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DEPARTMENT OF CHEMISTRY

Investigation of Solvent and Concentration Effects on the Tautomeric Equilibrium of Acetamide

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Investigation of Solvent and Concentration Effects on the Tautomeric Equilibrium of Acetamide

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This is to certify that the thesis prepared by Hailu Wolde entitled **“*Investigation of solvent and concentration effects on tautomeric equilibrium of acetamide*”** and submitted in partial fulfillment of the requirements of the degree of Master of Science in 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 tautomeric equilibria of acetamide have been investigated by Infra-red spectroscopic technique. IR absorption spectra of solvents of varying polarity were recorded at different concentrations. The solvents used were chosen to cover wide polarity ranges that include cyclohexane, 2-propanol, methanol and acetonitrile. Increasing the solvent polarity, a shift in absorption maxima to lower frequency (bathochromic shift) was observed. Dilution studies on acetamide showed that the relative intensity of the bands with respect to the main antisymmetric stretching bands were concentration dependent which was attributed to intermolecular association (aggregation).From the results obtained, when the acetamide concentration was diluted, the third band disappeared and the second band decreased steadily. This indicated that the carbonyl absorption band in acetamide was concentration dependent. Further, as the concentration was decreased, the relative intensity of the bands gradually decreased. The presence of a concentration dependent second band (band II) was a clear sign of intermolecular aggregation resulted in dimer that is favored when the amount of acetamide molecule in the medium was higher. As expected, the aggregation of acetamide molecule was higher in non-polar solvents. The presence of isosbestic point in cyclohexane indicated the monomer dimer coexisted in equilibrium. The relative stability of amide-imidol tautomeric equilibrium has been studied over a wide range of solvent polarity. In polar solvents the tautomeric equilibrium shifted towards amide tautomer and in non-polar solvents the tautomeric equilibrium shifted in favor of the imidol tautomer due to formation of self-association.

Keywords: Solvent and concentration effects, Dimerization, Tautomerism, Acetamide, FT-IR

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List of abbreviation

ACN	Acetonitrile
CT	Charge transfer
CXN	Cyclohexane
E_{el}	Electronic energy
E_{rot}	Rotational energy
E_{tot}	$_{t}$ Total energy
E_{vib}	Vibrational energy
FT-IR	Fourier-transform infrared
HBA	Hydrogen bond acceptor
HBD	Hydrogen bond donor
HOMO	Highest occupied molecular orbital
IPL	Iso-propanol (2-Propanol)
LSER	Linear solvation energy relation
LUMO	Lowest unoccupied molecular orbital
MeOH	Methanol
NMR	Nuclear magnetic resonance
PCM	Polarizable continuum model
UV	Ultraviolet
Vis	Visible light
V_{max}	Maximum vibrational frequency
ZnSe	Zinc Selenide

1. Introduction

Solvent effects on organic reactivity and on absorption spectra have been considered for more than a century. It is well known that the photo-physical behavior of a dissolved solute depends on the nature of its environment, i.e. the intensity, shape, and maximum absorption wavelength of the absorption band of solute (chromophore) in solution depends powerfully on the solvent-solute interactions and solvent nature [1–4]. This effect is closely related to the nature and degree of solute–solvent interactions. The solvent dependent spectral shifts can arise from their non - specific (dielectric enrichment or specific hydrogen bonding) solute-solvent interactions. Solvent polarity is a commonly used term related to the capacity of a solvent for solvating dissolved charged or neutral, a polar or dipolar, species. The study of solvent effects on the structure and spectroscopic behavior of a solute is vital for the advancement of solution chemistry. The presence of specific and non-specific interaction between the solvent and the solute molecules are responsible for the change in the molecular geometry, electronic structure and dipolar moment of the solute. These solute-solvent interactions affect the solute’s electronic absorption band and this phenomenon is referred to as solvatochromism [5-6].

Spectroscopic solvent polarity parameters have been derived from solvent sensitive standard compounds absorbing radiation in spectral ranges corresponding to UV-Vis, IR, and NMR spectra [7–11].Considering solvation phenomena is of great importance in order to explain experimental results obtained when a molecule interacts with a liquid environment. This is an everyday need in chemistry laboratory where most molecular spectra are recorded in a specific solvent. In addition, solvation is fundamental in most biochemical studies. With the great development achieved in theoretical quantum chemistry for isolated molecules a natural attention is now dedicated to solution problems. In recent years, this has become a central concern in theoretical physical chemistry. These are essentially three major theoretical lines of development to include solvent effects in the quantum chemical models: continuum, discrete and explicit approaches. In the continuum model the solvent is considered implicitly as a polarizable medium characterized by its dielectric constant. The polarizable continuum model (PCM) has been found to be successful in a large number of applications and is perhaps the most used model at present. Polarity is essential solvent property to explain solvent effects on solutes in many chemical processes. Polarity parameters have been proposed over the years to account for solute-solvent interactions. Some Solvatochromism equations tried to measure solvent polarity; however, the main difficulty is found when specific interactions such as hydrogen bonds are needed for a proper treatment [12].

Solvatochromism is generally interpreted in the context of dielectric continuum correlate spectroscopic peaks shifts with the solvent reaction field. The results from the response of the dipolar solvents are characterized by dielectric constant and refractive index, in the presence of dipolar solutes. Commonly, the solvent dependent absorption band shift expressed as a function of dielectric constant. However, it is not consistent and adequate since the dielectric constant regard solvents as anon-structural isotropic continuum, not composed of individual solvent molecules with their own solvent-solvent interactions, which does not consider other interactions such as quadrupole and so forth, they do not take into account specific solute–solvent interactions hydrogen bonding and electron pair acceptor/electron pair donor interactions. Thus, instead of changing the solvatochromism equation, the best solution is the solvent polarity parameter ε_r with solvent dependent dielectric parameter and ignored expression solvent polarity with ε_r to overcome the problem [13].

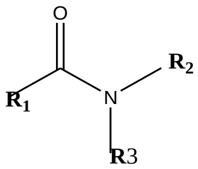
Tautomers are the chameleons of chemistry, capable of changing by a simple change of phase an apparently established structure to another, and then back again when the original conditions were restored. Intermolecular hydrogen bonding is the main factor that governs the kinetics and influences the structure of amide-imidol tautomerism in solution. The nature of hydrogen bonding and shift of established equilibria in different solvents have substantial influence on IR absorption bands. The thermodynamics and kinetics of electrons are to a large extent governed by redox centers, equally important protons motion can be viewed as extended series of tautomerization reactions. Tautomers are very interesting technological as well as fundamental [14, 15].

The solute-solvent interactions not only affect the tautomeric structure of ace amide but also include solvent dependent band shift and band shape. Though various potential applications of amides are discussed in literature, however; the solvent dependent amide-imidol tautomerism of primary amides, little or not been deeply studied on the structural changes that may arise due to the concentration of solutes and polarity of solvent. Therefore, it is necessary to conduct more systematic study of solvent and concentration effects on the tautomeric equilibrium of primary amides. Hence, the objective of the present study was to investigate the solvent and concentration effects on tautomeric equilibrium of ace amide which is one of the primary amides.

2. Literatures Review

2.1. Amides

Amides are organic molecules, whose bond formation is a basically important reaction in organic synthesis, in pharmaceutical industries, in addition amide bond plays a major role in composition of biological system such as proteins, nucleic acids; Proteins are large molecules which contain repeating amide units. They are formed when carboxylic acid group of one amino acid condenses with the amino group of another to form an amide linkage, also known as a peptide bond(-CO-N). Therefore an amide has a functional groups that consists of a carbonyl(C=O) to nitrogen, N, of the amide [16].



Where; R1, R2, R3 are alkyl, 1aryl or hydrogen.

Scheme 1: General structure of amides.

2.1.1 Structure and Classification of Amides

Amides can be classified as primary, secondary and tertiary on the basis of substituent on nitrogen as shown in the figure 2.

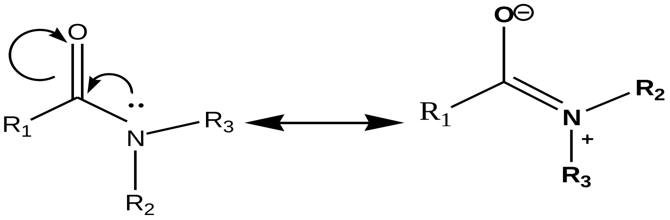
R-CO-NH_2	**R-CO-NHR_1**	**R-CO-NR_2**
a) Primary amides	(b) Secondary amides	(c) Tertiary amides

Where R is hydrogen, alkyl, or aryl group, and R_1, and R_2 are alkyl or aryl group.

