Solvatochromic Effect on the Ultraviolet Absorption Spectra of Chalcone Derived from Acetyl Benzo Oxazinone

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***Abstract* - The ultra violet absorption spectra of chalcone derived from acetyl benzo oxazine have been recorded in various solvents in the range 200–400nm and the effects of solvents on the absorption spectra of title compound are interpreted by correlating the of absorption frequencies with Kirkwood function$\{\varepsilon$, $1/\varepsilon$ and $f(\varepsilon) = \}$. Absorption maxima observed in alcohol water mixtures and hexane is found to be the direct measure of the excited state stabilization energy of the Chalcone under investigation in various percentage of alcohol-water mixture.**

***Index Terms* - Chalcone, cetyl benzo oxazinone, absorption maxima, Kirkwood function, stabilization energy.**

INTRODUCTION

Ultraviolet absorption spectroscopy concerned with the study of absorption of uv radiation in the range of 200-400nm.This absorption depends on the nature chromophoric group present in the analyte. Chalcones are-unsaturated ketone involving the reactive keto-ethylenic group (CO-CH=CH-) which gave colored compounds due to the presence of (CO-CH=CH) the chromophore group [1-5]. The UV–Visible spectral study reveals that the crystal is transparent in the entire visible region and the absorption is observed at 325.40 nm. The study of the solvent effect on molecular properties is of immense scientific and technological interests. The solvent effect plays a dominant role in many forefront areas such as synthetic chemistry, molecular biology and material design, because most of the chemical reactions as well as structure characterizations are performed in various solutions[6&7]. The solvent plays an important role in several processes, powering molecular properties, accelerating chemical reactions, and making feasible innumerous biological processes[8-10]. The influence of the solvent on spectroscopic properties and reactivity was conventionally rationalized by molecular properties of the solvent, such as dipole moment, electronic polarizability, hydrogen bond (HB) donor and acceptor capability, intermolecular electrostatic interactions, etc[11-13]. Onsager and Kirkwood developed[14], in the early days 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 in turn polarized by the field of the induced charges of the dielectric. The solvatochromic shift can provide vital information regarding charge distribution in the solute molecule, geometry of the molecule, nature of transition in the ground and excited states .These effects are predominantly electrostatic and may of induced dipole-induced dipole, dipoledipoleor hydrogen bonding types[15-17]. Hence in this aspect we planned to investigate the effect of solvent on the electronic absorption spectra Chalcone derived from acetyl benzo oxazinone.

Experimental section

The reaction and the purity of the product is assessed by performing TLC. The reported melting point is taken in open capillaries and it is uncorrected.

General procedure for the synthesis of Chalcone

The ethanolic solution of 6-Acetyl-2H-1,4-benzoxazin-(4H)-3one (0.4716g) and p-methylbenzaldehyde (0.7642g) was stirred with a small quantity of N/10 sodium hydroxide solution for 4 hours. The resulting solution was poured into ice-water and the formed precipitate was filtered. The crude Chalcone was recrystallized from ethanol.

Reaction

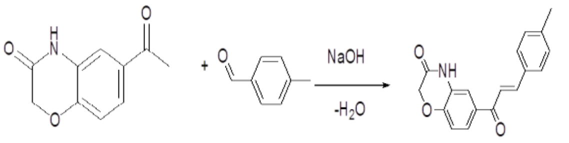

Table 1

Compound	Molecular formula	Molecular weight	Melting point(^{0}C)
6TABO	$C_{18}H_{17}NO_3$	295.3	148.9

RESULTS AND DISCUSSION

UV ABSORPTION SPECTRUM

The recorded UV spectrum for the new compound is shown in Fig.1& 2. Most of the absorption spectroscopy of organic compounds is based on transitions of n or π electrons to the π* excited state which takes place in the range 200–700 nm. In this point of view, the max absorption peak observed at 325.40 nm (Fig. 2) can be assigned to n → π* transition and may be attributed to the excitation in the aromatic ring and C=O group [9]. The Hammett correlation is made with σ and σ+ constants in the region of principle maximum of absorption for the new Chalcone.

Effect of solvents on the ultraviolet absorption spectra

The л* ← л electronic transition of the C=O group in the α , β unsaturated ketone (chalcone)is expected to shift its wavelength of maximum absorption to longer wavelength when polarity of the solvent is increased[18&19]. Hence the ultraviolet absorption spectra of the Chalcone derived from acetyl benzooxazinone is recorded in hexane and in ethanol-water mixtures of varying dielectric constant. The absorption maximum in hexane is considered that it is due to electronic transition from a non-solvated ground state to a non-solvated excited state. The difference in absorption maxima between those in alcohol-water mixtures and those in hexane is a direct measure of the excited state stabilization energy of the Chalcone under investigation in various percentage of alcohol-water mixture. The difference absorption maximum [Δλmax] values and the dielectric parameters of the solvent mixture are given in Table 1.

