



Solvent Effects on the Electronic Absorption Spectra of Benzene and Paranitroaniline in UV-Vis Spectroscopy

Lejalem Abeble Dagnaw

Ethiopian Institute of Agricultural Research (EIAR), Debre Zeit Agricultural Research Center, Debre Zeit, Ethiopia

Email address:

lijab2010@gmail.com

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Abstract: A UV-Vis spectrophotometer is simple, quick and low cost analytical technique used for the qualitative and quantitative determination of solutes (190 - 800 nm wavelength in the electromagnetic radiation) in both vapour and liquid phase. Depending on the nature of the chromophore, auxochrome, the conjugation, unsaturation properties, steric hindrance, concentration, pH and temperature of the solute and the polarity difference of solvents as well as the interaction of solute-solvent; the intensity, shape and position of maximum electronic absorption spectra of benzene and paranitroaniline influenced in UV/Vis spectroscopy measurement. The main focus of this study were (1) To optimize the working range of plastic and quartz cuvette and the effect of slit width in the spectrum of vapour phase of benzene (2) To determine the interaction effects of benzene with acetonitrile and cyclohexane, and paranitroaniline with water and cyclohexane. Plastic and quartz cuvette optimum working ranges from 300 -800 nm and above 250 nm respectively. The vapour phase with slit width of 0.1 nm and 2 nm and liquid phase in polar (acetonitrile) and non-polar (cyclohexane) of benzene maximum electronic absorption spectrum is observed at 254 nm. In the vapour phase of benzene using 2 nm slit width resolves the smooth spectrum, well resolved and high intensity as compared with 0.1nm slit width. The higher peak and vibration peak in liquid phase of benzene well resolved as compared to vapour phase. In the case of paranitroaniline, the maximum electronic absorption at 380nm shows a bathochromic shift (in water due to dipole-dipole interaction of PNA and water) and at 320nm which shows a hypsochromic shift (in cyclohexane since dipole-induced dipole interaction of PNA and cyclohexane). Therefore, as indicated in benzene and PNA the interaction of solvents matters the shape, position and intensity of maximum absorption spectra in UV/Vis spectroscopy.

Keywords: UV/Vis, Solute, Solvent, Bathochromic Shift, Hypsochromic Shift, Auxochrome

1. Introduction

Spectroscopy is any analytical techniques that use the interaction of light with matter to identify/determine the interest of analyte qualitatively/quantitatively. Light can be expressed in terms of its wave length and frequency. The molecular absorption of electromagnetic radiation results the electronic transition, vibration and rotation [1].

A UV/Vis spectrophotometer measures the intensity of light passing through a sample solution and compares it to the intensity of the light before it passes through the sample. The main components of a UV/Vis spectrophotometer are a light source, a sample holder, a dispersive device to separate the different wavelengths of the light (e.g. a monochromatic), and a suitable detector. In general, the UV/Vis spectrum is graphically expressed as absorbance versus wavelength. The

advantage of this representation is obvious; the height of the absorption peaks is directly proportional to the concentration of the species. According to Lambert-Beer law, the absorbance is expressed as a function of concentration, cuvette length and extinction coefficient [2].

Ultraviolet – visible spectroscopy, it is the fundamental concept which ranges mainly (λ 290 - 800 nm) [3] in electromagnetic radiation that studies the changes in electronic energy levels within the molecule arising due to transfer of electrons from π or non-bonding orbitals. It commonly provides the knowledge about π -electron systems, conjugated unsaturation's, aromatic compounds and conjugated non-bonding electron systems.

In absorption spectroscopy a beam of electromagnetic radiation passes through a sample. Much of the radiation is transmitted without a loss in intensity. At selected

frequencies, however, the radiation's intensity is attenuated. This process of attenuation is called absorption. Two general requirements must be met if an analyte is to absorb electromagnetic radiation. The first requirement is that there must be a mechanism by which the radiation's electric field or magnetic field interacts with the analyte. For ultraviolet and visible radiation, this interaction involves the electronic energy of valence electrons. A chemical bond's vibrational energy is altered by the absorbance of infrared radiation. The second requirement is that the energy of the electromagnetic radiation must exactly equal to the difference in energy, ΔE , between two of the analytes quantized energy states [4].

Solvents have different effects on the absorption spectra of organic compounds; the interaction of solute with different solvents depends on the nature and properties of both solute and solvents. Depending on the nature of the chromophore, auxochrome, the conjugation, unsaturation properties, steric hindrance, concentration, pH and temperature of the solute and the polarity difference of solvents. As a result of this interaction the maximum absorption spectra intensity, shape and position may shift either to the longer or shorter wave length in the spectrum of UV/Vis. This can also explained in terms of hypsochromic or blue shift, shorter wave length and higher energy and bathochromic or red shift which is also expressed in terms of longer wave length or lower energy/frequency [5-8].