Scheme 2: General classification of amides.

Amides have different types of hydrogen: hydrogen on the carbonyl side, hydrogen attached to the carbon atom on the alkyl (or aryl) group on the carbonyl side, which is called α-hydrogen,

hydrogen those attached to the nitrogen atom of the amide. Amides in IR spectroscopic studies fundamental absorptions of N-H in the range of 3450-3200 cm^{-1}.Primary amides have two N-H absorption bands near 3350 cm^{-1} and 3180 cm^{-1}, secondary amides show one N-H absorption band tertiary amides have no N-H absorption band but show only C=O in the range of 1680-1530 cm^{-1}.The conformation of the amide bond plays an important role in determining the backbone structure of the proteins and related compounds. Most of the properties of amides are readily rationalized by postulating amide resonance structures. The resonance reduces the double bond character of the C=O of amide, so its absorption band is displaced towards a rather smaller wave number. So that all amides have IR absorption frequencies lower than 1690 cm-^{1} [16, 17].



Where; R1, R2 and R3 are hydrogen, aryl or alkyl

Scheme 3: Resonance structure of amides.

2.2. Fundamentals of Spectroscopy

Spectroscopy is the study of the interaction of electromagnetic energy with matter. In organic chemistry, usually deals with molecular spectroscopy, i.e. the spectroscopy of atoms that are bound together in molecules [18]. Molecular spectroscopy is a means of probing molecules by absorption of electromagnetic radiation. The absorbed electromagnetic spectrum results in transitions between eigenstates of a molecule. The type of eigenstates involved in a transition depends on the energy of the spectrum absorbed. Figure 1 shows an electromagnetic spectrum along with the relative energies, wavelengths, and frequencies associated with each types of radiation. The absorbed ultraviolet and visible radiation generally results in transitions among electronic eigenstates, the absorbed IR radiation results in changes in vibrational eigenstates, and the absorbed microwave radiation results in changes in rotational eigenstates. The specific wavelengths of radiation that are absorbed in each region of the electromagnetic spectrum depend on the energy difference between the eigenstates of a molecule. The absorbed radiation in a spectrum provides information on the energy differences among various eigenstates of a molecule; however, it does not provide any information on the actual eigenstates involved in the transitions. Quantum mechanics is needed in order to analyze a spectrum in terms of assigning an absorption in a spectrum to a specific transition in eigenstates of a molecule [19].

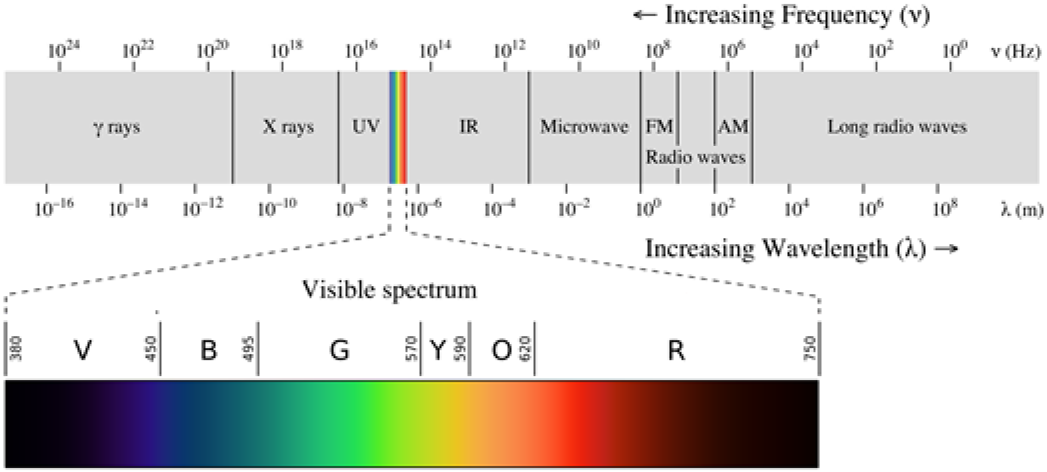


Figure1: Electromagnetic spectrum indicating the regions commonly used for ultraviolet /visible and infrared absorption spectroscopy.

The energy of a photon of electromagnetic radiation is inversely proportional to its wavelength, λ

$$E_{photon} = \frac{hc}{\lambda} \tag{2.1}$$

Where, the h in Equation 2.1 is Planck's constant of action, $6.62606957 \times 10^{-34}$ J s, and c is the speed of light. The wavelength of the photon absorbed in the infrared region is recorded in micrometers (microns, µm) or in terms of wave numbers (1/λ, in cm^{-1})

2.3. UV–Visible Spectroscopy

UV-Vis spectroscopy is the study of interaction of UV-Visible radiation with matter. Electromagnetic radiations such as visible light is commonly treated as a wave phenomenon, and characterized by a wavelength or frequency. Visible wavelength covers in a range from nearly 400 nm to 800 nm. And the ultraviolet radiation is an electromagnetic radiation with a wavelength nearly from 10 nm to 400 nm, which is shorter than visible light but longer than X-rays.

UV-visible spectroscopy is a technique that readily allows one to determine the concentrations of substances and therefore empowers scientists to study the rates of reactions, and determine rate equations for reactions, from which a mechanism can be proposed. As such UV spectroscopy is used extensively in teaching, research and analytical laboratories for the quantitative analysis of all molecules that absorb ultraviolet and visible electromagnetic radiation [20].

When radiation interacts with matter, a number of processes can cause, including reflection, scattering, absorbance, fluorescence/phosphorescence (absorption and reemission), and photochemical reaction (absorbance and bond breaking). In general, when measuring UV-visible spectra, we want only absorbance to occur [21].

The origin of spectral lines in molecular spectroscopy is the absorption, emission, and scattering when the energy of a molecule changes. In atomic spectroscopy, all transitions reflect changes in the configuration of electrons. In molecules, in addition there are energy states corresponding to nuclei vibrations and rotations. In consequence, the molecular spectra are more complex than atomic radiations and contain information on the molecular structure and the bond strength. They also provide a way of determining a variety of molecular properties, like dipole and quadrupole moments and the quantum numbers characterizing all molecular degrees of freedom. The molecular spectroscopy is also important for astrophysical and environmental science, for investigation of chemical reactions, for biology, and in many other areas of science and technology which requires detailed investigation of properties of microscopic atomic and molecular objects.

2.3.1. Nature of Electronic Transitions (Electronic Spectra)

In unsaturated system, pi-electrons predominantly determine the state of electron sheath which are excited by the absorption of UV-Vis light. The solvent effect on spectra, resulting from electronic transitions, is primarily dependent on the chromophore and the nature of transition ($\partial\rightarrow\partial^*$, $n\rightarrow\partial^*$, $n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$,) and charge transfer (CT) absorption. The electronic transitions of particular interest in this respect are $n\rightarrow\pi^{*},\boldsymbol{\pi}\rightarrow\boldsymbol{\pi}^{*}$and charge transfer (CT) absorptions. Organic molecules composed of directly attached electron donor and electron acceptor moieties have received considerable attention as possible models for a number of photochemical and photo biological processes. Excitation of such molecules induces transfer of an electron [22].

The total energy of a molecule is the sum of its electronic, vibrational energy and rotational energy. Energy absorbed in the UV region provides changes in the electronic energy of the molecule. As a molecule absorbs energy, an electron is promoted from an occupied molecular orbital (usually a non-bonding n or bonding π orbital) to an unoccupied molecular orbital (an ant bonding π∗ or ∂*orbital) of greater potential energy (Figure 2). For most molecules, the lowest-energy occupied molecular orbitals are ∂ orbitals, which correspond to ∂ bonds. The π orbitals lie at relatively higher energy levels than ∂ orbitals and the non-bonding orbitals that hold unshared pairs of electrons lie even at higher energies. The anti-bonding orbitals (π* and ∂*) are orbitals of highest energy [23].

The most likely transition would appear to involve the promotion of one electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), but in many cases several transitions can be detected, giving several absorption bands in the spectrum. We can have an overall view of the possible transitions prevailing in organic compounds [24].

