, and applying the identity $\nabla \times \nabla \times \mathbf{E} = \nabla(\nabla . \mathbf{E}) - \Delta \mathbf{E}$:

The electric field in vacuum can be written

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \tag{9}$$

For a wave propagation in +z –direction in a weakly absorbing medium:

$$\mathbf{E}(z, t) = \mathbf{E}_0 \exp\left(-\frac{1}{2}\alpha z\right) \cos(\omega t - kz) \tag{10}$$

Where α is the natural absorption coefficient and $k.(k = 2\pi n / \lambda)$ is the magnitude of the wave vector. Both α and n represent the linear response of the medium and linked to the imaginary and real part of $\chi^{(1)}$.

$$\alpha = \frac{\omega \operatorname{Im}\{\chi^{(1)}\}}{c_0} \tag{11}$$

$$n^2 = 1 + \operatorname{Re}\{\chi^{(1)}\} \tag{12}$$

2.2 Macroscopic polarization

The electric nth-order susceptibilities (χ^n) describe the polarization of a macroscopic portion of matter (for example, a dielectric medium) in the presence of an electric field.

If we consider an experimental situation in which a macroscopic (or Maxwell) field **E** (t) is generated in a medium by the superposition of a static and one optical component, that is

$$E(t) = E^0 + E^{\omega}\cos(\omega t) \tag{13}$$

then the response of the medium can be represented by the dielectric polarization vector (dipole moment per unit volume) P(t), which, in terms of Fourier components, yields

$$P(t) = P^0 + P^{\omega}\cos(\omega t) + P^{2\omega}\cos(2\omega t) + \ldots. \tag{14}$$

Each Fourier amplitude can be expanded as a power series with respect to the electric field, so that

$$\begin{aligned}
P^0 &= \chi^{(0)} + \chi^{(1)}(0;0)\cdot E^0 + \chi^{(2)}(0;0,0) : E^0E^0 + \\
&\quad \frac{1}{2}\chi^{(2)}(0;-\omega,\omega)E^{\omega}E^{\omega} + \chi^{(3)}(0;0,0,0)\vdots E^0E^0E^0 + \ldots \\
P^{\omega} &= \chi^{(1)}(-\omega;\omega)\cdot E^{\omega} + 2\chi^{(2)}(-\omega;\omega,0) : E^{\omega}E^0 + 3\chi^{(3)}(-\omega;\omega,0,0)\vdots E^{\omega}E^0E^0 + \ldots \\
P^{2\omega} &= \frac{1}{2}\chi^{(2)}(-2\omega;\omega,\omega) : E^{\omega}E^{\omega} + \frac{1}{3}\chi^{(3)}(-2\omega;\omega,\omega,0)\vdots E^{\omega}E^{\omega}E^0 + \ldots
\end{aligned} \tag{15}$$

where the argument in the parentheses of the susceptibility tensors, $\chi^{(n)}$, describes the nature of the frequency dependence at the given order; in all cases, the frequency of the resulting wave is stated first, followed by the frequency of the incident interacting waves (two in a first-order process, three in the second-order analogue, and four in the third-order case) [14].

2.3 Microscopic polarization

The molar polarizabilities can be interpreted microscopically in terms of the NLO response of a molecule to an electric field [14]. Through linear and nonlinear optical processes in the medium, the field of Eq. (13) will give rise to Fourier components $E^{L\Omega}$ of the local electric field E^L at frequencies $\Omega = 0, \omega, 2\omega, \ldots$

$$E^{L}(t) = \sum_{\Omega=0,\omega,2\omega} E^{L\Omega}\cos(\Omega t), \tag{16}$$

and the total dipole moment $p(t)$ of the solute molecule will exhibit a time dependence of the general form Eq. (14).

For the derivation of the local-field corrections and effective polarizabilities below, we consider the Fourier amplitudes of $p(t)$.

$$P^{0} = \mu^{0} + \alpha(0;0)\cdot E^{L0} + \frac{1}{2}\beta(0;0,0) : E^{L0}E^{L0} + \frac{1}{4}\beta(0;-\omega,\omega) : E^{L\omega}E^{L\omega} + \ldots.$$

$$P^{\omega} = \alpha(-\omega;\omega)\cdot E^{L\omega} + \beta(-\omega;\omega,0) : E^{L\omega}E^{L0} + \frac{1}{2}\gamma(-\omega;\omega,0,0)\,\vdots\, E^{L\omega}E^{L0}E^{L0}$$
$$+ \frac{1}{8}\gamma(-\omega;-\omega,\omega,\omega)\,\vdots\, E^{L\omega}E^{L\omega}E^{L\omega} + \ldots.$$

$$P^{2\omega} = \alpha(-2\omega;2\omega)\cdot E^{L2\omega} + \frac{1}{4}\beta(-2\omega;\omega,\omega) : E^{L\omega}E^{L\omega} + \frac{1}{4}\gamma(-2\omega;\omega,\omega,0)\,\vdots\, E^{L\omega}E^{L\omega}E^{L0}$$
$$+ \frac{1}{4}\delta(-2\omega;\omega,\omega,0,0)\,\vdots\, E^{L\omega}E^{L\omega}E^{L0}E^{L0} + \ldots.$$

Where μ^{0} is the permanent dipole moment and $\alpha,\beta,\gamma,\delta,\ldots$ are (hyper) polarizabilities of the isolated solute molecule [15].

2.4 Electrochromism

The optical properties of molecules can be influenced by an external electric field; this phenomenon is known as electrochromism or stark effect. Changes in optical absorption due to the action of an external electric effect are basically attributable to three effects, i.e. orientation, band shift and direct field-dependence of the transition moment effect.

2.4.1 Orientation Effect

In an ordinary solution the molecules are distributed isotropically, and polarized and unpolarised excitations give the same absorption curve, which can be represented as a plot of the extinction coefficient, $\varepsilon^{sol}(\tilde{v})$, against the wave number, $\tilde{v}$,. The extinction coefficient is a measure of the intensity of the optical absorption at a given wavelength.

The measure of the intensity of an absorption band is the transition moment, $\mu_{eg}^{so\ln}$, of the dissolved molecule, which is related to the molar decadic extinction coefficient, ε^{sol}, by the integral absorption.

$$\int_{Band\,(e\leftarrow g)} \frac{\varepsilon^{soln}(\tilde{\nu})}{\tilde{\nu}}\,\mathrm{d}\tilde{\nu} = \frac{8\pi^3 N_A}{2.303\times 3hc}\left|\mu_{eg}^{soln}\right|^2 \qquad (17)$$

For a single molecule or for an assembly of molecules having a definite orientation, the extinction coefficient ε_{orient} with light polarized in the direction of the unit vector e is

$$\varepsilon_{orient} = 3\varepsilon^{soln}\left|\mu_{eg}^{soln}\right|^{-2}\left|\boldsymbol{\mu}_{eg}^{soln}\boldsymbol{e}\right|^2 = 3\varepsilon^{soln}\cos^2\theta \qquad (18)$$

Partial orientation of molecules in solution can be achieved by means of an external electric field, F_b. The direction of the transition moment can be found from the change in optical absorption due to this field.

The total electric dipole moment μ_g^F of a molecule in the electronic ground state $\left|g\right\rangle$ in the electric field is

$$\mu_g^F = \mu_g + \alpha_g F_e \qquad (19)$$

μ_g is the permanent dipole moment α_g is the polarization tensor, and $\mathbf{F}_e$ is the effective field strength at the position of the molecule. For molecules having a sufficiently large dipole moment, $\left|\mu_g\right\rangle\rangle\left|\alpha_g F_e\right|$, and the polarizability term may be disregarded. In this approximation the energy E_g^F of a dissolved molecule in the electronic field is

$$E_g^F = E_g^{so\ln} - \mu_g\mathbf{F}_e = E_g^{so\ln} - \mu_g F_e\cos\vartheta \qquad (20)$$

$E_g^{so\ln}$ is the energy of the dissolved molecule in the ground state with no external field, and ϑ is the angle between the vectors μ_g and F_e.

The energy E_g^F depends on the direction of the dipole moment μ_g in relation to the field F_e . The orientation distribution of the molecules in a homogeneous field, e.g. between parallel electrodes, is therefore no longer isotropic. There will be more molecules with their dipole moments parallel to the field direction than with their dipole moments opposing the field direction. The extinction coefficient ε_F of the dissolved molecules in the electric field is found from Eq. (18) by multiplication of the Boltzmann factor $C\exp(-E_g^F / KT)$ and integration over all orientations.

The relative change in the extinction coefficient as a result of the orientation effect in an electric field is found to be

$$\left(\frac{\varepsilon_F - \varepsilon^{sol}}{\varepsilon^{sol}}\right)_{orient} = \frac{1}{30}\left(\frac{F_e}{KT}\right)^2 (3\cos^2\theta - 1)[3(e\mu_g)^2 - \mu_g^2] \qquad (21)$$

θ is the angle between the direction of the external field $\mathbf{F}_b$ and the polarization direction e of the incident light, k is the Boltzmann constant, and T is the absolute temperature.

For the case in which the transition moment μ_{eg} of a band is parallel to the dipole moment, and the polarization direction $\boldsymbol{e}$ of the incident light chosen parallel to the external field $\mathbf{F}_b$, it follows from Eq. (21) that

$$\left(\frac{\varepsilon_F - \varepsilon^{sol}}{\varepsilon^{sol}}\right)_{orient} = \frac{4}{30}\left(\frac{\mu_g F_e}{KT}\right)^2 \approx 3\times10^{-4} \qquad (22)$$

and for the case in which μ_{eg} is perpendicular to μ_g and $\boldsymbol{e}$ is again chosen parallel to F_b, we obtain

$$\left(\frac{\varepsilon_F - \varepsilon^{sol}}{\varepsilon^{sol}}\right)_{orient} = \frac{4}{30}\left(\frac{\mu_g F_e}{KT}\right)^2 \approx -1.5\times10^{-4} \qquad (23)$$

i.e. the absorption coefficient of a band whose transition moment is parallel the dipole moment increases in an electric field, while that of a band whose transition moment is perpendicular to the dipole moment decreases [1].

