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Ultraviolet and Visible Spectrometry: Structural Applications and Solvent Effects

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ABSTRACT

Ultraviolet and visible (UV-vis) spectrometry is routinely used for the quantitative determination of different analytes, such as drug compounds, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied. UV-vis absorption band positions, intensity and shape of solvent-sensitive molecules show changes in solvents of varying polarity. In this article a general overview of recent progress in the field of solvent effects on the electronic absorption spectra of a variety of molecules is presented. Moreover, the behavior of various compounds in different solvents and the effects of these solvents on the intramolecular charge transfer bands have been discussed using various solvent parameters such as solvatochromic behavior i.e. hypsochromic or bathochromic shifts in wavelength of maximum absorption, solute-solvent interactions and dielectric constant effects.

Keywords: Solvents effects, Absorption spectra, solvatochromism, chromophore.

INTRODUCTION

Absorption of Ultraviolet and Visible Radiation: Absorption of light in the ultraviolet and visible region of the spectrum is due to the presence of a chromophore in the absorbing molecule. The term chromophore was originally used for unsaturated groups of atoms which were thought to be essential for color. Now that light absorption studies have been extended into the UV region, the term includes multiple bonds as those of –ene, –yne and carbonyl and other groups in which the electrons are more loosely bound than those in fully saturated compounds. Unfortunately, these simple chromophores absorb in a region inaccessible to ordinary spectrophotometers and special instruments and light sources are needed to obtain reliable results

at wavelengths less than 210 nm [1].

The absorption of two or more chromophores which are separated by more than one bond is usually additive but when such chromophores are conjugated, i.e. separated by a single bond, pronounced effects are produced. The maximum absorption is shifted to longer wavelengths thus bringing into the working range of spectrophotometers. Such an effect is called a bathochromic shift and the increase in λ_{\max} which often accompanies such a shift is known as hyperchromic effect. The reverse changes are known as hypsochromic shift and hypochromic effect respectively, and occur quite often when a chromophoric system is changed, e.g. by alteration of pH [1,2].

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USE OF SOLVENTS

Solvents for Spectrometry: The solvent used to prepare the sample must not absorb appreciably in the wavelength region where the measurement is being made. In the visible region, this is no problem. There are many colorless solvents and, of course, water is used for most substances. Water can be used in the ultraviolet region. Many substances measured in the UV region are organic compounds that are insoluble in water and so an organic solvent must be used. Table.1 lists a number of solvents used in the UV region. The cutoff point is the lowest wavelength at which the absorbance approaches unity using a 1 cm cell with water as the reference. These solvents can all be used at least up to the visible region [3].

Choice of Solvents: The choice of solvent will sometime affect the spectrum in the UV region due to the solvent-solute interaction. Working from a non-polar to a polar solvent, loss of fine structure may occur and the wavelength of maximum absorption may shift (either bathochromic or hypsochromic depending on the nature of transition and the type of solute-solvent interactions) [3].

Solvatochromism: The solvatochromism is one of the phenomenon that permit to estimate the local field of forces in the interior of liquids, indirectly, by the energy of the intermolecular interactions [4]. 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 dipole moment of the solute. These solute-solvent interactions affect the solute's electronic absorption spectrum and this phenomenon is referred to as solvatochromism [5]. Each solvent has its own characteristic polarity. Since it is known that all electronic transitions modify the charge distribution of the compound in solution, it is obvious that the position and intensity of the absorption bands will vary a little with the nature of the solvent used.

Table 1. Lower transparency limit of solvents in the ultraviolet region [6].

Solvent	Cutoff point (nm)
Water	190
Acetonitrile	190
Glycerol	207
Methanol	210
Ethanol	210
2-methoxy ethanol	210
Pentane	210
n-propyl alcohol	210
n-Hexane	210
Cyclohexane	210
Methyl cyclohexane	210
1,4-Dioxane	215
Diethyl ether	218
Tetrahydrofuran	220
Ethyl acetate	225
1,2-Dichloroethane	226
Chloroform	245
Acetic acid	260
2-butanol	260
Carbon tetrachloride	265
Dimethylsulfoxide	265
N,N-Dimethylformamide	270
Benzene	280
Toluene	286
Tetrachloroethylene	290
Xylene	290
Pyridine	330
Acetone	330
Carbon disulfide	380

The nature of the solvent-solute interactions are a greater indication of the type of transition [2].