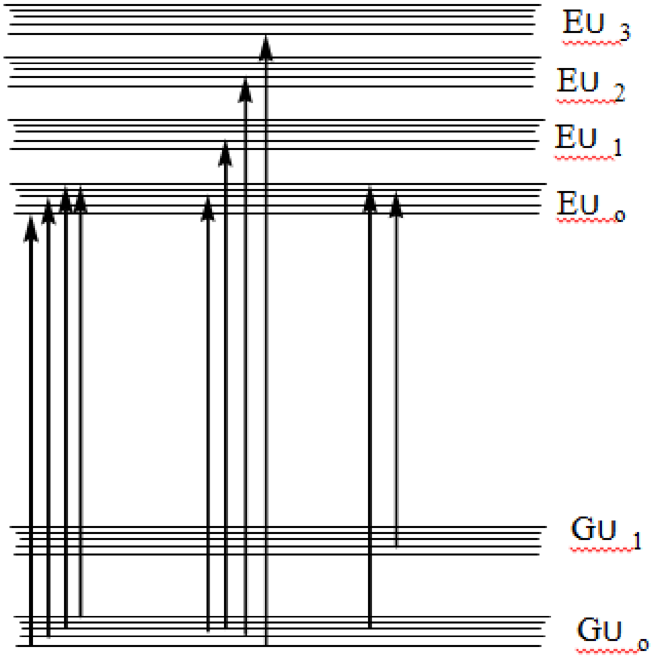


Figure 2: Energy level diagram showing excitation between different vibrational and rotational levels of two electronic states [23].

In the Born-Oppenheimer approximation the energy of a molecule can be presented as sum of electronic energy Eel, vibrational energy Evib and rotational energy E_{tot} energy.

$$E_{tot} = E_{el} + E_{vib} + E_{rot} \qquad 2.2$$

The amount of energy a molecule possesses in each form is not a continuum but a series of discrete levels or states. The differences in energy among the different states are in the order:

$$E_{el} > E_{vib} > E_{rot} \qquad 2.3$$

In some molecules and atoms, photons of UV and visible light have enough energy to cause transition between the different electronic energy levels. The wave length of light absorbed is that having the energy required to move an electron from lower energy to higher energy level.

2, 3, 2.Trasmittance and Absorbance

When light passes through or is reflected from a sample, the amount of light absorbed is the difference between the incident radiation (Io) and the transmitted radiation (I). The amount of light absorbed is expressed as either transmittance or absorbance. Transmittance usually is given in terms of a fraction of 1 or as a percentage and is defined as follows:

$$T = \frac{I}{I_O}, \%T = \frac{I}{I_O}.100 \qquad 2.4$$

Absorbance is defined as follows:

$$A = -\log T \qquad 2.5$$

For most applications, absorbance values are used since the relationship between absorbance and both concentration and path length normally is linear.

The absorbance of a sample also follows Beer-Lambert Law which states that the fraction of incident radiation absorbed is proportional to the number of absorbing molecules in its path and is given by the equation [25].

$$A = \varepsilon c l \qquad 2.6$$

Where, Ɛ is molar absorption coefficient having the units of $dm^3mol^{-1}.cm$. It is a constant and is a characteristic of a given absorbing species (molecule or ion) in a particular solvent at a particular wavelength, c is the concentration in mol /dm^3, and l is path length in cm.

2.4. Infrared Spectroscopy

Infrared refers to that part of the electromagnetic spectrum between the visible and microwave regions. It is one of the classical instrumental techniques for structure determination of molecules. This is because of its sensitivity to the chemical composition and architecture of molecules. The absorption of infrared radiations causes vibrational frequencies (transitions) of molecules.IR radiation absorption causes when the frequencies of light and vibrations are equal and when the molecular dipole moment changes during the vibration. Vibrational frequency and probability of absorption depend on the strength and polarity of vibrating bonds, i.e. they are affected by intramolecular and intermolecular effects. The strength of absorption increases with increasing polarity of the vibrating bonds.

Infrared spectroscopy is one of the oldest and well established experimental techniques for the analysis of secondary structure of polypeptides and proteins and the method is convenient, non-destructive, requires less sample preparation, and can be used under a wide variety of conditions. Fourier-transform infrared (FT-IR) spectroscopy is a fast, sensitive and precise method which is used to determine protein content in food, and has been used as worldwide instrument to analyze varieties of samples because of its ability to identify functional group of chemical compounds, such as hydroxyl, carbonyl, amine and ester. Fourier- transform infrared (FT-IR) spectroscopy has radically improved the quality of infrared spectra and minimized the time required to obtain data [26].

Electromagnetic radiation refers to the superficially diverse collection of radiant energy, from cosmic rays to X-rays to visible light to microwaves, each of which can be considered as a wave or particle traveling at the speed of light. These waves differ from each other in the length and frequency, as illustrated in Figure 3.

Frequency, ν (nu), is the number of wave cycles that pass through a point in one second. It is measured in Hz, where 1 Hz = 1 cycle/sec. Wavelength, λ, is the length of one complete wave cycle. It is often measured in cm (centimeters). Wave- length and frequency are inversely related**:**

$$v = \frac{c}{\lambda} \quad and \qquad \lambda = \frac{c}{v}, \qquad 2.7$$

Where c is the speed of light, 3 x 10^{10} cm/sec

Energy is related to wavelength and frequency by the following formulas:

$$E = h\nu = \frac{hc}{\lambda}, \qquad 2.8$$

Where h = Planck’s constant of action, 6.6 x 10–34 joules-sec

Note that energy is directly proportional to frequency and inversely proportional to wavelength.

The IR region is allocated into three regions: the near, mid, and far IR (see Figure 3.). The mid IR region is of greatest practical use to the organic chemist. This is the region of wavelengths between 3 x 10^{-4} and 3 x 10^{-3} cm. Chemists prefer to work with numbers which are easy to write; therefore IR spectra are sometimes reported in µm, although another unit, ν (nu bar or wave number), is currently preferred**.**

A wave number is the inverse of the wavelength in cm:

$$\tilde{\nu} = 1/\lambda \qquad 2.9$$

Where ν is in units of cm^{-1}, λ is in units of cm and now:

$$E=hc\tilde{\nu} \qquad 2.10$$

Wave number corresponds to an increase in energy. In wave numbers, the mid IR range is 4000–400 cm^{-1}. An increase in Eq. 2.10

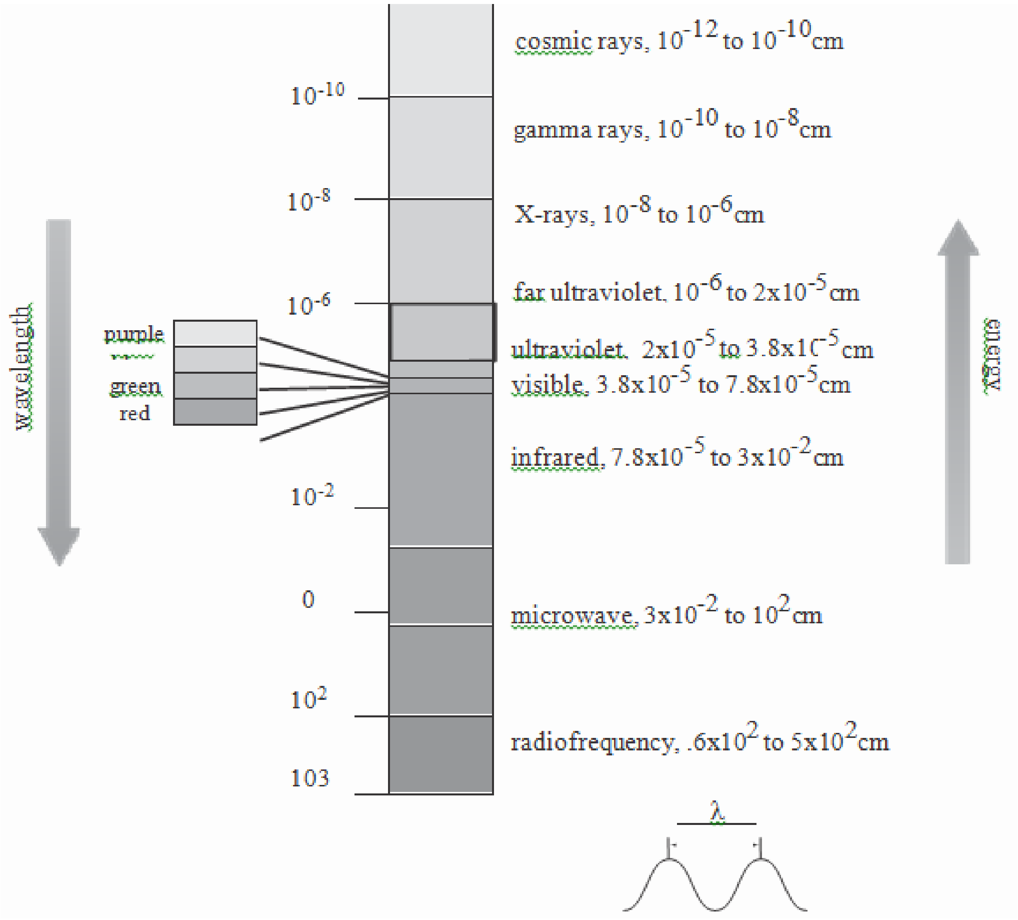


Figure 3: The electromagnetic spectrum [26].