2.4.2 Band Shift Effects

In the excited state, the energy of the molecule under the applied external electric field may be expressed as

$$E_e^F = E_e^{sol} - \mu_e \mathbf{F}_e = E_e^{sol} - \mu_e \mathbf{F}_e \cos\vartheta \qquad (24)$$

E_e^{soln} is the energy of the dissolved molecule in the excited state with no external field. In the following equations, it is assumed, for simplicity that the dipole moment μ_e in the excited state is parallel to the dipole moment μ_g in the ground state.

For a given transition having the absorption wave number $\tilde{v}_e^{soln}$ in solution with no external field $\left(hc\tilde{v}_e^{sol} = E_e^{sol} - E_g^{sol}\right)$ the absorption wave number $\tilde{v}_e^{F}$ in an electric field is given by

$$\tilde{v}_e^{F} = \frac{E_e^F - E_g^F}{hc} = \tilde{v}_e^{sol} - \frac{\left(\mu_e - \mu_g\right) F_e \cos\vartheta}{hc} \tag{25}$$

The change in the dipole moment $(\mu_e - \mu_g)$ thus leads to a field-dependent shift of the band, which also depends on the angle ϑ between the dipole moment and the field direction.

If the dipole moment of the dissolved molecule is oriented parallel to the field, $\cos\vartheta = 1$. So that the energy in the ground state is reduced by $\mu_g F_e$ and that in the excited state by $\mu_e F_e$. Under the consideration of $\mu_e \rangle \mu_g$, the distance between the levels E_e^F and E_g^F thus decreases, and the absorption wave number $\tilde{v}_{\uparrow\uparrow}$ (parallel orientation) < $\tilde{v}_e^{sol}$. If the dipole moment is oriented perpendicular to the field, $\cos\vartheta = 0$ and the energy level will be the same as in the absence of an external field; thus $\tilde{v}_{\perp}$ (perpendicular orientation) $= \tilde{v}_e^{sol}$. Finally if the dipole moment is oriented antiparallel to the field, i.e. $\cos\vartheta = -1$, the energy in the ground state will be increased by $\mu_g F_e$ and that in the excited state by $\mu_e F_e$; in this particular case, therefore $\tilde{v}_{\uparrow\downarrow}$ (antiparallel orientation) > $\tilde{v}_e^{sol}$ [1].

2.4.3 Direct Field-Dependence of the Transition moment

If the wave function of a molecule is known, the dipole moment can be calculated by an integration process; for example the dipole moment μ_g^F of the molecule in the ground state in an electric field is

$$\mu_g^F = \int \psi_g^{F*} \left(\sum_i e_i \hat{r}_i \right) \psi_g^F \, d\tau \tag{26}$$

where r_i are the coordinates of the positions of the nuclei and electrons of the molecule, their charges being e_i ,and ψ_g^F is the wave function in the electric field.

Similarly, the electric dipole transition moment μ_{eg}^F for a transition between the ground state $|g\rangle$ and an excited state $|e\rangle$ in an electric field is

$$\mu_{eg}^F = \int \psi_e^{F*} \left(\sum_i e_i \hat{r}_i \right) \psi_g^F \, d\tau \tag{27}$$

The transition moment μ_{eg}^F in an electric field can also be expressed with the aid of the polarizability tensor α_{eg} as

$$\mu_{eg}^F = \mu_{eg} + \alpha_{eg} F_e \tag{28}$$

The relative change in the extinction coefficient due to the field dependency of the transition moment may be of the same order of magnitude as the changes due to the orientation effect and the band shift [1].

2.5 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 [12, 16]. Solvent parameters such as dielectric constant and refractive index are involved in representing various solvent properties [3, 4]. 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 [17].

These changes 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 [3]. 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 (S_0), as compared to that of the excited state (S_1), results in the negative solvatochromic shift of the spectral maximum. Alternatively, the stronger solvation of the 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 [18].

The reaction field acts on the dissolved molecule in the same way as an external field (in the case of electrochromism), *i.e.*, it is capable of causing a band shift and hence in the intensity of the band. The reaction field depends on the nature and arrangement of the surrounding solvent molecules. The accurate determination of the (mean) field, still presents difficulties that have not yet been overcome. Useful approximations have however been developed. In the simplest approximation the solvent is regarded as a homogeneous isotropic dielectric continuum having a dielectric constant ε_r. The dissolved molecules are assumed to be located in the center of the spherical cavity with radius a. The dipole moment is represented by a point dipole located. In this approximation, the reaction field F_{Rf} of a dissolved molecule in the electronic ground state is given by

$$F_{Rf} = \frac{2(\varepsilon_r - 1)}{a^3(2\varepsilon_r + 1)} \mu'_g \tag{29}$$

μ'_g is the total dipole moment (permanent plus induced moment) of the molecule [19, 20].

2.5.1 Solvent effect on Vibrational frequency

The vibrational spectrum of a molecule A-B not only depends on the strength of the bond between A and B, but may also be markedly affected by environmental factors. Such 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 [3]. 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 [21].

In particular, the vibrational frequencies and transition dipole strengths of molecular oscillators are known to be highly sensitive to local electric field in solutions. Although the vibrational frequencies are known to be strongly affected by solute-solvent electrostatic interactions in general [16].

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 [22]. 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 [23].

Intramolecular 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 [24].

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 semiempirical 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-dipolarity) 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 nonpolarizable dipole (solute molecule) immersed in a dielectric continuum [8].

2.5.2 Solvent effect on electronic absorption

The modification of the electronic spectra during the transition from gaseous phase to liquid solutions, can offer information on the interactions between the spectrally active molecule and the solvent molecules [23]. According to Bayliss and McRae, four limiting cases can be distinguished for intramolecular electronic transitions in solution [3].

(1) Nonpolar solute in a nonpolar solvent: In this case, only dispersion forces contribute to the solvation of the solute. Dispersion forces, operative in any solution, invariably cause a small bathochromic shift, the magnitude of which is a function of the solvent refractive index, n, the transition intensity, and the size of the solute molecule. The function $(n^2-1)/(2n^2+1)$ has been proposed to account for this general red shift.

(2) Nonpolar solute in a polar solvent: In the absence of a solute dipole moment there is no significant orientation of solvent molecules around the solute molecules, and again a general red shift, depending on the solvent refractive index, n, is expected. Solute quadrupole/solvent dipole interactions also have to be taken into account in this case.

(3) Dipolar solute in a nonpolar solvent: In this case, the forces contributing to solvation are dipole-induced dipole and dispersion forces. If the solute dipole moment increases during the electronic transition, the Franck–Condon excited state is more solvated by dipole-solvent polarization, and a red shift, depending on the solvent refractive index, *n*, and the change in solute dipole moment, is expected. The Franck–Condon excited state is less solvated if the solute dipole moment decreases during the electronic transition, and a blue shift, again proportional to the two above mentioned factors, is expected. In the latter case, the resultant shift may be red or blue depending on the relative magnitude of the red shift caused by polarization and the blue shift.

(4) Dipolar solute in a polar solvent: Since the ground-state solvation results largely from dipole-dipole forces in this case, there is an oriented solvent cage around the dipolar solute molecules, resulting in a net stabilization of their ground state. If the solute dipole moment increases during the electronic transition ($\mu_g < \mu_e$), the Franck–Condon excited state is formed in a solvent cage of already partly oriented solvent dipoles. The better stabilization of the excited state relative to the ground state with increasing solvent polarity will result in a bathochromic shift. Its magnitude will depend on the extent of the change in the solute dipole moment during the transition, the value of the solvent dipole moment, and the extent of interaction between the solute and solvent molecules.

2.6 Solute-solvent interaction

The term solvation refers to the surrounding of each dissolved molecule or ion by a shell of more or less tightly bound solvent molecules. This solvent shell is the result of intermolecular forces between solute and solvent [3]. Intermolecular interactions determine changes in the position of the molecular energy levels, which usually leads to electronic band shifts in the frequency scale [23].

If we mix a solute and a solvent, both being constituted by solvated, their molecules attract one another as they approach one another. This interaction can only be electrical in its nature, given that other known interactions are much more intense and of much shorter range of action (such as those which can be explained by means of nuclear forces) or much lighter and of longer range of action (such as the gravitational force) [18].

A solvent should not be considered a macroscopic continuum characterized only by its macroscopic physical constants such as boiling point, vapour pressure, density, index of refraction, relative permittivity, thermal conductivity, surface tension, etc. From the molecular-microscopic point of view, a solvent is a discontinuum which consists of individual, mutually interacting solvent molecules, characterized by their molecular properties such as dipole moment, electronic polarizability, hydrogen bond donor (HBD) and hydrogen-bond acceptor (HBA) capability, electron-pair donor (EPD) and electron-pair acceptor (EPA) capability, etc [3, 22].

The analysis of solute-solvent interactions is usually based on the following partition scheme:

$$\Delta E = \Delta E_i + \Delta E_{ij} + \Delta E_{jj} \tag{30}$$

Where i stands for the solute and j for the solvent. This approach can be maintained while the identities of the solute and solvent molecules are preserved. The first term in the above expression is the energy change of the solute due to the electronic and nuclear distortion induced by the solvent molecule and is usually given the name solute polarization. ΔE_{ij} is the interaction energy between the solute and solvent molecules. The last term is the energy difference between the solvent after and before the introduction of the solute. This term reflects the changes induced by the solute on the solvent structure. It is usually called cavitation energy in the framework of continuum solvent models and hydrophobic interaction when analyzing the solvation of nonpolar molecules.

The calculation of the three energy terms needs analytical expressions for the different energy contributions but also requires knowledge of solvent molecules distribution around the solute which in turn depends on the balance between the potential and the kinetic energy of the molecules. This distribution can be obtained from diffraction experiments or more usually is calculated by means of different solvent modeling. The first two terms in Eq. (30) can be considered together by means of the following energy partition:

$$\Delta E_i + \Delta E_{ij} = \Delta E_{el} + \Delta E_{pol} + \Delta E_{d-r} \tag{31}$$

Analytical expressions for the three terms (electrostatic, polarization and dispersion-repulsion energies) are obtained from the intermolecular interactions theory [18].