Δλmax = [λmax (ethanol-water) - λmax (hexane

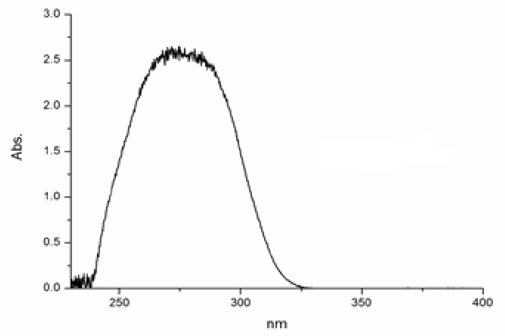

Fig-1

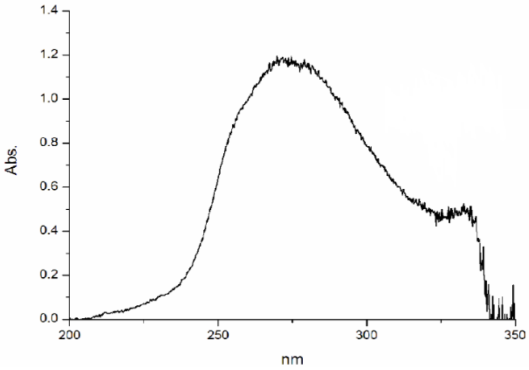

Fig-2

Table 1: The observed absorption maxima of chalcone

Ethanol (%) in ethanol-water	Δmax (nm)	Δλmax(nm)
100	285	15
90	289	19
80	292	22
70	297	27
60	302	32
50	304	34

Hexane = 270nm

The plots of Δλmax *versus* ε, 1/ε and f(ε) = $\frac{\varepsilon - 1}{2\varepsilon + 1}$, Kirkwood[14] function dielectric constant are shown in Figs. 1-6. In all the plots there is a perfect linearity between the stabilization energy and the dielectric constants of the alcohol-water mixtures establishing the fact that the stabilization energy is increased by solvation of the excited state. Dielectric constant of various percentage of ethanol-water mixtures are given in Table 2.

Table 2-Dielectric constant of various percentage of ethanol-water mixtures

Ethanol (%) in ethanol-water	ε	1/ ε	f(ε) = $\frac{\varepsilon - 1}{2\varepsilon + 1}$
100	24.30	0.041	0.469
90	29.80	0.033	0.475
80	35.48	0.028	0.479
70	41.07	0.024	0.482
60	46.66	0.021	0.484
50	52.25	0.019	0.486
40	57.84	0.017	0.488

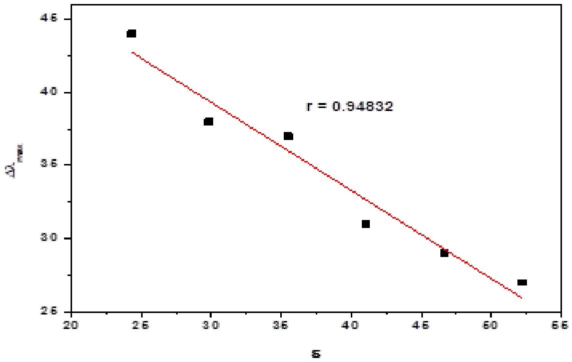

Fig-1.The plot of $\Delta\lambda_{max}$ of Chalcone versus ε.

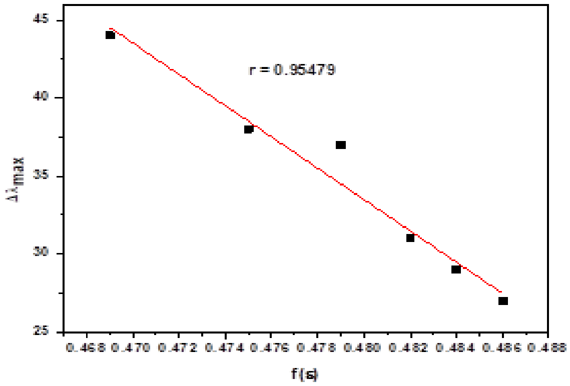

Fig-2.The plot of $\Delta\lambda_{max}$ of Chalcone versus 1/ ε

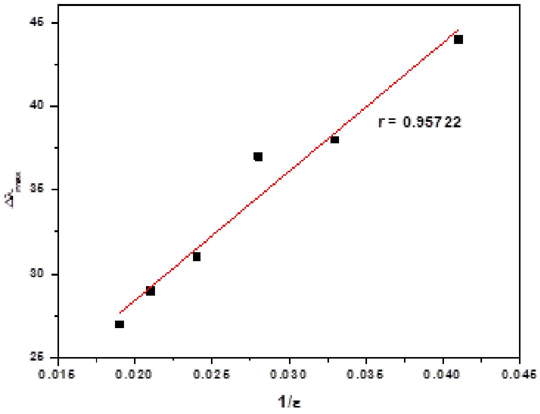

Fig-3.The plot of $\Delta\lambda_{max}$ of Chalcone versus 1/ ε

There is a perfect correlation between the stabilization energy of the excited state and dielectric constant of the medium hence it was thought worthwhile to see the correlation existing between stabilization energy of the excited state and dielectric constant(ε) of the medium by varying the alcohols.