The effects of solute-solvent interaction in liquid phase can be expressed in non-specific solvent interactions (dipolarity/polarizability) and specific solvent interactions (hydrogen bonding) on the electronic absorption spectra are interpreted using liner solvation energy relationship, the phenomena is solvatochromism. The specific solute-solvent interaction expressed the solvent acidity and basicity (intramolecular or intermolecular hydrogen bond donor and hydrogen bond acceptor) whereas the non-specific solute-solvent interactions expressed in the solvent dipolarity and polarizability [9-13].

Acetonitrile is a polar, aprotic solvent with high solvating ability. It has a high affinity for water and can be difficult to dry [14]. Ethylacetate is a dipolar aprotic solvent and cyclohexane is non-polar solvent which have low dielectric constant and not miscible with water which is polar protic solvent.

The objectives of this research were conducted to address (1) To optimize the working range of plastic and quartz cuvette and the effect of slit width in the spectrum of vapour phase of benzene (2) To determine the interaction effects of benzene with acetonitrile and cyclohexane, and paranitroaniline with water and cyclohexane in UV/Vis. Spectroscopy.

2. Materials and Methods

2.1. Instruments and Equipment's

Equipment's and instruments used were UV/Vis.

Spectrophotometer (UV/Vis 1900i, Shimadzu), Cuvettes (quartz and plastic), micro Pipette (Dragon Lab, China), rubber pipette filler, Conical flask and washing bottle were also used for the experiment.

2.2. Chemicals and Reagents

All reagents and chemicals used in this research were analytical grade. Water, Acetonitrile (Wego Chemical Group Inc, NY), Ethylacetate (fisher scientific), Cyclohexane (Analytical Grade, Indian) were used as a solvent in the measurements. Benzene (Sigma Aldrich) and Paranitroaniline (China) were used as a solute.

3. Methods and Procedure

UV/Vis spectroscopy methods were applied. The spectrometer and the operating software were turned on. The working range of cuvettes (plastic and quartz) and solvents (acetonitrile, cyclohexane, ethylacetate) determined in the UV/Vis. Region. Benzene and PNA dissolved in acetonitrile & cyclohexane and cyclohexane & water respectively. Then the sample transferred in plastic and quartz cuvette and inserted to the instrument. The analysis started and the peak of the interest of analyte uv/vis. Spectrum with the same and different slit width were measured.

4. Experimental Results and Discussion

4.1. Effects of Cuvette in UV/Vis. Spectrometer Measurement

Plastic cuvette and the quartz cuvette can be used as sample holder from (300nm- 800nm) and above 250nm in UV/Vis. Region of EMR respectively. The selection of cuvette for UV/Vis measurement should be based on the indicated working range of the cuvette in (Figure 1) as well as the nature of solvent and solute interaction with cuvette.

4.2. Solvent Effect in UV/Vis. Spectrum Measurement

As indicated in (Figure 2), it shows the UV/Vis spectrum of Cyclohexane and ethylacetate. The working ranges of the solvents are from (250nm-800nm) in the UV/Vis. Region.

4.3. The Effects of Slit Width in the Spectrum of Vapour Phase Benzene

The vapour phase of benzene absorbs uv/vis. below 275nm. And the vibration peak is not well resolved due highly tighting of electron in the molecule. The spectrum of smooth curve indicates the vapour phase of benzene with slit width 0.1nm. It has lower intensity of peaks compared with slit width having 2 nm of vapour phase benzene. Therefore, running of UV/Vis with larger slit width resolve the smooth curve observed in smaller slit width as indicated (Figure 3).