From another point of view, the solvation energy of a molecule, E_{solv}, in a given solvent can be divided into the following terms

$$E_{solv} = E_{cav} + E_{disp} + E_{elst} + E_{H-bond} \quad \ldots\ldots\ldots\ldots \quad (32)$$

Each of which corresponds to a certain type of intermolecular interaction in the condensed media. Thus, E_{cav} denotes the energy of the cavity formation for the solute in the solvent, E_{disp} is the dispersion energy and E_{elst} the electrostatic energy of the interaction of the solute with the surrounding solvent molecules. The term E_{H-bond} accounts for the energy of the hydrogen bond formation between the solute and solvent molecules. The value of each of the above terms will change as a result of the Franck-Condon excitation of the solute molecule.

First, the size of the molecule increases, as a rule, during the excitation. However, as the excitation process is practically instantaneous, the position and orientation of the solvent molecules in the solvation sheath of the chromophoric solute will not change. This means that the average distance between the surface of the solute and the solvent molecules will decrease in the Franck-Condon excited state of the former that normally causes the enhanced solute-solvent repulsion in that state. At the same time, the dispersion energy that stabilizes the solute-solvent system will also increase in the absolute value, but to the opposite direction. In consequence, both effects may cancel each other and the net effect will be close to zero. For the polar solutes, both in the ground and in the excited state, the electrostatic solvation energy is therefore often considered as the most important term in Eq. (32) [18].

Intermolecular forces are usually classified in to two distinct categories. The first category comprises the so-called directional, induction, and dispersion forces, which are non-specific. The second group consists of hydrogen bonding forces, and charge-transfer or electron-pair donor–acceptor forces. The latter group are specific, directional forces, which can be saturated and lead to stoichiometric molecular compounds [3].

2.6.1 Electrostatic

The electrostatic contribution arises from the interaction of the unpolarized charge distribution of the molecules. If both the solute and the solvent are considered to be formed by neutral polar molecules (with a permanent dipolar moment different from zero), due to an asymmetric distribution of its charges, the electric interaction of the type dipole-dipole will normally be the most important term in the electrostatic interaction [18]. When two dipolar molecules are optimally oriented with respect to one another at a distance r as shown in Fig. 2.1a, then the force of attraction is proportional to $1/r^3$. An alternative arrangement is the anti-parallel arrangement of the two dipoles as shown in Fig. 2.1b [3]. The most stable orientation is the antiparallel, except in the case that the molecules in play are very voluminous [3, 18].

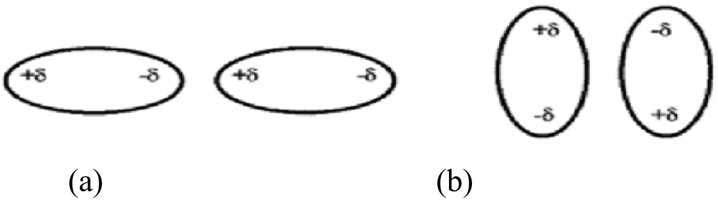


Figure 2.1: (a) ‘‘Head-to-tail’’ arrangement of two dipole molecules; (b) Antiparallel arrangement of two dipole molecules.

Two dipoles in rapid thermal movement will be orientated sometimes in a way such that they are attracted and at other times in a way that they are repelled. On the average, the net energy turns out to be attractive. It also has to be born in mind that the thermal energy of the molecules is a serious obstacle for the dipoles to be oriented in an optimum manner. The average potential energy of the dipole-dipole interaction, or of orientation, is, therefore, very dependent on the temperature [18].

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 favoured leads to a net attraction, which is strongly temperature dependent, according to Eq. (33).

$$E_{d-d} = -\frac{2}{3}\frac{\mu_1^2 \mu_2^2}{(4\pi\varepsilon)^2 \kappa T r^6} \qquad (33)$$

μ_1, μ_2 dipole moments

κ Boltzmann constant

ε Dielectric constant

T absolute temperature

r intermolecular distance

However, the intermolecular interaction energy rapidly falls off at higher orders of the multipole. The anomalous behavior of the chair-configure, non–dipolar solvent 1, 4-dioxane, which often behaves like a polar solvent even though its relative permittivity is low (ε_r = 2.2), is caused by its large nonideal quadrupolar charge distribution [3].

In the event that one of the species involved were not neutral (for example an anionic or cationic solute) the predominant term in the series which gives the electrostatic interaction will be the ion-dipole interaction [18].

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 μ = 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 ion, and the other repulsive end directed away. The potential energy of an ion-dipole interaction is given by

$$E_{ion-dipole} = -\frac{1}{4\pi \cdot \varepsilon_0} \cdot \frac{z \cdot e \cdot \mu \cdot \cos\theta}{r^4} \qquad (34)$$

Where ε_0 is the permittivity of a vacuum, $z \cdot e$ 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 r joining the ion and the centre of the dipole [3, 18].

2.6.2 Polarization

If we dissolve a polar substance in a nonpolar solvent, the molecular dipoles of the solute are capable of distorting the electronic clouds of the solvent molecules inducing the appearance in these new dipoles [18]. This induced moment always lies in the direction of the inducing dipole and will be attracted to each other. The net dipole/induced dipole energy of interaction for two different molecules, each possessing a permanent dipole moment μ_1 and μ_2 and polarizabilities α_1 and α_2, often referred to as the induction or Debye interaction and is given by Eq. (35) [3].

$$E_{d-id} = -\frac{1}{(4\pi\cdot\varepsilon_0)^2}\cdot\frac{\alpha_1\cdot\mu_2^2+\alpha_2\cdot\mu_1^2}{r^6} \tag{35}$$

2.6.3 Dispersion

Even when solvent and solute are constituted by nonpolar molecules, the continuous electronic movement results, at any instant, in a small dipole moment, μ, which can fluctuatingly polarize the electron system of the neighboring atoms or molecules. This coupling causes the electronic movements to be synchronized in such a way that a mutual attraction results. The energy of this dispersion or London interaction can be given, to a first approximation, by:

$$E_{dispersion} = -\frac{1}{(4\pi\cdot\varepsilon_0)^2}\cdot\frac{3\alpha_1\cdot\alpha_2}{2r^6}\cdot\left(\frac{\mathrm{I}_1\cdot\mathrm{I}_2}{\mathrm{I}_1+\mathrm{I}_2}\right) \tag{36}$$

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.

The dispersion forces are often more intense than the electrostatic forces and, in any case, are universal for all the atoms and molecules, given that they are not seen to be subjected to the requirement that permanent dipoles should exist before hand [3, 25].

2.6.4 Hydrogen Bonding

Liquids possessing hydroxyl groups or other groups with a hydrogen atom bound to an electronegative atom X are strongly associated and have abnormal boiling points. This observation led to the contention that particular intermolecular forces apply here. These are designated as hydrogen bridges, or hydrogen bonds, characterized by a coordinative divalency of the hydrogen atom involved [3]. Hydrogen bonds appear in substances where there is hydrogen united covalently to very electronegative elements (e.g., F, Cl, O and N).

2.7 Basic solvatochromism equation

In different solvatochromic theories different solvent polarity parameters appear. The concept of reaction field theory is useful in relating solvent effects with the change of electronic transition energy and frequency shifts in various spectroscopic applications [4].

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:

$$\vec{F} = \vec{E}_c + \vec{E}_r = g(\varepsilon)\vec{E} + f(\varepsilon)\frac{\vec{\mu}}{2a^3} \tag{37}$$

Here, $\vec{E}_c$ and $\vec{E}_r$ 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 (MO), 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

$$\hat{H}_p = \hat{H}_0 - \hat{\mu}\frac{\mu}{2a^3} f(\varepsilon) \qquad (38)$$

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 $f(\varepsilon)$ has been used, such as the liptay, Lippert-mataga, MacRae, Bakhshiev and Kawski-Chamman-Viallent [8, 26].

2.7.1 Liptay equation

For a molecule having a permanent dipole moment $|\mu_g| = \mu_{gz}$ in the electronic 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 $\widetilde{\nu}_a^{sol}$ of the absorption maximum is given to a good approximation by the following equation.

$$\widetilde{\nu}_a^{sol} = \widetilde{\nu}_a^{0} - \frac{(\mu_{az} - \mu_{gz})(F_{RM})_z}{hc} - \frac{2(n^2-1)}{a^3(2n^2+1)} D \qquad (39)$$

$\widetilde{\nu}_a^{0}$ is the wave number of the absorption maximum in the free molecule (gas 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. (39) is the mean of the reaction fields of the dissolved molecule in the ground state and in the Franck-Condon excited state, i.e. the primary state after the excitation process. The Z-component of F_{RM} is

$$(F_{RM})_z = \frac{1}{a^3}\left[\frac{\varepsilon_r - 1}{2\varepsilon_r + 1}\left(1 - \frac{2\alpha_{gz}(\varepsilon_r - 1)}{a^3(2\varepsilon_r + 1)}\right)^{-1} 2\mu_{gz} + \frac{n^2-1}{2n^2+1}\left(1 - \frac{2\alpha_{gz}(n^2-1)}{a^3(2n^2+1)}\right)^{-1}(\mu_{az} - \mu_{gz})\right] \qquad (40)$$

ε_r - Dielectric constant of the solution

n - Refractive index

α_{gz} - Z-component of the polarizability tensor, α_g, of the molecule in the ground state, transformed to principal axes.

The Eq. (40) can be represented by a function that depends on the properties of the dissolved molecule ($\mu_{gz}, \mu_{az}, \alpha_{gz}$, 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, F_{RM} disappears, leaving only the term containing the refractive index n in Eq. (40) , 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 (μ_{az} - μ_{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 [1, 27].

2.7.2 Lipert-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. These 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) of the solvent, and is described by the Lippert-Mataga equation [28, 29].

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 a homogeneous and isotropic dielectric with relative permittivity ε_r [3] and neglecting the mean solute polarizability α in the states involved in the transition ($\alpha \cong \alpha_e \cong \alpha_g \cong 0$) [28]. Lippert–Mataga equation is as follows:

$$\Delta\tilde{\nu} = \tilde{\nu}_a - \tilde{\nu}_f = \frac{1}{4\pi\cdot\varepsilon_0}\cdot\frac{2}{h\cdot c\cdot a^3}\cdot(\mu_e-\mu_g)^2\cdot\Delta f + const. \qquad (41)$$

$$\text{With } \Delta f = f(\varepsilon_r) - f(n^2) = \left[\frac{\varepsilon_r - 1}{2\varepsilon_r + 1} - \frac{1}{2}\left(\frac{n^2-1}{2n^2+1}\right)\right] \qquad (42)$$

Where $\Delta\tilde{\nu}$ 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, respectively [29, 30].