Infrared radiation is absorbed by organic molecules and converted into energy of molecular vibration. In IR spectroscopy, an organic molecule is exposed to infrared radiation. When the radiant energy equals the energy of a specific molecular vibration, absorption occurs. A characteristic IR spectrum is shown in such a way that the wave number, plotted on the X-axis, is related to energy; therefore, the highest energy vibrations are on the left. The percent transmittance (%T) is plotted on the Y-axis. Absorption of radiant energy is therefore characterized by a “trough” in the curve: zero transmittance corresponds to 100% absorption of light at that wavelength.

The necessary requirement for infrared activity, leading to absorption of infrared radiation, is that there must be a net change in dipole moment during the vibration for the molecule or the functional group under study. That means the electric dipole moment must change during vibration, i.e. The vibration frequencies of a chemical bond depend on the strength of this bond (characterized by a proportionality constant termed the force constant) and the masses of the atoms at each end of the bond. There are two types of molecular vibrations: one that changes the bond length (stretching) and other that changes the bond angle (bending.)

From Hooke's law, the fundamental vibrational frequency of a molecule can be expressed by equation (2.11).

$$V = \frac{1}{2\Pi C}\sqrt{\frac{K}{\mu}} \qquad 2.11$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad 2.12$$

Where, ʋ is fundamental vibration frequency, C is speed of light, k is force constant, and μ is reduced mass. The reduced mass, where m_1 and m_2 are the component masses for the chemical bond under consideration.

The vibrational wave number (frequency) depends on force constant and the effective mass, and 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 the attached atoms the lower the IR frequency at which the bond will absorb[27].

When the frequency of a specific vibration is equal to the frequency of IR radiation directed on the molecule, the molecule absorbs the radiation i.e. each atom has three degrees of freedom, corresponding to motions along any of the three Cartesian coordinate axes(x, y, z). A polyatomic atomic molecule of n atoms has total of 3n degrees of freedom, corresponding to the Cartesian coordinates of each atom in the molecule. In a nonlinear molecule, 3 of these degrees are rotational and 3 are translational and the remaining corresponds to fundamental vibrations; in a linear molecule, 2 degrees are rotational and 3 are translational. The net number of basic vibrations for nonlinear and linear molecules is therefore;

Molecule	degree of freedom	
Linear	$3n-5$	2.13
Nonlinear	$3n-6$	2.14

Where n is the number of component atoms in the molecule [27].

2.5. Factors Affecting IR Absorption Spectra

2.5.1. Intermolecular Forces

At the most basic level, it is clear that molecules attract one another when they are far apart since liquids and solids exist and repel each other when they are very close since densities are finite. The mutual potential energy (u) of a pair of molecules is positive for small intermolecular distances and negative for large intermolecular distances. At some intermediate distance the potential energy is a minimum and at this point the attractive and repulsive forces balance [28].

All solvent effects induced in the physical absorption of electromagnetic spectrum depend on the intermolecular forces between solute and surrounding solvent molecules. Intermolecular forces include nonspecific force such as purely electrostatic columbic forces of charged ions and dipolar molecules (ion/ion, ion/dipole, dipole/dipole) and polarization forces that come from dipole moment induced in molecules by nearby ions dipolar molecules(ion/non- polar molecules, dipole/non- polar molecules, two non-polar molecules (dispersion force),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 decide quantitatively. The intermolecular forces not only permit solute-solvent interactions explanation but also determine the properties of gases, liquids and solids. The main and commonly used intermolecular forces are categorized in to the followings [29, 30].

2.5.1.1. Ion-Dipole Forces (Electrostatic Forces)

If the magnitude of the two equal and opposite charges of the molecule dipole is denoted by q, and the distance of separation l, the dipole moment is given by μ = q.l Electrically neutral molecules with an unsymmetrical charge distribution possess a permanent dipole moment μ.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 equation (2.15).

$$U_{ion-dipole} = -\frac{1}{4\Pi\varepsilon} \cdot \frac{ze\mu\cos\theta}{r^2} \qquad 2.15$$

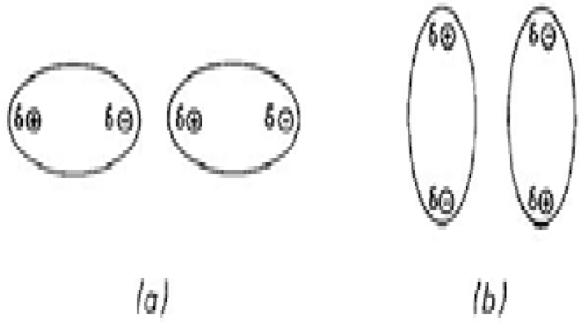
Where ε is the permittivity of vacuum, z. e the charge on the ion, r the distance from the ion to the center of the dipole, and θ the dipole angle relative to the line r joining the ion and the center of the dipole. Cos θ= 1 for θ= 00, i.e. in this case the dipole is positioned next to the ion in such a way that the ion and the separated charges of the dipole are linearly arranged. Equation (2.15) 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.

2.5.1.2. Dipole-Dipole Forces

Directional forces depend on the electrostatic interaction between molecules possessing a permanent dipole moment μ due to their opposite charge distribution. When two dipolar molecules are optimally oriented with respect to one another at a distance r as shown in scheme 4 (a) 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 Scheme: 4(b).

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 Eq. (2.16) (k_B= Boltzmann constant; T =absolute temperature).

$$U_{dipole-dipole} = \frac{1}{(4\Pi\varepsilon)^2}\cdot\frac{2\Pi\mu^2}{3k_BTr^3} \qquad 2.16$$



Scheme 4: (a) “Head to tail” arrangement of two dipole molecules ;(b) Antiparallel arrangement of two dipole molecule

2.5.1.3. Dipole-Induced Dipole Forces

When polar substances dissolve in non-polar solvent, the molecular dipoles of the solute are capable of interfere with the electronic clouds of the solvent molecules inducing the appearance in these of new dipoles. The dipoles of solutes and those induced will line up and will be attracted and the energy of this interaction (also called interaction of polarization or induction)[30].

$$U_{diple-induceddipole} = \frac{a_1\mu^2}{\left(4\Pi\varepsilon_o\right)^2 r^6} \qquad 2.17$$

Where a_1 is polarizability, μ is dipole moment and r is intermolecular distance.

2.5.1.4. Instantaneous Dipole-Induced Dipole Forces

In atoms and molecules possess in no permanent dipole moment, the continuous electronic movement in an instant and small dipole moment, which can fluctuatingly polarize the electron structure of the neighboring atoms or molecules. This coupling effects the electronic movements to be synchronized in such a way that a mutual attraction results. The energy of such so-called dispersion or London interactions can be expressed as [31].

$$U_{dispertion} = -\frac{1}{(4\Pi\varepsilon_o)^2}\cdot\frac{3a_1a_2}{2r^6}\cdot\left(\frac{I_1I_2}{I_1+I_2}\right) \qquad 2.18$$

Where α_1 and α_2 are the electronic polarizability and I_1 and I_2 are the ionization potentials of the two different interacting species

Dispersion forces are common for all atoms and molecules; they alone are responsible for the aggregation (association) of molecules which possess neither free charges nor electric dipole moments. Because of the greater polarizability of π-electrons, especially strong dispersion forces exist between molecules with conjugated π-electron systems (e.g. aromatic hydrocarbons). For many other dipole molecules with high polarizability as well, the main part of the cohesion is due to dispersion forces [32].

2.5.1.5. Hydrogen Bonding

Hydrogen bonding is important due to the effects they have on the properties of compounds. If hydrogen boding is possible between solute-solvent, solute-(solute-solvent) mixed solvent, this property increase solubility and other consequences in large or even in infinite solubility. There is evidence that the double and triple bond aromatic rings, and cyclopropane rings can form hydrogen bonds with polar functional group. But these bonds are very weak.