SOLVENT EFFECT ON THE ABSORPTION SPECTRA OF ORGANIC MOLECULES

The study of the solvent effect on molecular properties of organic compound is of immense scientific and technological interests. The solvent plays an important role in several processes, powering molecular

properties, accelerating chemical reactions, and making feasible innumerable biological processes [7,8]. The modifications induced by a solvent in the electronic spectra of molecules can provide information on the local electric field acting on the spectrally active molecules [4]. In solutions, the solvent environment determines important changes in the electro-optical properties of the spectrally active molecule compared to those in its gaseous phase. Several reports are now available on the correlation of UV absorption frequencies with the solvent parameters [4, 9, 10]. Study of the effect of solvents on the electronic absorption and fluorescence spectra of a variety of molecules e.g. anthraquinone derivatives, azo compounds, azo disperse red dyes [11] forms an important subject of research in past years because it can play a significant role in the photophysics of the excited states [12]. Solvent effects on organic reactivity and on absorption spectra have been studied for more than a century [13]. 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 [14]. Solvent polarity is a commonly used term related to the capacity of a solvent for solvating dissolved charged or neutral, apolar or dipolar species. Attempts to express it quantitatively have mainly involved physical solvent properties such as relative permittivity, dipole moment, or refractive index but these parameters cannot effectively account for the multitude and specific interactions of solute-solvent on the molecular-microscopic level [8]. Spectroscopic solvent polarity parameters have been derived from solvent sensitive standard compounds absorbing radiation in spectral ranges corresponding to UV-vis, IR, ESR and NMR spectra [13]. The effect of solvent on the UV-visible absorption of some organic compounds would be dealt in the following sections.

Flavone and 7-Hydroxyflavone

Solvent effects on the electronic absorption spectra of flavone and 7-hydroxyflavone in neat and binary solvent mixtures have been investigated. Analysis

indicates that both specific hydrogen bond donor ability and non-specific dipolar interactions of the solvents play an important role in absorption maxima of flavone in pure solvents. The hydrogen bond acceptor ability of the solvent was the main parameter affecting the absorption maxima of 7-hydroxyflavone. The spectroscopic behavior in binary solvent mixtures was analyzed by the preferential solvation approach using ethanol which was detected in cyclohexane-ethanol and acetonitrile-ethanol mixtures for flavone and in acetonitrile-ethanol mixtures for 7-hydroxyflavone. The results indicated that intermolecular hydrogen bonds between solute and solvent are responsible for the non-linear variation of the solvatochromic shifts on the mole fraction of ethanol in the analyzed binary mixtures. The solvatochromic shifts observed in pure solvent were evaluated using linear solvation energy relationships (LSER) [15].

Crystal Violet

Effects on the visible absorption spectrum of crystal violet were studied after the addition of polar solvents to non-polar solutions of crystal violet which resulted in dramatic changes in the visible absorption spectra. The observed changes were explained in terms of crystal violet existing as an ion-pair in non-polar solutions and as a solvated ion in polar solutions. Over a wide temperature range the spectrum of crystal violet in toluene and in acetone solution remained virtually unchanged. However, in methanol and ethanol, the short wavelength component of the absorption in the visible region disappeared as the temperature is lowered. The spectral behavior in alcoholic solutions suggests a decreasing solvent-solute interaction around the dye cation due to increased self-association of the solvent molecules as the temperature is decreased. These studies have a direct application in interpreting some of the results of the photodynamics of crystal violet in solution [16].

Barbiturate dye and block copolymers

A general overview of solvent effects on the electronic absorption and fluorescence spectra was presented