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) 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 [29].

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 [3, 29].

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 $\alpha = \left(a^3/2\right)$. 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 [26, 31, 32].

$$\widetilde{\nu}_a - \widetilde{\nu}_f = \frac{2\left(\mu_e - \mu_g\right)^2}{4\pi\varepsilon_0 hca^3}\Delta f \tag{43}$$

The approximation $\alpha = a^3/2$ yields $\Delta f = \left[\frac{\varepsilon_r - 1}{\varepsilon_r + 2} - \frac{n^2 - 1}{n^2 + 2}\right]$ (44)

By combining Eq. 43 and 44 $\widetilde{\nu}_a - \widetilde{\nu}_f = \frac{2\left(\mu_e - \mu_g\right)^2}{4\pi\varepsilon_0 hca^3}\left[\frac{\varepsilon_r - 1}{\varepsilon_r + 2} - \frac{n^2 - 1}{n^2 + 2}\right]$ (45)

2.7.4 Bakhshive equation

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

$$f(\varepsilon, n) = \frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \tag{46}$$

$$f(n) = \frac{n^2 - 1}{n^2 + 2} \tag{47}$$

Usually, one checks multiparameter linear correlations of the type:

$$\nu^a = \nu_0^a + C_1^a f(\varepsilon, n) + C_2^a f(n) + C_3^a \delta_H \tag{48}$$

where the correlation coefficient ν_0^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. (48) signifies the wavenumber 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. (48) was added to take into consideration the contribution of the specific interactions to the total spectral shift [23].

In Bakhshiev theory, the correlation coefficients C_1^a from Eq. (48) 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:

$$C_1^a = \frac{2}{a^3}\frac{2n^2+1}{n^2+2}(\mu_g \mu_e \cos\varphi - \mu_g^2) \tag{49}$$

But in order to determine the polarity function equation proposed by Bakhshiev the last term in Eq. (48), which is the contribution of the specific interactions, excluded and one gets the equation Eq. (50); [23, 30].

$$\widetilde{\nu}^a = \widetilde{\nu}_0^a + \frac{2\mu_g(\mu_e - \mu_g)}{4\pi\varepsilon_0 hca_0^3}\left[\frac{\varepsilon_r - 1}{\varepsilon_r + 2} - \frac{n^2-1}{n^2+2}\right]\frac{2n^2+1}{n^2+2} \tag{50}$$

3. Objectives

3.1 General objective

The general objective of this study is to determine solvation dependent Empirical Dielectric constant of solvents with apparent quadrupole moments from vibrational and electronic spectra.

3.2 Specific objectives

The specific objectives of this study include:

- To empirically determine the solvation dielectric constant ($\varepsilon_{r,solv}$) of dioxane (a compound with quadrupole moment) using picolinamide as a solute compound in order to account the quadrupole moment induced increase in the dipolar dielectric constant ($\varepsilon_{r,}$).

- To apply the empirically calculated solvation dielectric constant of dioxane to other compounds.

- To investigate the universality of the solvation dielectric constants of dioxane in electronic transition.

4. Experimental Part

4.1 Materials

4-(dimethylamino)benzaldehayde (DMABA) (99%, Sigma-Aldrich), Nitrobenzaldehayde (NBA) (Sigma-Aldrich), Bromobenzaldehayde (BBA) (99%, Sigma-Aldrich), propylamide (Analytical grade, Sigma-Aldrich 97%), picolinamide (98%, Sigma-Aldrich), 2-chloroacetamide (≥ 98%, Sigma-Aldrich), acrylamide (≥ 99%, Sigma-Aldrich), and 2-chloro-benzamide (98%, Sigma-Aldrich), were used as received. Solvents including, 1, 4-dioxane (stabilized with 2.5 ppm of 2,6-Di-tert-butyl-4-methylphnol(BHT) and GC grade), dichloromethane (GC grade), were obtained from (BDH chemical ltd). Acetonitrile (HPLC grade), heptane, chloroform (GC grade), were obtained from (Sigma-Aldrich). 1, 2-dichloroethene (GC grade), methylacetate (GC grade), tetrahydrofuran (GC grade), obtained from (Riedel de Haen). Methanol (GC grade), cyclohexane (GC grade), obtained from (Acros, USA) benzene, carbon tetrachloride, o-Xaylene, diethylether, toluene, pentane, water and acetic acid.

4.2 Methods and Instrument

UV/Vis absorption spectroscopy:

UV/Vis spectra of the aldehaydes were recorded with double-beam spectrophotometer (Lambda9-UV/Vis/NIR, PerkinElmer, USA) in solvents of varying polarity. The spectral resolution was 1nm and in a spectral range 200 nm-400 nm. A cell width 1 cm optical path length and quartz-cell was used for transmission measurements. The excitation light source was Deutrium and Tungesten arc lamp. All measurements were performed under room temperature and pressure.

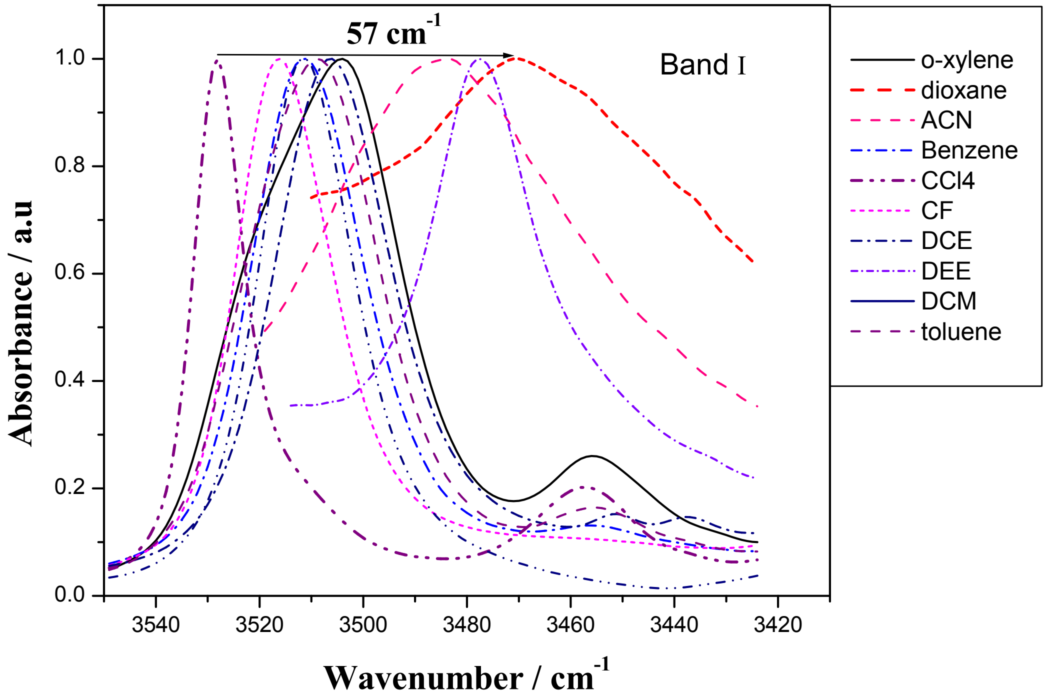
FT-IR spectrophotometer:

IR spectra of the amides were recorded with PerkinElmer Spectrum 65 FT-IR spectrophotometer in solvents of varying polarity. The spectral resolution was 1 cm^{-1} and in a spectral range 3600 cm^{-1} to 3280 cm^{-1}. A cell width 2.1 mm optical path length and ZnSe ATR crystal was used for transmission and reflection measurements, respectively. Transmission mode IR measurements were preferred for less concentrated solutions and the reflection technique were employed for the concentrated solutions. All measurements were performed under room temperature and pressure.

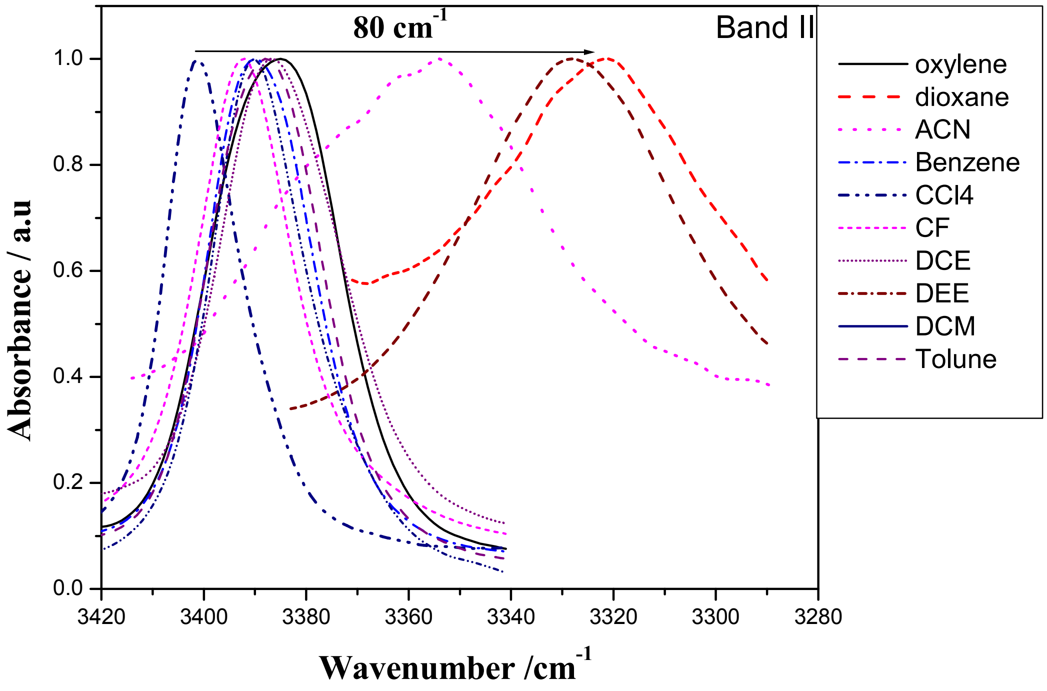
5 Results and Discussions

5.1 Determination of Solvation Dielectric Constant ($\varepsilon_{r,solv}$) of Dioxane Using IR spectra of Picolinamide

Infrared spectra of Picolinamide were recorded in a series of solvents of differing polarities for determining the solvation dielectric constant. The concentrations were kept relatively high in order to get peak absorbance values above 0.1. The observed spectra are presented in Figures 5.1a and b.