Hydrogen bonding is formed between functional group and an atom or group of atoms in very similar or different molecules. It can exist in the form of solid and liquid phase or in solutions. Hydrogen bonding can be detected in many ways but the most important way is by the infrared spectroscopy. In many cases, there is some functional groups that are free and some are hydrogen bonded. In such cases two IR absorption bands appear. IR spectroscopy can also distinguish between inter-molecular and intra- molecular hydrogen bondings are investigated by an increase in concentration. Intermolecular hydrogen bonding can be influenced by the dilution or temperature while intra- molecular hydrogen bonds are unaffected [33].i.e. The strength of hydrogen bond decreases as distance between proton donor and proton acceptor group increases, and hence, the effect of concentration on intermolecular and intramolecular hydrogen bonding is obviously different in that bands result from intermolecular bonding generally disappears at low concentration but intramolecular hydrogen bonding exists at very low concentration[34].Molecules possessing hydroxy 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 bivalency of the hydrogen atom involved. A general definition of the hydrogen bond is: when a covalently bonded hydrogen atom forms a second bond to another atom, the second bond is referred to as a hydrogen bond. A hydrogen bond is formed by the interaction between the partners R—X—H and: Y—R’ according to Eq. (2.19).

$$R-X-H+:Y-R^{I} \leftrightarrow R-X-H...Y-R^{I} \qquad 2.19$$

R–X–H is the proton donor and: Y–R makes available an electron pair for the bridging bond. Thus, hydrogen bonding can be considered as a preliminary step in a Brønsted acid-base reaction which would cause a dipolar reaction product R–X-.....H–Y+–R’. X and Y are atoms of higher electronegativity than hydrogen (e.g. N, O, S, F, Cl, Br, I). Both intramolecular and intermolecular hydrogen bondings are probable, the latter when X and Y belong to the same molecule. A special class is ionic hydrogen bonds formed between neutral molecules and ions to give cationic or anionic hydrogen-bonded systems such as R–X+–H….Y–R’ and its anionic counterpart R–X–H…. -Y–R’; R–X+–H is usually a protonated base and -Y–R’ a deprotonated Brønsted acid [35].

2.5.2. Mesomeric Effects

Mesomeric effect is caused due to the delocalization of electrons. A group that can donate electrons in to a neighboring bond has a positive mesomeric effect, +M and is called electron donor by mesomeric effect, one that attracts electrons out of the bond has a negative mesomeric effect, -M and is an electron acceptor . This causes lengthening or the weakening of a carbonyl bond leading to lowering of absorption frequency because of conjugation as shown in case of Acetamide[35].The resonance reduces the double bond character of the C=O of amide, so its absorption band is displaced towards a rather smaller wave number. All amides have an IR absorption frequency lower than 1690cm^{-1}

2.5.3. Concentration Effects

In measurement of absorption spectra by spectroscopic method is done under dilute solutions. This is because, concentrated solutions undergo solute-solute interactions other than solute-solvent interactions, in that the solute-solute interactions may cause change in the intensity and frequency of bands. Thus, intermolecular interactions are enhanced if hydrogen bonding exists. All amides except tertiary, exhibit formation of hydrogen bonding with that of carbonyl (C=O) of oxygen and hydrogen of nitrogen (N-H).Hence, all amides have the vibrational frequency lower than 1690 cm^{-1} [36].

2.6. Solvent Effects on Absorption Spectra

The study of solvent effect on properties is of vast scientific and technological interests. The solvent plays an important role in several processes, powering molecular properties, speed up chemical reactions, and making feasible innumerous biological processes. Onsager and Kirkwood developed, in the early period of quantum mechanics, a model in which the solvent is treated as a continuum dielectric. These ideas were developed further to the concept of a self-consistent reaction field, where the dielectric is polarized by the charge distribution of the solute, which is one by one polarized by the field of the induced charges of the dielectric.

One drawback of the continuum models is that the specific interactions between the solute and the solvent need special attentions that are not always justified. An alternative approach where the solvent is treated explicitly has been developed. This approach recognizes the need for a statistical treatment of the liquid, and for a proper description, a large number of molecules must be involved in the calculations [37].

The wave length and intensity of absorption bands are both affected when a molecule is in solvent environment. This is due to unequal perturbation of the ground and exited electronic state of molecule which depends on the nature of the solute-solvent interactions. The interpretation of solvent effect is often made difficult, since they are small and not easy to measure precisely and also because several individual effects, superimposed on one another, contribute to the observed changes. The dipole moment difference between exited state and ground state shows the solvent effect on solvatochromic shift. The ground state dipole moment µg was calculated using a method of Gaussian software. The exited state of dipole moment µe was determined by Lippert-Mataga method, that is based on the measurement of the absorption spectrum shift with respect to solvent polarity function Δf.

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{1}{2}\left(\frac{n^2 - 1}{2n^2 + 1}\right) \qquad 2.20$$

Where; ε is dielectric constant, n refractive index, The Lippert-Mataga equation has form [24].

$$\Delta v_{ab} = v_a - v_f = \frac{2}{hca^3} . (\mu_e - \mu_g)^2 \Delta f + cons\tan t \qquad 2.21$$

Where: h, Planck's constant of action, a, Onsager radius Vsol and v_0, absorption maxima wave numbers Solvent effect on absorption spectra has both qualitative and quantitative. Quantitatively, the spectra shifts to the refractive index while the qualitative and comprehensive treatment of solvent effect have been sought to deduce spectra shift in terms of combination of dipole polarization of solute molecule and hydrogen bonding effect[38].

Solvent effects on organic reactivity and on absorption spectra have been considered for more than a century. It is well known that the photo-physical behavior of a dissolved dye depends on the nature of its environment, i.e. the intensity, shape, and maximum absorption wavelength of the absorption band of solute in solution depends mainly on the solvent-solute interactions and solvent nature. This effect is closely related to the nature and degree of solute–solvent interactions. The solvent dependent spectral shifts can arise from either non-specific (dielectric enrichment) or specific (e.g. hydrogen-bonding) solute–solvent interactions. The solvent effect can be determined by Solvent polarity scale or solvatochromic parameters.

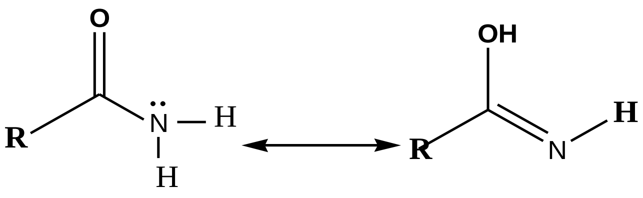
Solvent polarity is a commonly used term related to the ability of a solvent for solvating dissolved charged or neutral, a polar or dipolar, species. Efforts to express it quantitatively have mainly involved physical solvent properties such as relative permittivity, dipole moment, or refractive index, but these considerations cannot effectively account for the multitude and specific interactions of solute-solvent on the molecular- microscopic level.

Spectroscopic Solvent polarity parameters have been derived from solvent sensitive standard compounds absorbing radiation in spectral ranges corresponding to UV-Vis, IR, and NMR spectra. In spite of the observation that single empirical parameters may serve as good approximations of solvent polarity in the sense defined, but there are many examples of solvent-sensitive processes known, which cannot be correlated to one empirical solvent parameter. However, multi parameter solvent polarity scale for quantitative assessment of the solvent/solute interface and the absorption shifts can be used. The effect of solvent polarity on the absorption spectra are inferred by means of linear solvation energy relationship (LSER) using a Kamlet–Taft Eq.2.22.

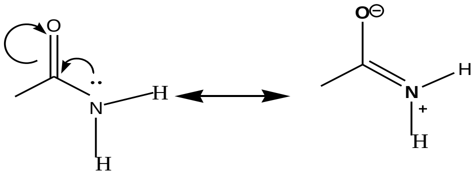
$$v = v_o + s\Pi^* + b\beta + a\alpha \tag{2.22}$$

2.7. Solvent Effects on Tautomeric Equilibrium

Tautomers are capable of changing phase from an apparently established structure to another and then back again when the original conditions are restored disconcerting. A change in structure means changes in properties. Intramolecular hydrogen bonding is the major factor that governs the structure of keto-enol, amide-imidol tautomerism, etc. in solution and in β-ketoamides, internal hydrogen bonding is possible to be established in numerous tautomeric forms [40] Tautomerism should not be confused with resonance, in that resonance structures differ in position of electrons whereas tautomerism involves the movement of hydrogen or another atom that may causechange in molecular geometry.