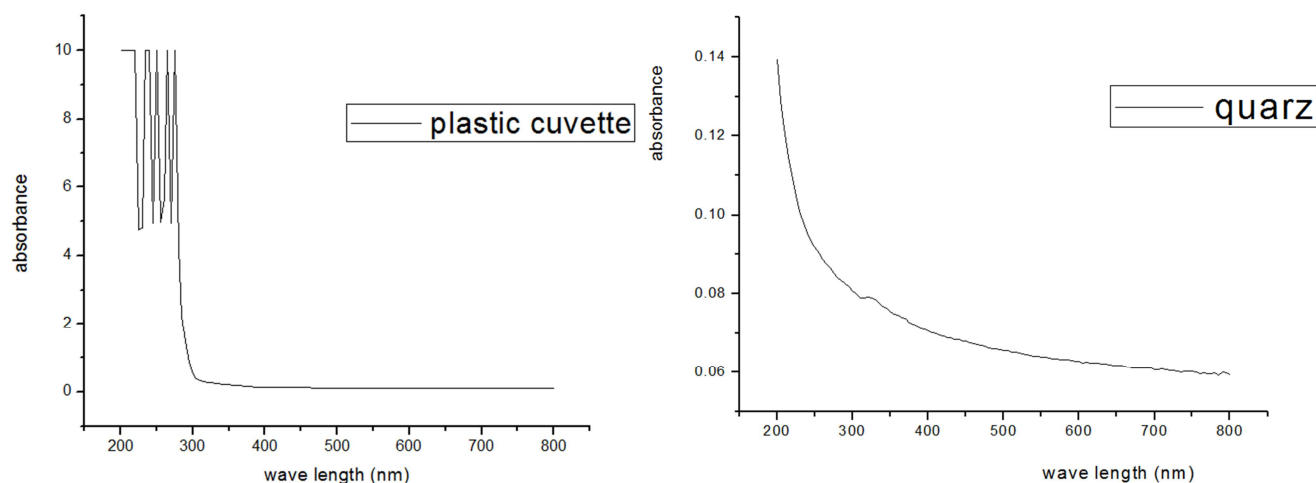


Figure 1. Plastic and quartz cuvette Spectrum in UV/Vis.

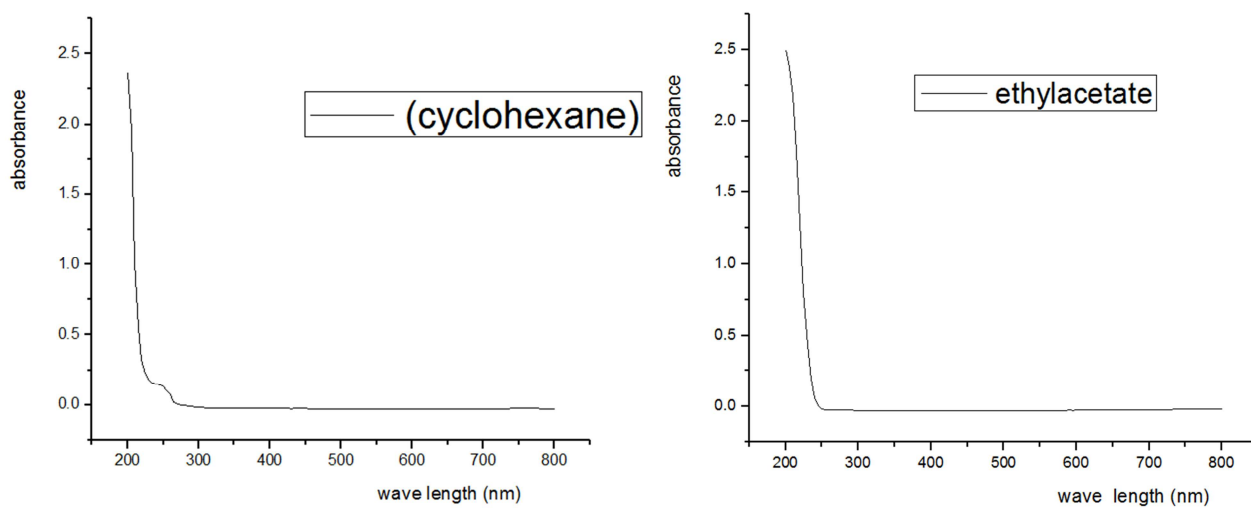


Figure 2. The spectrum of cyclohexane and ethylacetate in UV/Vis. region.