by Homocianu et al. (2011) [4]. In order to describe the behavior different solvents were selected. The solvent effects on the intramolecular charge transfer bands were explained using the possible correlations (with advantages and disadvantages) between adsorption/fluorescence maxima and various solvent parameters. Solvatochromatic effect has been used to determine the magnitude of the solute-solvent interactions such as the polarizability / dipolarity parameter, π^* of the solvent, as well as giving information about hydrogen bond donor, acceptor ability of the solvent. The barbiturate dye in aprotic solvents, showed a single absorption band in the visible range, whereas in protic solvents this band is considerably broadened and was split into two bands. This fact can be attributed to the protonation reactions. The monitoring of the absorption and fluorescence properties in different solvents of the PPO-block-PpPE (poly(propylene-oxide)-poly(p-phenylene-ethynylene)) block co-polymers can be used to establish the aggregation tendency of these compounds. Thus, the absorbance spectra of PPO-block-PpPE copolymers at same concentrations in different solvents were taken. In chloroform, a more than 50% increase in absorbance (at 349 nm) was observed, probably due to best solubility and least degree of aggregation of the block copolymer. In hexane and methanol, which solvate the aromatic PpPE segment less, leading to enhanced aggregation, the absorbance maximum displayed a hypsochromic shift to 335 nm and in methanol-water mixtures the maxima was further shifted to 331 nm. It was concluded that solvent effects on the electronic absorption and fluorescence spectra can contribute in elucidation of the internal structure of liquids, in classification of the solvents by their role in intermolecular interactions and in estimation of some electro-optical molecular parameters, such as dipole moments or polarizability [4].

Benzophenone

A comparative study of UV-vis absorption spectrum of benzophenone in water and the same spectrum in gas phase was carried out by Georg et al. (2007) [7]. The corresponding solvatochromic shifts were

obtained and compared considering five transitions. The influence of the solute polarization in the solute-solvent interaction and, in particular, in solute-solvent hydrogen bonds was analyzed. This study gives the first full description of the entire UV-vis absorption spectrum of benzophenone in water. The results suggest that a careful consideration of the solute polarization is essential to describe the solute-solvent interaction and the electronic properties of polar molecules in polar environment. Also, the conventional description of solvent shells might be revised for molecular solutes with a general shape. This could be done using the minimum-distance distribution function [7].

Aminoazobenzene dyes

Azo dyes are one of the important classes of colorants. The advantage of azo colorants is the simplicity of their synthesis, high molar extinction coefficient and to the medium to high light and wet fastness properties. In this study absorption spectra of three aminoazobenzene dyes with various molecular size and alkyl tails have been recorded in solvents in the range between 200 to 600 nm. The photophysical 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 dye in solution depends strongly on the solvent-solute interactions and solvent nature. The solvatochromic behaviors of aminoazobenzene dyes and solvent-solute interactions were analyzed by means of linear solvation energy relationships concept proposed by Kamlet et al. (1981) [17]. Bathochromic shift of absorption maxima of these dyes, λ_{\max} occurs in solvent with the highest proton acceptor ability and dipolarity / polarizability. The results showed that the solvent effect on UV-vis absorption spectra of investigated amino azo dyes were very complex and strongly depended on the nature of the substituent on the amino group. This phenomenon was caused by the difference in the conjugational or migrating ability of the electron lone pairs on nitrogen atoms and azo-hydrazotautomerism of amino azo dyes. It was also suggested that the electronic behavior of the nitrogen atoms of azo group was somewhat

different between derivatives with electron-donating substituents [13].

Substituted dimethylhydantoins

The aim of the study was to investigate solvent effects on the UV absorption spectra of 1,3-bis-substituted-5,5-dimethylhydantoins. The absorption spectra of the 1,3-bis-substituted-5,5-dimethylhydantoins were recorded in twelve solvents in the range 200–400 nm. The effects of the solvent polarity and hydrogen bonding on the absorption spectra were interpreted by means of linear solvation energy relationships (LSER), using a general equation a concept proposed by Kamlet et al. (1981) [17]. Most of the solvatochromism was ascribed due to the solvent acidity rather than the solvent polarity / polarizability. The results indicated that steric effects between the substituents and the carbonyl groups were important factors in the correlations between the structures in addition to solvent effects and the electronic transition energies of the studied compound. The UV-vis absorption spectrum of 1,3-bis-substituted-5,5-dimethylhydantoins in different solvents presented in this work may be utilized to quantitatively estimate and separate the overall solvent effect [10].