Tautomerism

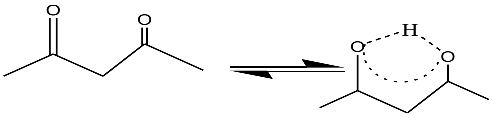


Resonance

Scheme 5: Tautomeric equilibrium & resonance structure of primary amides

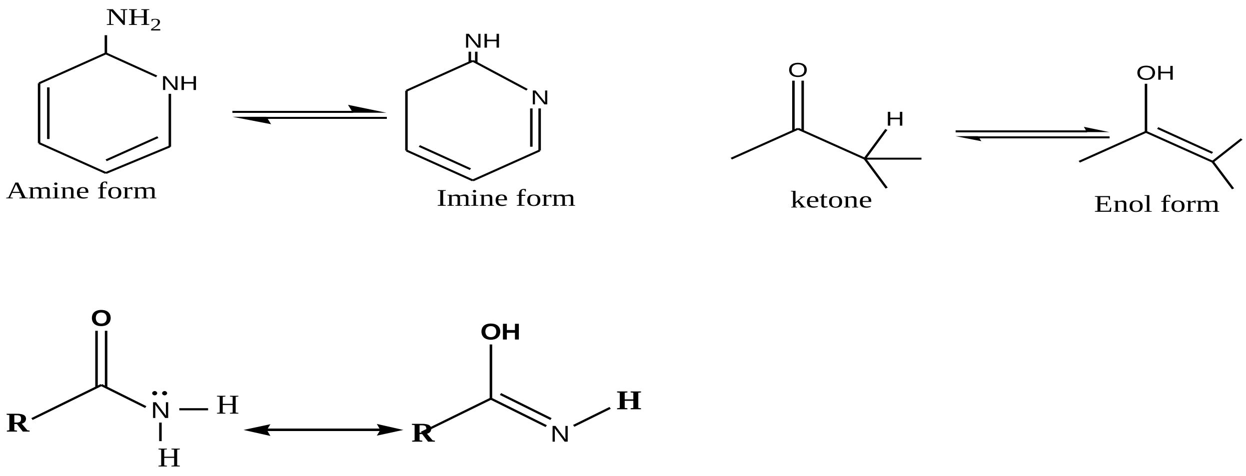
The position of the tautomeric equilibrium is powerfully influenced by the formation of hydrogen bonds, either inter- or intramolecularly, because of the considerable enthalpy of hydrogen bond formation. Numerous examples are known where intramolecular hydrogen bonding may alter the tautomeric equilibrium of a species; a well-known example is the intramolecular hydrogen bond that shifts the equilibrium in a number of β-diketones towards a singly enolized species, particularly in polar solvents[40].It is expected that the enol tautomer stabilization would be attained in the neutral state as a result of the strong intramolecular hydrogen bonding between the tautomeric OH group and the carbonyl group in the ionophore part.

Prototropic tautomerism involves the relocation of an H atom and a double bond. One example of prototropic tautomerism is that between keto and enol forms (figure10). The keto tautomer possesses a C=O group, while the enol form has a vinylic alcohol structure. Increasing acidity of the α-H affects this tautomerism, favoring the enol form. Conjugated double bonds andintramolecular H-bonds can also stabilize the enol form [41].



Scheme 6: Keto-enol tautomerism and stabilization of enol form through intramolecular H-bonding.

Other types of prototropic tautomerism are amine-imine tautomerism (e.g. in adenines [43].Amide-imidol acid tautomerism (related to asparagine-linked glycosylation and, as a special case, lactam-lactim tautomerism (present in uracil and thymine [42].



Amide form imidol form

sScheme: 7: Types of protropictautomerism.

Proton transfer in the course of tautomerization is typically a very fast process. The equilibrium between tautomers is dynamic. Few information have been found on the occurrence of amides in equilibrium with the corresponding tautomers, the imidol ones

2.8. Isosbestic Point

If two or more species are in equilibrium in solution and if the absorption spectra of the two species overlap, then there will be a point known as the isosbestic point at which irrespective of the concentration of the two species, the absorption of the solution will remain unchanged. At the isosbestic point, the total absorbance does not change with time. However, the absorbance on either side of the isosbestic point changes as the reaction continues. At the isosbestic point, the molar absorptivities of the reactant and the product are equal. If the absorption spectra of the reactants and products do not cross, there will be no isosbestic [43].

2.9. Dimerization Constant

Dimerization is the process by which molecules tend to aggregate (associate) in concentrated solutions. This self-association phenomenon plays an important role in biological processes.

Such aggregation processes has been extensively studied on the dimerization of ionic dyes [44].In diluted systems, generally, dissolved molecules exist as monomers surrounded by solvent molecules, i.e. there is little or no interaction between them. In a concentrated solution, however**,** the interaction between the dissolved molecules can be very strong and association to the extent of dimmer formation.

$$M + M \leftrightarrow D \qquad 2.23$$

of where M and D represent the monomer and dimer species the dissolved molecule, respectively. K_{dim} is known as a dimerization constant and is expressed as

$$K_{\mathrm{dim}} = \frac{C_D}{C_M{}^2}$$

2.24with c_D and c_M the concentrations of the dimer and monomer, which are related to the absorbance through Lambert-Beers Law

$$A = \varepsilon_M C_M l + \varepsilon_D C_D l \qquad 2.25$$

In dimerization, the total weighed concentration c_0 is simply the sum of the monomer and dimer concentrations

$$C_O = C_M + 2C_D \qquad 2.26$$

Note that the dimmer concentration is multiplied by two, since two monomers are consumed in forming one dimmer. Rearranging, one may express the dimer concentration in terms of monomer concentration as

$$C_D = \frac{1}{2}\left(C_0 - C_M\right) \qquad 2.27$$

Using the above expressions (expressions in equation 2.25 and 2.27) one may derive an express ε ion for the apparent (measured) molar decadic absorption coefficient

$$\varepsilon = \frac{C_M}{C_O}\left(\varepsilon_M\right) + \frac{C_D}{C_O}\left(\varepsilon_D\right) \qquad 2.28$$

One can simplify eq. (2.28) by introducing a new parameter $\alpha = \frac{C_M}{C_O}$ as

$$\varepsilon = \varepsilon_M \alpha + \frac{(1-\alpha)}{2} \varepsilon_D$$

2.29

Using the relationships in Eq. (2.27) and rearranging one obtains an expression for the dimerization constant K_{dim}

$$K = \frac{C_O - C_M}{2{C_M}^2} = \frac{(1-\alpha)}{2\alpha^2 C_D} \qquad 2.30$$

Inserting the expression obtained for (2.29) in eq. (2.30) it results for the apparent molar decadic absorption coefficient

$$\varepsilon = C_M \frac{\left(\sqrt{8C_D K_{\text{dim}} + 1}\right) - 1}{4C_o K_{\text{dim}}} \alpha + \frac{1}{2}\varepsilon_D - \frac{1}{2}\frac{\sqrt{(8C_D K_{\text{dim}} + 1)} - 1}{4C_D K_{\text{dim}}} \varepsilon_D \qquad 2.31$$

Apparent molar decadic absorption coefficient and weighed concentration are accessible experimentally whereas as monomer and dimer molar decadic absorption coefficients and the dimerization constants are not. From eq. (2.31) it is evident that there are three unknowns, and therefore the unknown quantities are need to be determined iteratively for determining the three unknown quantities of the spectra of a serious of concentration are necessary. In this project we have employed in house developed nonlinear regression analysis program [45].

The Gibbs free energy is defined as the difference between the free energy content of the reactants and the free energy content of products under standard conditions. It is used to predict whether a process will occur spontaneously at constant temperature. Under such conditions, it is mathematically related to equilibrium constant by the equation

$$\Delta G^O = -RT \ln K_{\text{dim}} \qquad 2.32$$

Where R is the gas constant (8.314K/ mol) and T is the absolute temperature.

3. Objectives of the Study

3.1. General Objective

The general objective of this study is to investigate solvent and concentration effects on the tautomeric equilibrium of acetamide by Infrared spectroscopic technique.

3.2. Specific Objectives

The specific objectives of this thesis are to:

- Investigate effects of solvent on the spectral position of vibrational frequency (V_{max}) of acetamide.
- Investigate the concentration dependence of acetamide using concentration variable spectra.
- Determine the existence of isosbestic point and compare it with theoretical aspects.
- Examine the existence of tautomer and equilibrium as a function of polarity.
- Compare V_{max} of acetamide at different solvents of varying polarity with Lippert Mataga polarity function.

4. Experimental Part

4.1. Instruments and Chemicals used

IR spectra of the solution were measured by using FTIR spectrometer (PerkinElmer Spectrum 65 FT-IR spectrometer).The chemical used was acetamide (99% BDH Ltd Poole England). The chemical was used without further purification. The solvents used were methanol and 2-propanol and Acetonitrile (99.9% Carlo Erbo HPLC grade) and cyclohexane (99.5% Riedel-De Germany). Solvents were used for the investigation of studying solvation power and band shift. Distilled water and acetone (laboratory reagent grade) were used for cleaning purpose all the times.