a



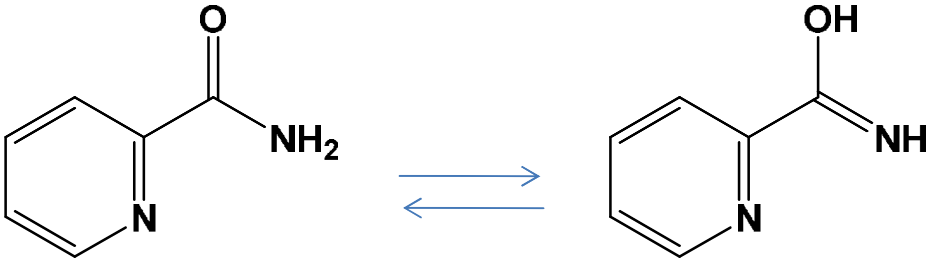
b

Figure 5.1: a) Band I b) Band II vibrational absorbance spectra of Picolinamide in o-xylene, Dioxane, ACN, benzene, CCl_4, CF, DCE, DEE, DCM and toluene.

In all solvents two peaks were observed. For the sole purpose of discussion, the peaks in the spectral ranges 3600 – 3420 cm^{-1} and 3420 – 3280 cm^{-1}are grouped as Band I and Band II, respectively. This nomenclature is used throughout this work. In addition a third additional peak was accordingly observed in the spectra of the compound in the spectral region of between Band I and Band II.

As the solvent polarity was increased, for both Band I and Band II peaks a solvent induced shift in wavenumber of maximum absorption ν_{max} to lower energy was observed, except for dioxane and DEE. The magnitude of the shift calculated, taking the ν_{max} values of the solvents with largest (ACN) and lowest polarity (CCl_4) was 57 and 80 cm^{-1} for Band I and II, respectively.

Generally, fundamental vibration absorption above 3300 cm^{-1} is due to X–H chromophore where X can be N or O. Looking at the molecular structure of the compound, only N-H vibration is expected unless one considers the existence of the compound in a tautomeric equilibrium as shown below



Picolinamide **Picolinimidic acid**

Scheme 1: Tautomeric equilibrium of picoline amide.

The existence of the two tautomers in various solvent polarities has been suggested through NMR analysis [33]. Therefore, the two peaks were attributed to N–H and O–H vibration. However, the exact assignment of a given peak to a specific chromophore vibration and also the third peak (shoulder peak in the spectral range of Band I) is difficult to impossible without additional information.

In order to determine the cause of the shoulder peak, the spectra of the compound was recorded at different concentrations [33]. As the concentration was increased an increase in the intensity of the shoulder peak, at the expense of the peak of Band I, was observed. This concentration dependence clearly demonstrated that the shoulder peak is due to dimerization and thus attributed to a dimer peak.

After assigning all the three peaks, the frequency of the two intense peaks in Band I and Band II were plotted against the Lippert-Mataga polarity function. The data used for the plot are summarized in Table 1.

Table 1: The vibrational absorbance maxima of Picolinamide, Acrylamide and propylamide in different solvent and with their polarity function, refractive index [34] and dielectric constant [34].

Solvents	Absorbance maxima, $v_{\max}(cm^{-1})$						ε_r	n_D^{20}	$f(\varepsilon_r, n^2)$
	Picolinamide		Acrylamide		Propylamide				
	Band I	Band II	Band I	Band II	Band I	Band II			
o-Xylene	3504	3385	3508	3392	3511	3396	2.57	1.5054	0.1416
Dioxane	3471	3321	3424	3342	3446	3347	2.25	1.4224	0.1257
ACN	3484	3354	3467	3363	3474	3373	37.5	1.3441	0.3926
Benzene	3511	3390	3516	3400	3518	3402	2.27	1.5011	0.1152
CCl_4	3528	3401	3538	3421	3539	3420	2.24	1.4601	0.1185
CF	3516	3392	3529	3413	----	----	4.81	1.4458	0.2538
DCE	3506	3387	3514	3399	----	----	10.36	1.4448	0.3260
DCM	3511	3390	3522	3407	3525	3408	8.93	1.4241	0.3184
Toluene	3509	3388	3514	3398	----	----	2.38	1.4969	0.1269

Using the data a linear fit was generated excluding (masking) the data for dioxane (Fig. 5.2).

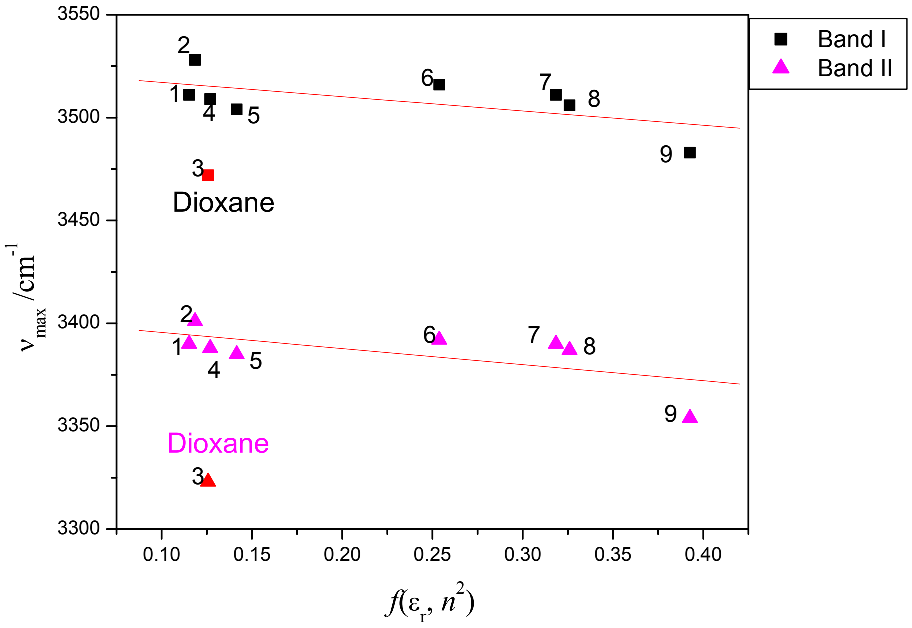


Figure 5.2: Plot of ν_{max} Band I and Band II *versus* polarity function for picolinamide in different solvents (as 1, 2, 3… for Benzene, CCl_4, Dioxane, Toluene, o-xylene, CF, DCM, DCE and ACN, respectively).

In fitting the data point the v_{max} value for dioxane were excluded. It resulted with correlation coefficient of $R = -0.61$ and -0.64 for the Band I and Band II, respectively. The correlation coefficient obtained using the data was poor (-0.20 and -0.06 for Band I and Band II, respectively), which may indicate the exclusion of Dioxane data point is justified from the perspective linearity.

Using the relationship generated from the fit and using the absorption wavenumber, it was tried to calculate the solvation dielectric constant. The determined solvation dielectric constant is unphysical since the values obtained for polarity function in both curves were out of the range expected for the polarity function between ‘0’ (in vacuum implying no shift) and ‘0.5’ (extreme shift in the case of the solvent polarity goes to infinity), which in consequence implies that the observed shift could not be described by the Lippert-Mataga solvatochromic equation.

The apparently anomalous large positive solvatochromic shift in 1, 4-dioxane may be attributed to both to the quadrupole interaction which is neglected in dipole-approximation used to derive the solvatochromic equations including that proposed by Liptay or the possible hydrogen-bonding specific interaction between the solvent dioxane and the solute picolinamide. In order to qualitatively estimate the extent of each contributions IR spectra of camphor molecule were carried out in different solvents, and the peak absorbance values in the solvents employed is summarized in Table 2 and are presented in Figure 5.3.

Table 2: The vibrational absorbance maxima of Camphor in different solvent and with polarity function, refractive index and dielectric constant.

Solvent	Absorption maxima, ν_{max}/cm^{-1}	Dielectric constant, ε_r,	Refractive index, *n*	Polarity function $f(\varepsilon_r, n^2)$
Heptane	1752	1.92	1.385	0.09516
CCl_4	1745	2.24	1.4601	0.11876
Dioxane	1742	2.25	1.4224	0.12589
MEAC	1743	7.30	1.361	0.31326
Butanol	1748	17.80	1.399	0.36163
Ethanol	1747	24.50	1.3614	0.37934
Methanol	1743	32.70	1.3284	0.393
ACN	1735	37.50	1.3441	0.39284