UV A and UV B Sunscreens

The effect of solvents on the ultraviolet absorbance of sunscreens was investigated by Agrapidis-Paloympis and Nash (1987) [18] due to the fact that effectiveness of sunscreens is often influenced by solvents in which they are dissolved. Therefore, in this regard the UV absorption spectra of 13 UV A and UV B sunscreen chemicals were determined in 12 solvents of varying polarity and cosmetic interest. Sunscreen-solvent systems were studied for the changes in both the wavelength of maximum absorbance (λ_{\max}) and molar absorptivity. The difference in structure and polarity of a number of sunscreens causes changes the shifts in λ_{\max} , polar solvents shifted λ_{\max} of polar sunscreen to shorter wavelength and less polar sunscreens to longer wavelengths. Sunscreens containing salicylates and anthranilates showed a minimum or no UV

absorbance shifts. However, most sunscreens showed increased absorbance in both polar and non polar solvents and decreased absorbance in semi-polar solvents such as hexylene glycol and C₁₂-C₁₅ alcohols benzoate. The study of the interaction between sunscreens and solvents provided practical information for the chemists which may be more beneficial in formulating sunscreen preparations [18].

Aminobenzimidazoles

Changes on the electronic absorption spectra of 2-aminobenzimidazoles by the effect of protic and aprotic solvents were examined. UV absorption spectra were recorded in five protic and four aprotic solvents. Bathochromic shifts of absorption maxima, λ_{\max} , occur from the solvent with highest proton-donor ability to the proton acceptor solvent i.e. from water to dimethylsulfoxide (DMSO). In order to explain the obtained results, the UV absorption frequencies of the electronic transitions of the compounds were correlated using total solvatochromic equation which is the sum of measure of solvent polarity, scale of solvent hydrogen bond acceptor basicities and scale of solvent hydrogen bond donor acidities. The spectroscopic data was analyzed by means of multiple linear regression analysis [19].

Styrene

Solvent effect on UV spectrum of styrene was studied by considering the absorption ratios at peak and valley of benzoid bands. These ratios varied with the change of electrical environment that could be monitored through the dielectric constant of the solvent. The ratio values of the solvent-induced bands of styrene decreased as the polarity of solvent increased, at higher temperature these ratio values turned out to be lower especially in polar solvents. This study basically depicts the effect of electrical environment from solvents on the absorption ratios of UV in the benzenoid region of styrene which were considerably sensitive to the variation in polarity of solvents of graded hydrophobic character namely heptane and some monohydric alcohols and water.

It was concluded that styrene molecule has similar behavior to benzene and this molecule could be disturbed by static electrical environment of solvents which was measured in terms of dielectric constant. This solvent induction caused the change in radiation less internal conversion of excited state electronic transition of styrene [20].

Flavins

Effect of solvent on UV and visible absorption maxima and the molar absorptivities of formylmethylflavin and its photoproducts i.e. lumichrome and lumiflavin were determined. Solvents used were water, acetonitrile, methanol, ethanol, 1-propanol, 1-butanol, dichloromethane and chloroform. The sensitivity of flavin spectra to solvent changes is probably due to a greater degree of solute-solvent interaction on increasing the solvent polarity. The band position was thought to be affected by relative stabilization of the ground and excited states by solvation. The increase in absorption maximum with an increase in the polarity of the solvent implied that the energy necessary for the $\pi-\pi^*$ transition is less in the more polar solvents due to stabilization of the excited states by interaction with the solvent. The precise position of the absorption maxima and the molar absorptivities depends on the environment of the flavin chromophore [21].

Phenol

The effect of solvent on the absorption spectrum of phenol was studied following the preparation of 0.002% w/v solution of phenol in water and cyclohexane. The absorption spectrum of each solution was recorded over a range 230–300 nm. It was observed that in cyclohexane, little interaction with fine vibrational structure occurred between solvent and solute. In water, however, solvation of the solute and hydrogen bonding are possible so that the fine structures are almost diminished, only the band envelope was obtained. Similarly, if the two solvents are aqueous and differ only in their ionic character, e.g. different strengths of the same buffer solution, it is possible for a salt effect to cause slight differences in the absorption band of a compound[1].

CONCLUSION

The study of the solvent effect on molecular properties of a compound is of immense scientific and technological interests. The solvent plays an important role in several processes, powering molecular properties, accelerating chemical reactions, and making feasible innumerable biological processes. The effect of solvent on electronic spectra can also contribute in elucidation of internal structure of liquids, solute-solvent interaction, estimation of dipole moments or polarizabilities. It can also be concluded that a correlation between the absorption maxima and solvent dielectric constants would help to understand the possible interaction between compound and solvents which would ultimately help in developing a rapid, economical, accurate and precise method for the determination of the drug in pharmaceutical systems incorporating organic solvents.

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