4.2. Methods and Procedures

For the IR spectra measurement PerkinElmer Spectrum 65 FT-IR spectrometer using ZnSe cell surface through reflectance was used. All sample solutions dissolved by polar solvents were prepared at room temptature and pressure stirred thoroughly by glass rod until dissolution complete and then filtered off using filter paper, but solution prepared by nonpolar solvent like cyclohexane was heated until dissolution completes and the solution stirred by magnetic stirrer then filtered off. The IR absorbance measurement was employed solutions of different concentrations from more concentrated solution to low concentrated solution i.e. . All the measurements were carried out at room temperature and pressure. Origin 8.0 software used to draw graphs for IR spectral data interpretation; similarly chemdraw ultra was used to draw structure of some interested compounds.

5. Results and Discussion

5.1. IR Absorption of Acetamide in Different Solvents

The IR absorption spectra of acetamide were measured with solvents of varying polarity, the solvents used were methanol, 2-propanol, acetonitrile and cyclohexane, the measurements were done with the spectral range of 1500 cm^{-1} to 1800 cm^{-1} and from which absorbance were recorded by stepwise dilution process qualitatively at varying concentrations of the solution to determine solvent effects upon absorption maxima and solvent concentration dependent was studied. And, therefore; the effect of solvent polarity variations on tautomeric equilibrium using IR absorption maxima (V_{max}) was examined. The observed absorption maxima (ν_{max}) of solutions at different solvents were correlated with their spectral shifts and Lippert-Mataga polarity function. The relationship between vibrational frequency shifts with different solvent polarity was examined. The spectra are presented in Fig.4.

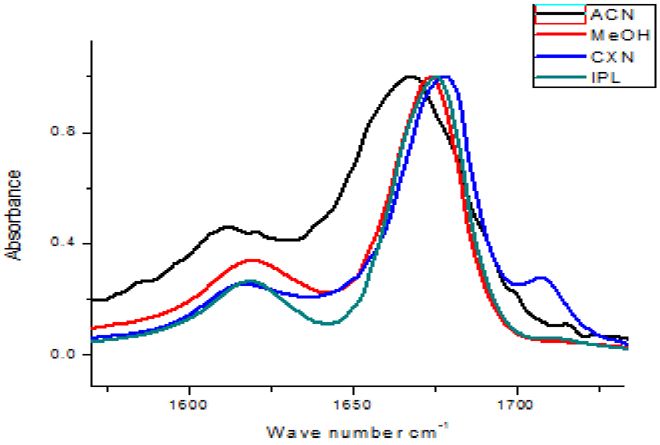


Figure 4: Normalized infrared spectrum of acetamide in different solvents of varying polarity.

The figure 4 indicated that there was a shift of absorption bands to lower frequency or lower energy with increasing solvent polarity i.e.bathochromic shift or red shift was observed. This indicated that the dipole moment in exited state is larger than in ground state. This means the neutral form is the dominant structure of the molecule. i.e. the change in dipole moment (μ_e-μ_g) is positive and thus, as expected the positive shift was observed. The spectral shifts observed in these different solvents depend on the difference in dipole moment of the exited and ground states and strength of the interaction between solute and solvents. Thus, the band shift was polarity dependent. The two, relatively strong absorption peaks were observed at (1667-1678) cm^{-1} and (1611-1620) cm^{-1} .It is commonly known as carbonyl absorption occurs comparatively at higher frequency than imine absorption, due to the higher bond strength. Thus, the bands at (1667-1678) cm^{-1} and (1611-1620) cm^{-1}wereassigned to C=O and C=N vibrations respectively in all spectra of the solvents. In general the bathochromic shift was observed as a function of an increased in solvent polarity between C=O, C=N and solvent molecules. These two bands were observed in all spectral absorption of solvents throughout the entire work. For the sake of simplicity, the bands were nominated as band I and band II respectively. The nomenclature was used throughout this work, and one additional band (band III) was observed in non- polar solvent like Cyclohexane.

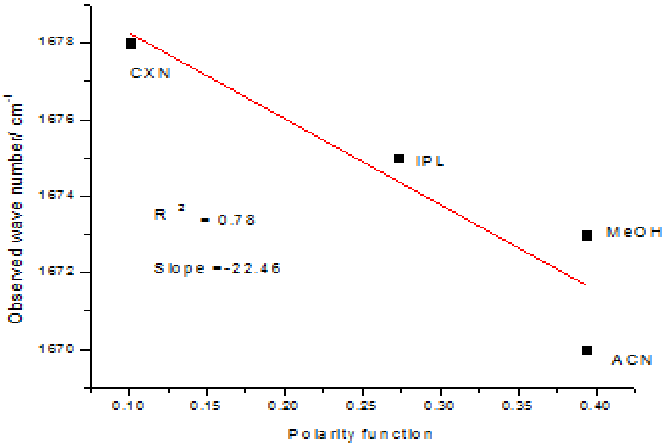
Table1: Absorption maxima of acetamide observed in different solvents. Dielectric constant, refractive index of solvents was taken from reference [46]; polarity function is calculated by using equation 2.20.

No.	Solvents	Band I(cm^{-1}) Observed	Band II(cm^{-1}) observed	Dielectric constant(ε_r)	Refractive index(n)	f ($\varepsilon_{r,n}^2$)
1	Acetonitrile	1670	1611	37.5	1.3441	0.3928
2	Methanol	1673	1615	32.6	1.3284	0.3930
3	2-propanol	1675	1617	18.3	1.3772	0.2730
4	Cyclohexane	1678	1622	2.02	1.4262	0.1004

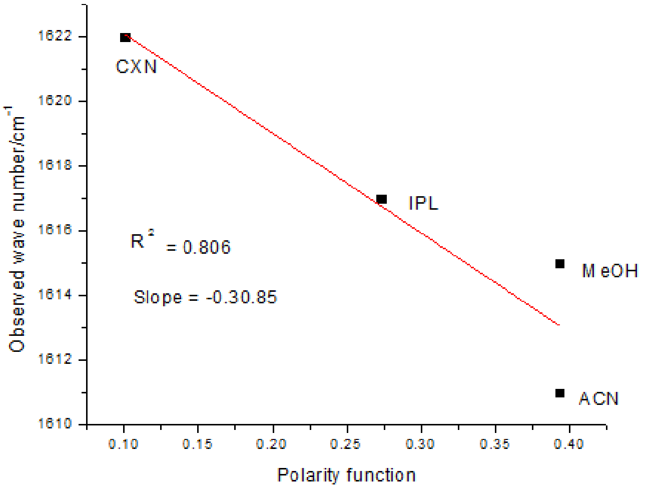
The absorption of the chromophore (solute) is mainly determined by the magnitude of a force constant k and effective mass. Thus, if a specific solute (chromophore) is considered, then shift induced through the interaction with solvent is related to the change in the force constant Therefore, the bathochromic shift or the red shift was observed when solvent polarity was increased, this could be explained that might be caused due to interaction of carbonyl (C=O), C=N and solvent molecules, the observed shift is consistent with the theory.

As the solvent polarity increased, dipolar interactions between solvent-solute also increased. The higher the solvent polarity, the greater dipolar interaction is. In comparison, using more polar solvents, the higher extent of complete solvation was observed, and hence the solute molecules in polar solvents existed as monomer, in contrast in non-polar solvents like Cyclohexane, due to association of solute molecules existed at higher concentration, consequently the third band was observed.

The wave number of the maximum absorbance (peak absorption v_{max}) of the two bands (band I and band II) in the solvents of varying polarity are plotted as a function of polarity function *f, and the* graph is presented in the figure 5. (a) and (b).



a)



b)

Figure5: Plot of (a) V(C=O) band I Vs polarity function of acetamide in different solvents and (b) V(C=N) Vs polarity function at band II.

The linear fit of the data points showed negative slopes. Poor correlation was observed. In fitting the data points the V_{max} for ACN and MeOH were excluded in both band I and band IIin comparison with IPL, CXN. The correlation coefficient obtained was 0.78 and 0.806 and slopes -22.46 and -30.85were observed for band I and band II respectively. From solvatochromism theoretical point of view, a single slope is expected from single vibrational transition and more than one slope is an indicator of the existence two or more chromophore resulting from isomeric structure. Accordingly the existences of two different slopes were observed for band I and band II with the value of -22.46 and -30.85 respectively. This implies that the existence of compounds under investigation of tautomeric isomers of amide-imidol in general and acetamide and actetionimidic acid tautomer in particular existed in equilibrium.