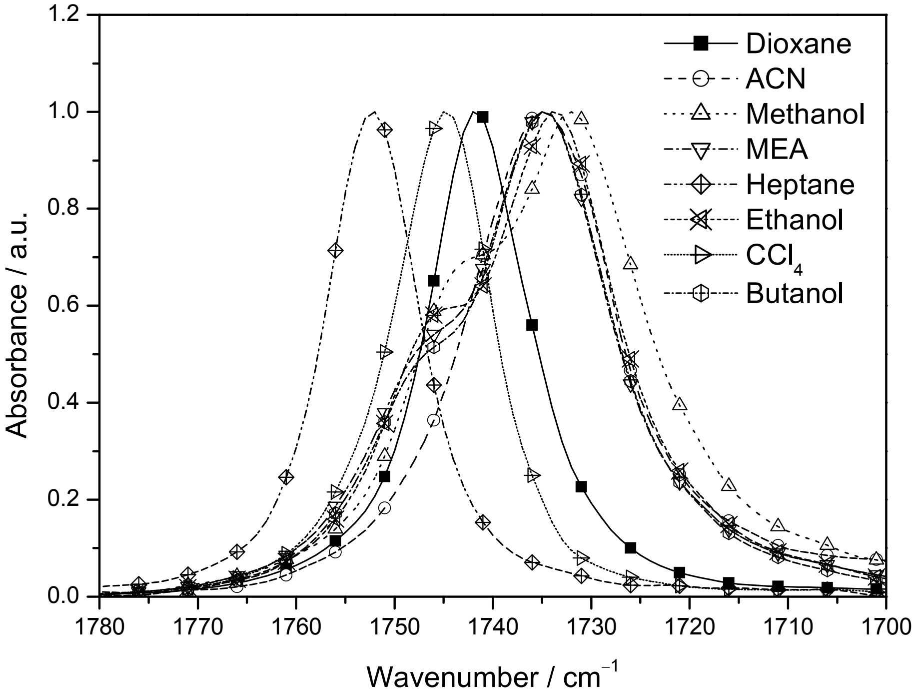
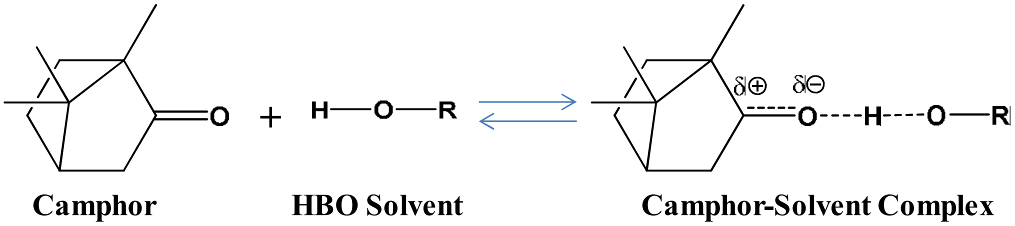


Figure 5.3: Normalized spectra of camphor in different solvents.

The peak absorption frequency of camphor was shifted to lower energy with increasing solvent polarity. Interestingly, there was a distinct different in the band-shape of the spectra in hydrogen bonding (HBO) forming (methyl acetate, methanol, ethanol and butanol) and the rest (Dioxane, heptane, CCl$_4$ and ACN) of the solvents. The energetically low lying peak in HBO solvents is attributed to the hydrogen bonding complex as shown in the scheme 2 [3].



Scheme 2: Hydrogen bonding complex of camphor.

In order to obtain the carbonyl band in camphor, the spectra of the compound in HBO solvents were Gaussian fitted (Note that the spectrum of an absorption band has generally a Gaussian shape). The values of the ν_{max} were then plotted against the Lippert-Mataga polarity function in the same way as was done for picolinamide (see Appendix Figure 7). Though the wavenumber obtained for dioxane is less that of acetonitrile, the calculated solvation energy is meaningless since it approaches infinite. The difficulty in establishing solvent induced shift with the polarity function is well known in the literature and various attempted have been made to generate a linear relationship by considering the contributions of orientation (which depends on ε_r) and electronic polarization (which depends on n) separately [3]. In either case however unrealistic and unphysical results obtained which lead us to question the validity of the Lippert-Mataga equation specifically and the commonly employed equations as a whole in their application for determining the solvation dependent dielectric constant.

The basic scientific principle in describing the solvatochromic shift is that the polarity of the solvent determines the extent of perturbation of the energy state of a molecule compared to the energy state in vacuum. Since in excitation there are two states (ground and excited states), the interaction of the two states in a given solvent environment may be different consequently this will lead to a change in excitation energy, i.e. the position of maximum absorption wavenumber. The comparatively extensive theoretical description of the energetic due to solvent-solute interactions is presented by Liptay equation. Therefore, examining the Liptay equation for any possible shortcomings may help to explain the apparently ‘unexpected’ large solvatochromic shift observed in dioxane, since all the other commonly in the literature employed solvatochromic equations are either simplification or modification of Liptay equation.

Liptay expresses the perturbing energy using the commonly employed ‘dipolar approximation’, in which all higher order polar interactions are neglected. The approximation is valid for longer wavelength radiation including ultraviolet, visible and infrared radiation, and when the solute and the solvent molecule don’t posses higher order poles. For solute/solvent molecules that have quadrupole moment like dioxane, equations derived based on ‘dipolar approximation’ usually underestimate the interaction stabilization and thus the extent of solvatochromic shift.

The unphysical result obtained for dioxane in infrared experiments suggests that the existing equations cannot be used to determine the solvation dielectric constant using the existing solvatochromic equations. This finding made us to question the applicability of from Baumann proposed solvation dielectric constant for dioxane irrespective of the nature of the solute.

5.2. Determination of Solvation Dielectric Constant ($\varepsilon_{r,solv}$) of Dioxane Using UV/Vis Spectra DMABA, NBA and BBA

Baumann *et al*. [11] suggested a solvation dielectric constant of 6.0 for dioxane. This value could not be verified in the vibrational analysis. Therefore, in order to investigate the universal, i.e. compound independent applicability 6.0 for dioxane determination of the solvation dependent dielectric constant for dioxane were carried out on DMABA, NBA and BBA in electronic spectroscopy. For this purpose electronic spectra of all the three compounds were recorded in solvents of varying polarity. Here the investigation on DMABA is presented, while the results obtained for NBA and BBA are brought to appendix part.

The concentrations were kept relatively high in order to get peak absorbance values above 0.1. The observed spectra are presented in Figure 5.4.

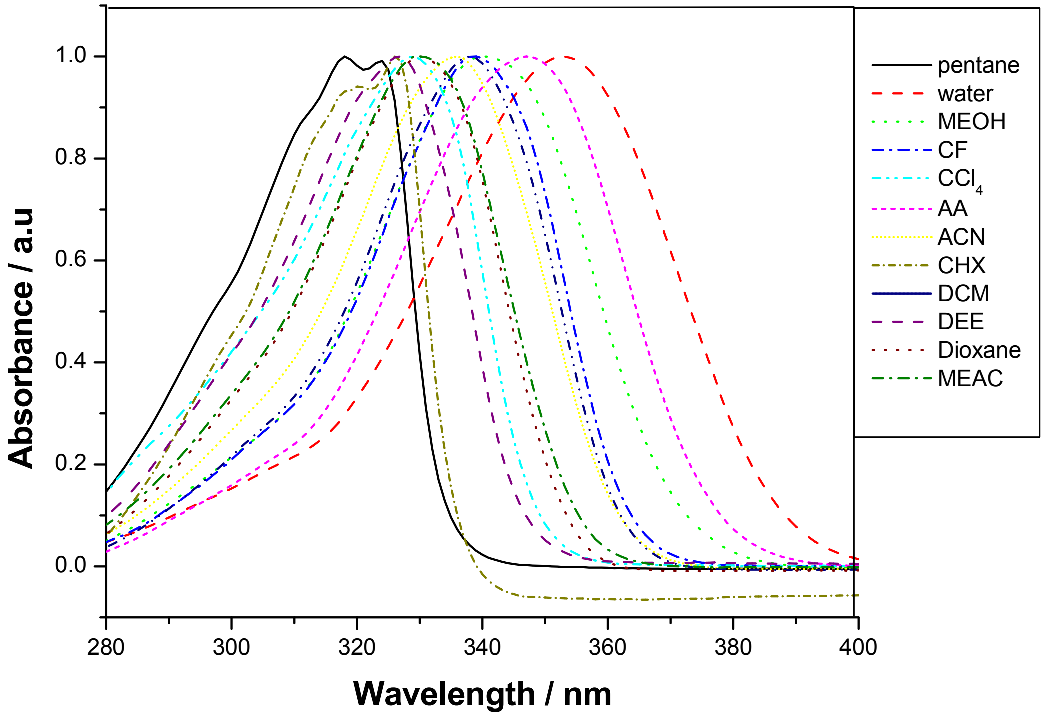
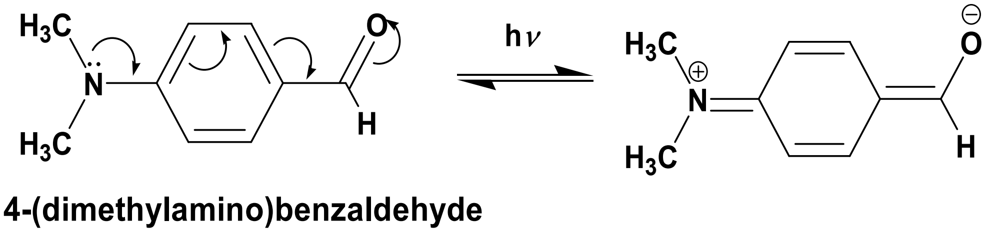


Figure 5.4: Electronic absorption spectra of DMABA in pentane, water, MEOH, CF, CCl$_4$, AA, ACN, CHX, DCM, DEE, Dioxane and MEAC.

In all solvents a single peak was observed in the spectral ranges between 280 – 400 nm. In addition, small shoulder peaks were observed in pentane and cyclohexane. Up on increasing solvent polarity, a solvent induced shift in wavelength of maximum absorption λ_{max} to lower energy were observed. The magnitude of the shift calculated considering the λ_{max} values of the most (water) and lowest (pentane) polar solvents was ≈ 35 nm.

Looking at the molecular structure of the compound, there are two possible electronic transitions. The electronic absorption at lower wavelength arises due to local electron transition (π-π^*) and at higher wavelength is due to charge transfer transitions. It is well known that the bands due to local transitions are solvent insensitive, whereas the charge transfer bands are sensitive to environmental changes [9]. Here the absorption band due to charge transfer is considered.



Scheme 3: Charge transfer of DMABA.

After assigning the bands, the electronic absorption maxima of the charge transfer band were plotted against the Lippert-Mataga polarity function. The data used for the plot are summarized in Table 3.

Table 3: The electronic absorbance maxima of DMABA, BBA and NBA in different solvent with their polarity function, refractive index and dielectric constant.