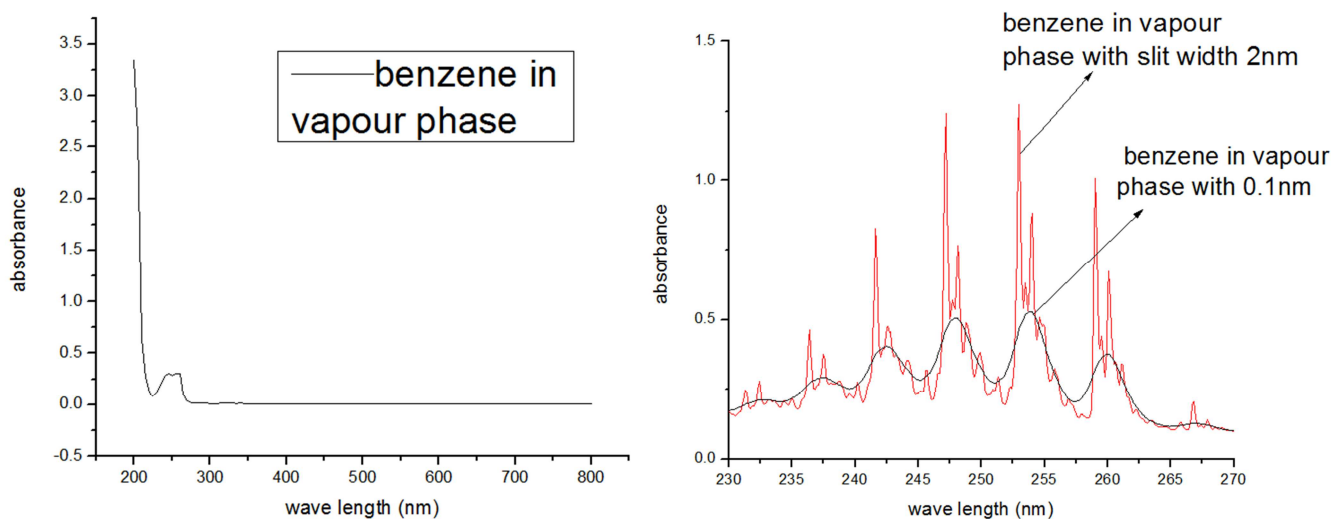


Figure 3. The spectrum of vapour phase benzene with 0.1 nm & 2 nm slit width.

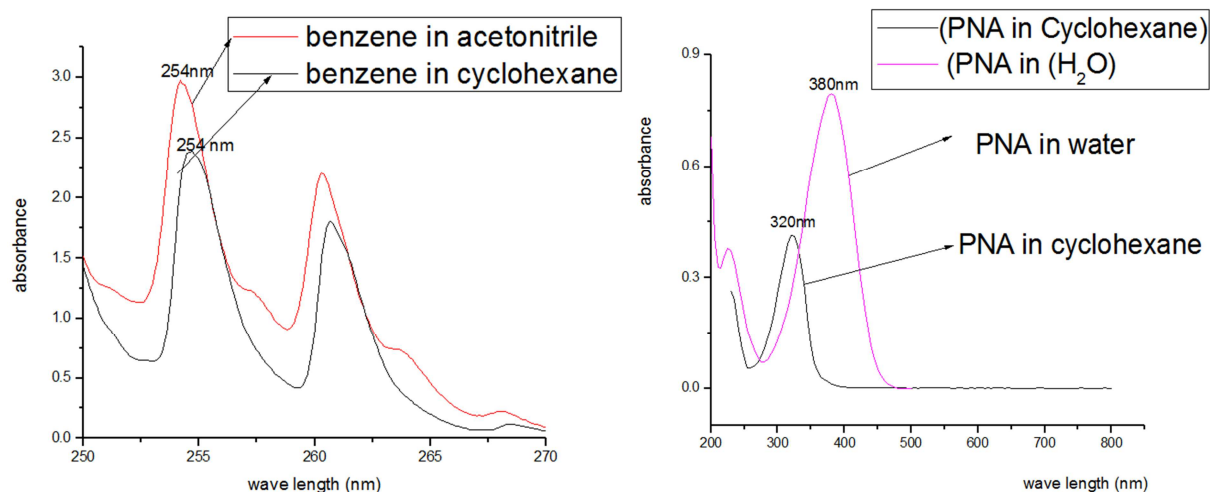


Figure 4. The spectrum of benzene in acetonitrile and cyclohexane, and PNA in water and cyclohexane.

4.4. Effects of Solute-solvent Interaction on UV/Vis Spectrum

Running benzene in liquid phase, well resolved the vibration peak which is smooth in vapour phase both in acetonitrile and cyclohexane. The shape, position and intensity of maximum electronic transition absorption of benzene are similar in both vapour and liquid phase (Figure 4).

The maximum absorption wave length of paranitroaniline in water shifts to higher wave length, due to higher interaction of PNA with water (dipole–dipole interaction). And the maximum absorption wave length of PNA shifts to lower wave length and higher energy in cyclohexane, due to the lower interaction of PNA and cyclohexane (dipole–induced dipole interaction) in this study as indicated in (Figure 4) and the solvatochromic shifts of the electronic state of PNA in water, 1,4-dioxane and cyclohexane is the result of solute-solvent interaction [15, 16]. The maximum absorption spectra of PNA in cyclohexane is 320 nm and 380 nm in water which is almost similar in the preferential solvation result reported in PNA [17].

5. Conclusion

In conclusion, the selection of cuvette for UV/Vis based on the type of solvent and solute. The plastic cuvette works most commonly in the visible and quartz cuvette works both in the ultraviolet and visible Spectrometry in this experiment. As a result of solvent–solute interaction, the vibration peak and maximum electronic absorption spectrum of a molecule well resolved in liquid phase (with solvents) than vapour phase (without solvent). In the case of paranitroaniline, high interaction with water shows bathochromic shift compared with in cyclohexane which is hypsochromic shift observed. In benzene, running of UV/Vis with larger slit width resolve the smooth curve observed in smaller slit width and running it in liquid phase well resolved the vibrational peak in both solvents. Benzene also has similar absorption maxima in vapour and liquid phase.

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