5.2. Concentration Effects on IR Spectrum of Acetamide in Different Solvents

The IR absorption spectra of acetamide in different solvents of varying polarity at different concentration are presented in the Figures 6, 7, 8 and 9 below. As it can be seen that in all Figures the two bands intensity increased as the concentration of acetamide increased, comparable weaker bands were observed at lower concentration. At very low concentration, the second bands vanished; this suggested that the amide molecule existed as monomer. One can deduce that from the concentration dependent absorption spectral bands seen in the figures below, all spectra shifted to the lower intensity (hypochromic shifts) were observed as far as the concentrations were decreased.

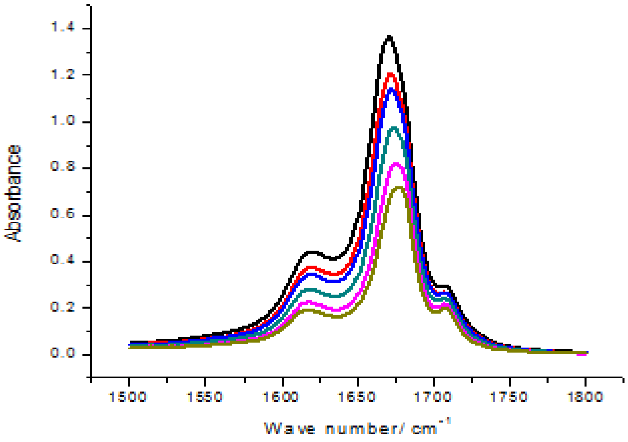


Figure 6: IR spectra of acetamide in acetonitrile at different concentrations.

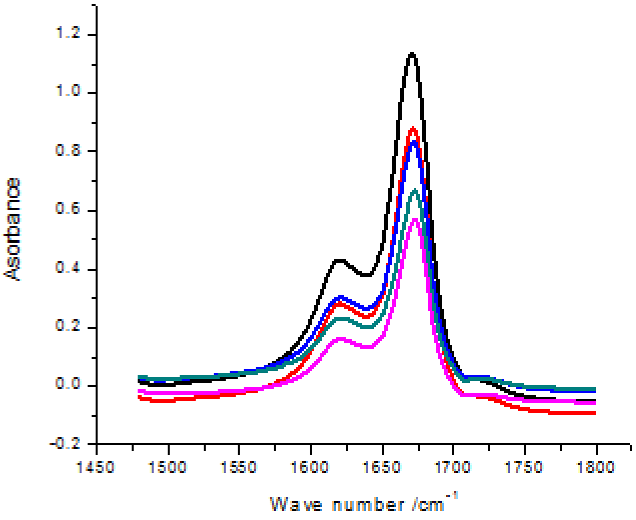


Figure 7: IR spectra of acetamide in methanol at different concentrations.

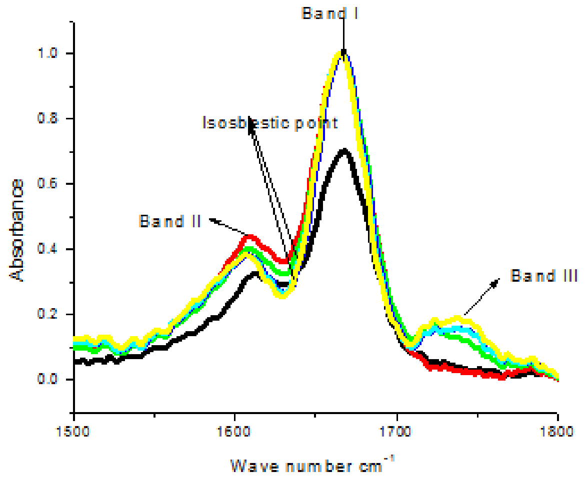


Figure 8: IR spectra of acetamide in CXN at different concentrations

The isosbestic point observed at 1636 cm^{-1} in CXN in the Figure 8 indicated the formation of aggregation (self-association) which is known as monomer dimmer species coexisted in equilibrium. The third band also observed at higher concentration at 1742 cm^{-1} due to self-association. This third band at very low concentration was disappeared. Because as it was already discussed above in dilute solution the molecule existed as monomer.

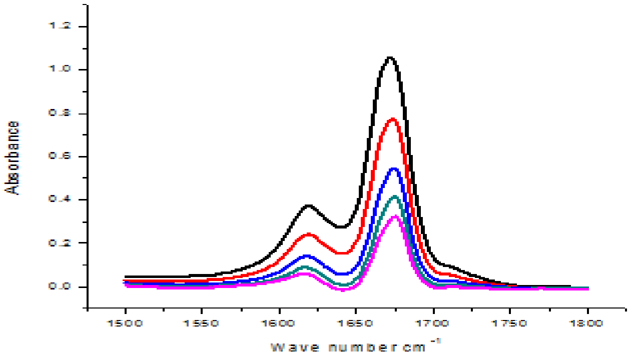


Figure 9: IR spectra of acetamide in IPL at different concentrations

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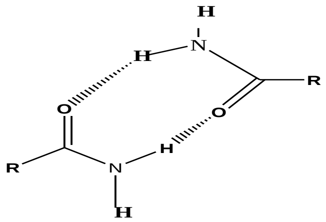
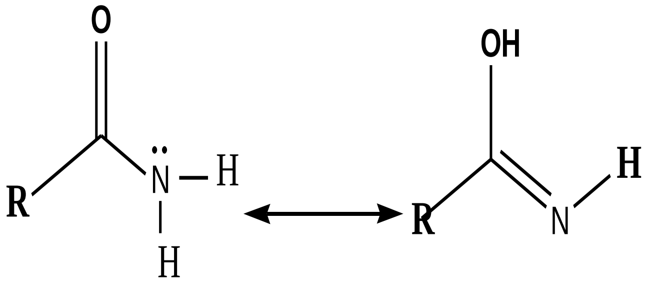
The acetamide in all solvents showed two peaks at different frequencies which are concentration dependent, the acetamide has shoulder at low concentrations i.e. monomeric effect was observed at low concentration .From the results obtained that when the acetamide concentration reduced the third band disappeared and the second band decreased steadily. This indicated that the C=O and C=N absorption band is concentration dependent. Thus, the relative stability of amide tautomerism decreased as the concentration was being decreased. The presence of band II was a clear indicator of intermolecular aggregation (association) was dimmer that is favored when the amount of acetamide molecule in the medium was higher. The dimmer concentration increased due to the higher probability of self-association at higher concentration. At very low concentration i.e.in dilute solution the band intensity was decreased due to the breaking of aggregation (self-association).



Scheme 8: Formation of aggregation in primary amides

The aggregation of amide molecules is higher in non-polar solvents because of the higher solute-solute interactions. Therefore it is possible to determine the relative stability of tautomerism of amides in general can be discussed in accordance with solvents of different polarity. Because of intermolecular hydrogen bonding or association effect, in polar solvents the tautomeric equilibrium shits to amide molecule since it exists as a monomer whereas in non-polar solvents the tautomeric equilibrium shifts to the imidol tautomer.



Scheme 9: Tautomeric equilibrium of amide-imidol formation.

6. Conclusion

Experimentally, the effects of solvents of different polarity, the effect of concentration on the absorption spectra and these effects on tautomeric equilibrium of acetamide were studied .The IR spectral shift results indicated that in polar solvents the spectra were shift to the lower frequency or lower energy. The spectral shifts observed in these different solvents depend on the difference in dipole moment of the exited and ground states and strength of the interaction between solute and solvents. Thus, the band shift was polarity dependent. Two absorption bands were observed in all spectral measurements of acetamide and a single isosbestic point was observed in CXN; this suggested that acetamide molecule coexisted in equilibrium as monomer and dimer. The effect of concentration on absorption spectra was also investigated such that when concentration was increased, absorption band intensity increased. In contrary, at very dilute solution not only the band intensity was decreased but also the second band gradually vanished. This is a clear indicator of C=O stretching frequency of acetamide is purely concentration dependent. From solvatochromism theoretical point of view, a single slope is expected from single vibrational transition and more than one slope is an indicator of the existence of two or more chromophore resulting from isomeric structure. Accordingly, the existences of two different slopes were observed for band I and band II with the value of -22.46 and -30.85 respectively. This indicated that the existence of compounds under investigation of tautomeric isomers of amide-imidol in general and acetamide and actetionimidic acid tautomer in particular existed in equilibrium. `

In the non- polar solvents more association or aggregation of amide (self-association)was observed, as the result of this the dimer was formed; this might be caused by intermolecular aggregation or hydrogen bonding. The relative stability of tautomerism of acetamide has been investigated in solvents of varying polarity. In polar solvents the tautomeric equilibrium shifted to amide molecule i.e. acetamide whereas in non-polar solvents the tautomeric equilibrium shifted to the imidol tautomer (actetionimidic acid).

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