Solvent	Absorbance maxima, $v_{\max}(cm^{-1})$			Dielectric constant (ε)	Refractive index (n)	$f(\varepsilon_r, n^2)$
	DMABA	NBA	BBA			
ACN	29762	38023	38760	37.5	1.3441	0.39284
AA	28818	38023	----	6.15	1.3716	0.2947
CHX	30675	38610	38760	2.02	1.4262	0.10037
CCl_4	30395	----	----	2.24	1.4601	0.11876
DCM	29586	37736	38314	8.93	1.4241	0.3188
DEE	30581	38461	38910	4.33	1.3524	0.25573
Dioxane	30303	38023	38610	2.25	1.4224	0.12589
MEAC	30303	38023	----	7.3	1.361	0.31326
MEOH	29412	37736	38610	32.7	1.3284	0.393
Pentane	31447	38760	39062	1.84	1.3564	0.08976
Water	28329	37313	37879	80.1	1.333	0.40539
CF	29499	----	38023	4.81	1.4458	0.25353
THF	30120	----	----	7.58	1.4072	0.30837

Using the data a linear fit was generated excluding (masking) the data for those solvents that form hydrogen bond (DEE, THF, AA, MEOH and Water) and also dioxane (Fig. 5.5).

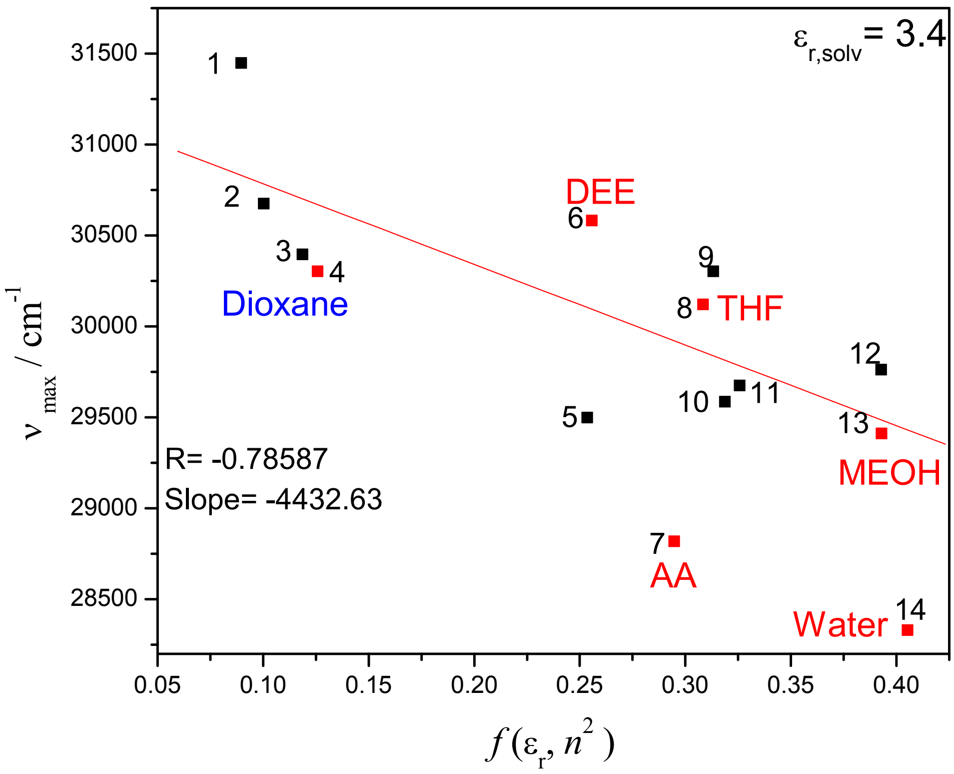


Figure 5.5: Plot of electronic absorption wavenumber maxima ν_{max} *versus* polarity function for DMABA in different solvents (as 1, 2, 3… for Pentane, CHX, CCl_4, Dioxane, CF, DEE, AA, THF, MEAC, DCM, DCE, ACN, MEOH and water respectively).

In fitting the data points the ν_{max} values for Dioxane, DEE, THF, AA, MEOH and Water solvents were excluded. It resulted with correlation coefficient of $R = -0.79$. The correlation coefficient obtained in the case of using the data obtained was poor (-0.74), which may indicate the exclusion of three data points is justified from the perspective linearity. The exclusion is scientifically justified since in the above mentioned solvents there are other contribution than mere nonspecific dipolar interaction that are considered in establishing the relationship between the electronic absorption wavenumber maxima and polarity function in Eq. (42).

Using the relationship generated from the fit and using the electronic absorption wavenumber, the solvation dielectric constant was calculated. The experimentally determined solvation dielectric constant for dioxane was ($\varepsilon_{r,solv}$ = 3.4). As expected, this value is higher than the value obtained from dipolar dielectric constant measurement (ε_r= 2.25). In dipolar dielectric measurement solute dipole-solvent quadrupole interaction (like in the case of dioxane) is not included. So that, it underestimate the interaction stabilization and it lowers the value of dielectric constant. From this point of view, it is reasonable to obtain higher value of dielectric constant from experimental data.

Though, the value obtained from this investigation is larger than that the dipolar dielectric constant, yet it is much smaller than the value suggested by Baumann *et al*. [11]. The values obtained in BBA and NBA investigations were 3.8 and 7.7 (Appendix Figure 5 and 6), respectively were also quite different than 6.0. The obtained values were not only inconsistent in all the cases of the three compounds investigated, but also different from the value proposed by Baumann *et al*. [11]. These observations clearly indicate that the assumption regarding the existence of a universal solvation dielectric constant is wrong. When the solute compound changes the value of solvation dielectric constant also changes. From this, it can be argued that the experimentally determined value of solvation dielectric constant for dioxane is not universally applicable to all compounds, and therefore it should experimentally determine for each compound.

6 Conclusions

In this work, the effect of solvent of different polarity on the vibrational absorption spectra of Picolinamide, Propylamide and Acrylamide and also the effect on electronic absorption of DMABA, BBA and NBA were studied. Up on increasing solvent polarity both the vibrational and electronic spectra bands were shifted to lower energy.

From the correlation of vibrational wave number *versus* Lippert-mataga polarity function, the solvation dielectric constant of dioxane was determined using picolinamide, propylamide and acrylamide as solute compound and the value obtained was goes to infinite ($\varepsilon_{r,solv}=\infty$) which is un physical. This result showed that from vibrational absorption spectra it is difficult to determine the solvation dielectric constant of solvent (that have quadrupole moment) using the existed solvatochromism equation. To overcome this problem the equation should modify in such a way that the solute dipole-solvent quadrupole interaction can consider.

From the correlation of electronic wave number maxima *versus* Lippert-mataga polarity function the solvation dielectric constant of dioxane was determined using DMABA, BBA and NBA as solute compound and the value was 3.4, 3.8 and 7.7, respectively, which is inconsistent. The empirically calculated value of solvation dielectric constant of dioxane does not apply to all compounds and optical spectroscopy methods. So from electronic spectra measurement the solvation dielectric constant of dioxane should empirically determine for each compound and in every optical measurement.

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Appendices

For the sake of simplicity, in the Figures the solvents are coded using the numbers appeared are represented 1, 2, 3,……. for Benzene, CCl_4, Dioxane, o-xaylene, DEE, DCM, ACN, Toluene, CF, DCE, Pentane, HEP., CHX, MEOH, water, MEAC and AA respectively.

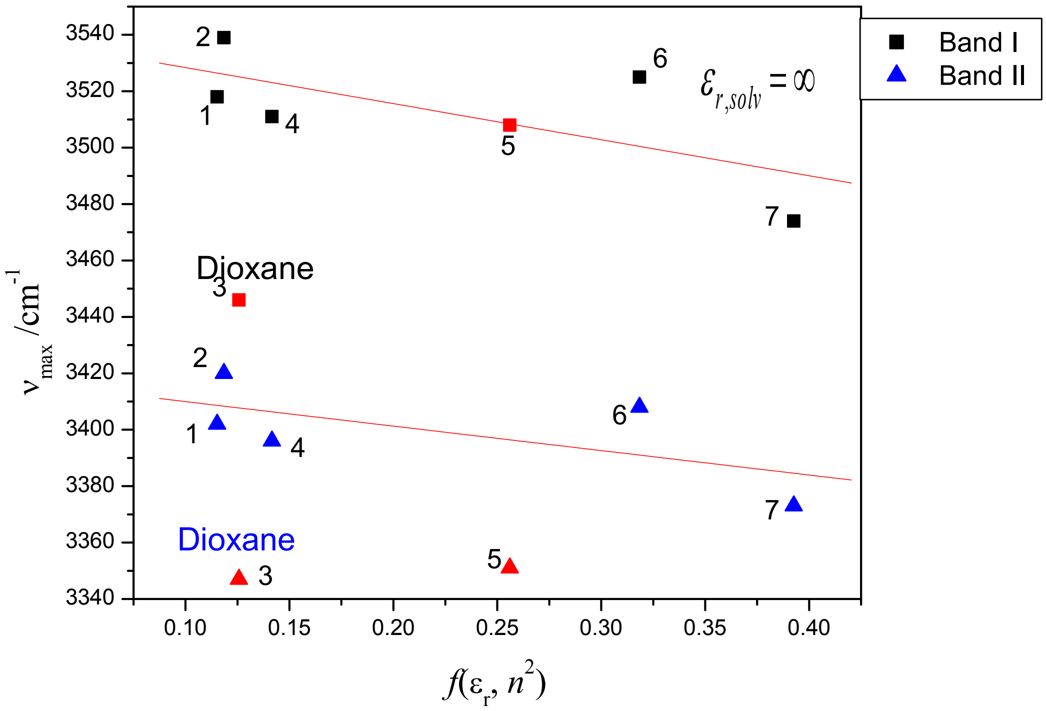

Figure 1: Plot of ν_{max} Band I and Band II *versus* polarity function for propylamide in different solvents.

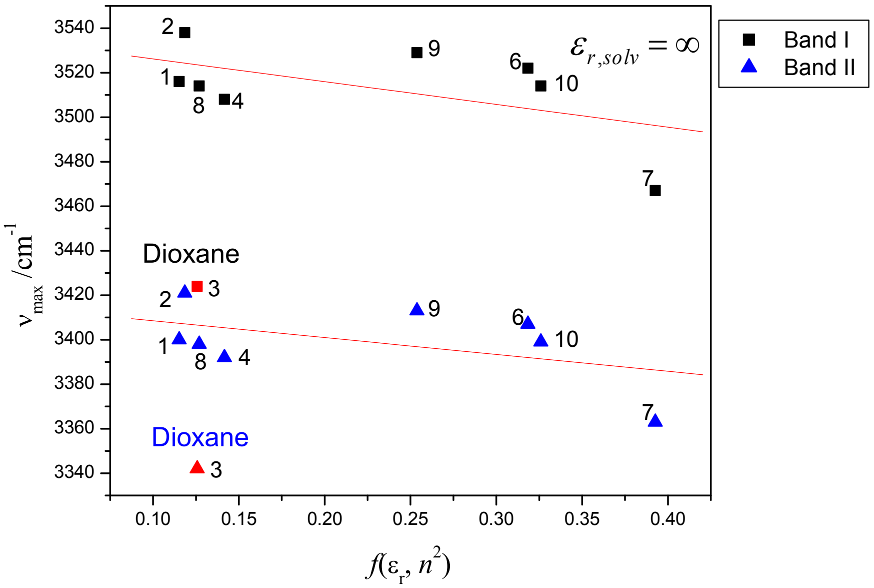

Figure 2: Plot of ν_{max} Band I and Band II *versus* polarity function for Acrylamide in different solvents.

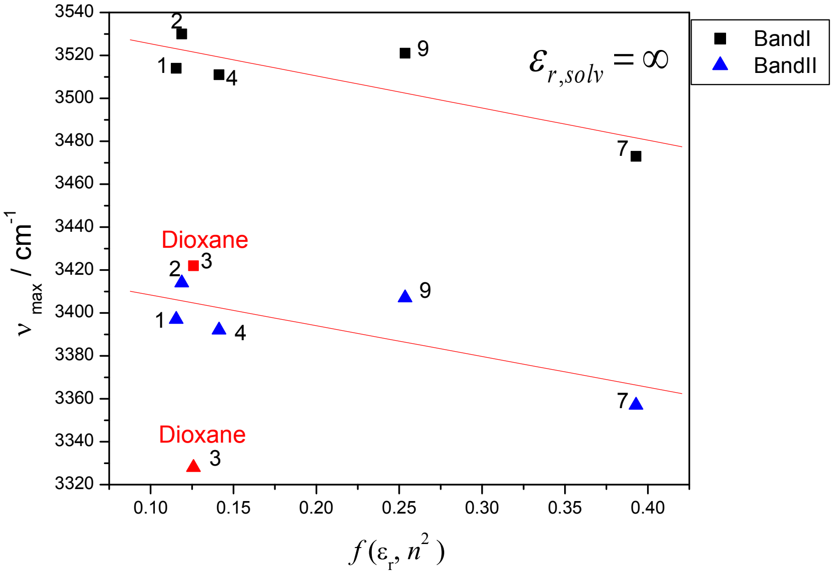

Figure 3: Plot of ν_{max} Band I and Band II *versus* polarity function for 2-Chloroacetamide in different solvents.

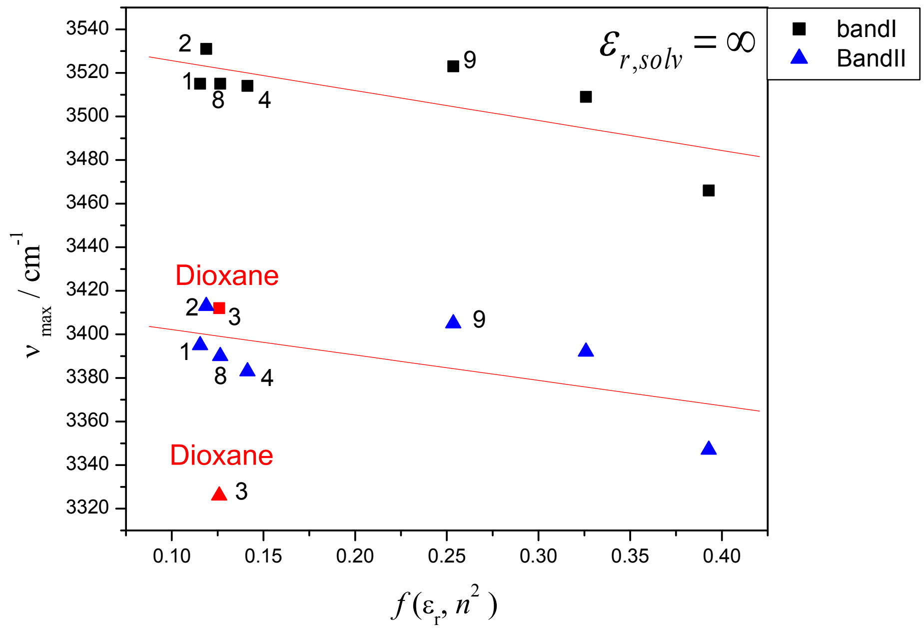

Figure 4: Plot of ν_{max} Band I and Band II *versus* polarity function for 2-Chlorobenzamide in different solvents.

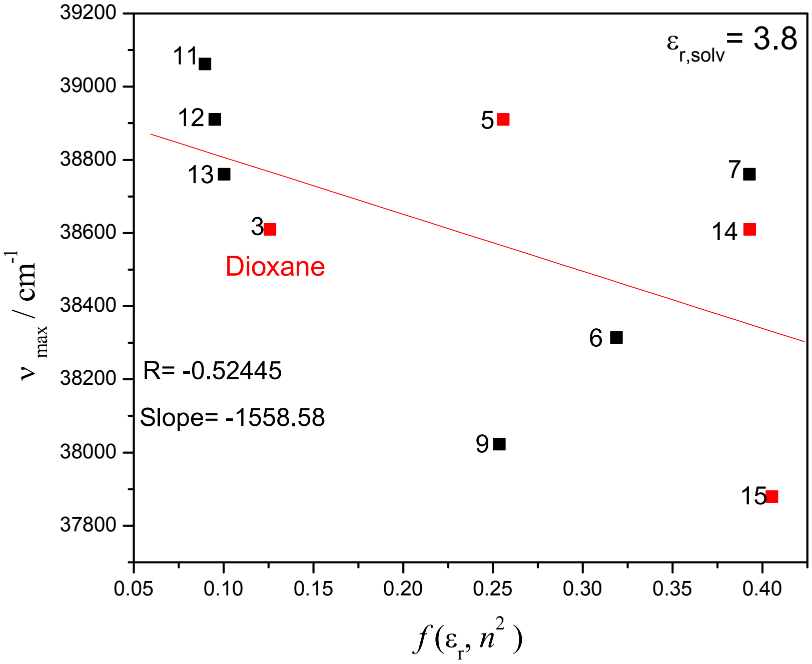

Figure 5: Plot of ν_{max} *versus* polarity function for BBA in different solvents.

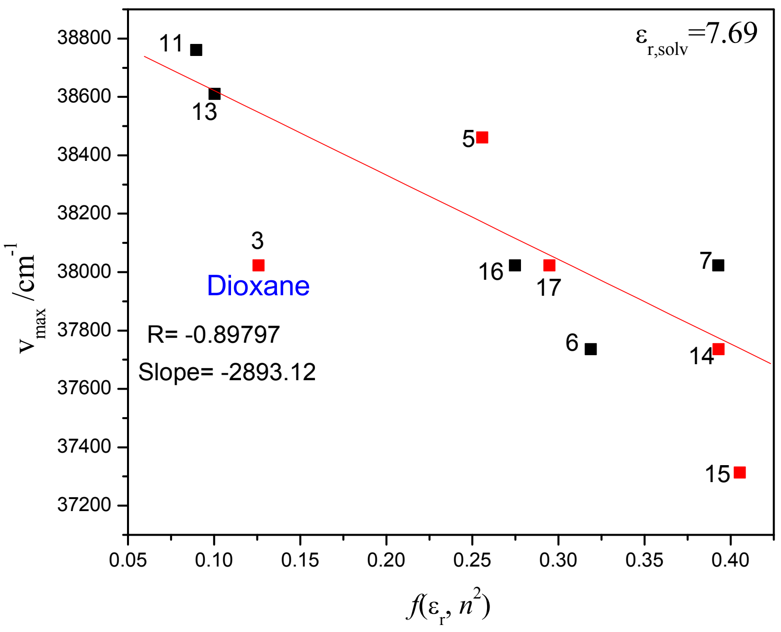

Figure 6: Plot of ν_{max} *versus* polarity function for NBA in different solvents.

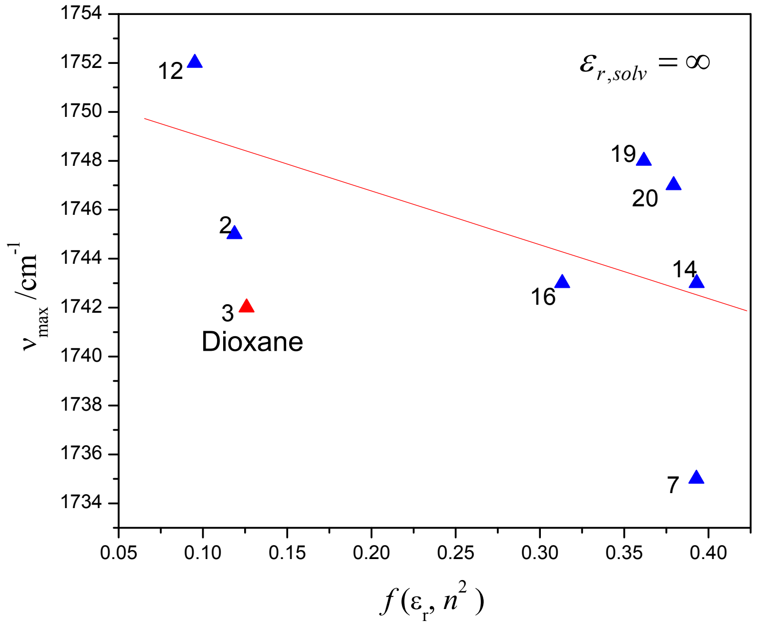

Figure 7: Plot of ν_{max} *versus* polarity function for Camphor in different solvents.