Table 3 λ_{max} , $\Delta\lambda_{max}$ and log $\Delta\lambda_{max}$ of chalcone in various alcohols

S. No.	Solvent	λ_{max} (nm)	$\Delta\lambda_{max}$ (nm)	log$\Delta\lambda_{max}$ (nm)
1.	1-Butanol	295	25	1.40
2.	2-Butanol	302	32	1.51
3.	2-Propanol	303	33	1.52
4.	Benzyl alcohol	309	39	1.60
5.	Methanol	329	59	1.80
6.	Ethanol	331	61	1.81
7.	Propanol	333	63	1.82

(n-Hexane = 281 nm

$\Delta\lambda_{max}$ = (λ_{max} ethanol - λ_{max} hexane)

Table 4 Solvent parameters for alcohols

S. No.	Solvent	ε	1/ε	f(ε)
1.	1-Butanol	17.1	0.0584	0.4574
2.	2-Butanol	15.8	0.0632	0.4540
3.	2-Propanol	18.3	0.0546	0.4601
4.	Benzyl alcohol	13.1	0.0763	0.4448
5.	Methanol	32.0	0.0312	0.4774
6.	Ethanol	24.3	0.0411	0.4698
7.	Propanol	20.1	0.0497	0.4636

There will be a charge separation in the excited state of the chalcone so it was expected that the excited state will be stabilized by increasing the polarity of the alcohols. Hence, we attempted to seek the correlations existing between log $\Delta\lambda_{max}$ versus ε, 1/ε and f(ε). Fair to good correlations were obtained in all the cases and are shown in fig (4-6)

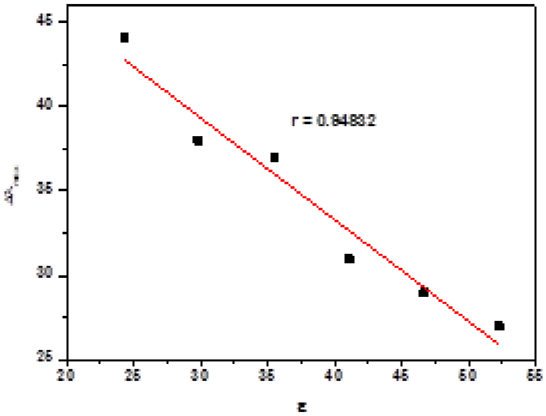

Fig-4.The plot of $\Delta\lambda_{max}$ of Chalcone versus ε

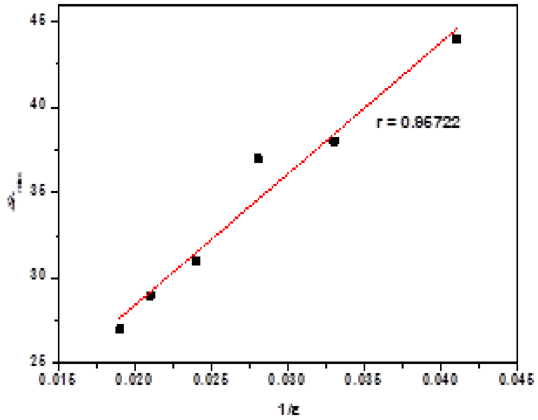

Fig-6.The plot of $\Delta\lambda_{max}$ of Chalcone versus 1/ ε

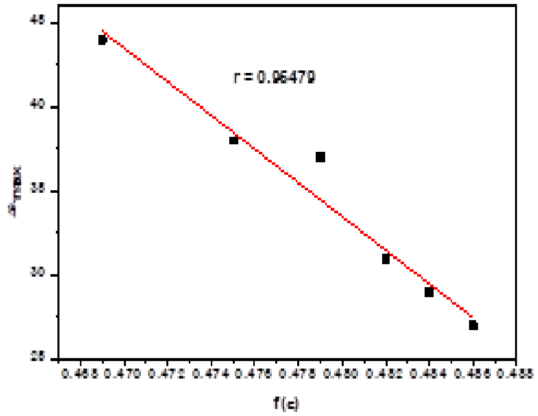

Fig-6.The plot of $\Delta\lambda_{max}$ of Chalcone versus f(ε)

To investigate the changes in the absorption maximum when we move from polar→ aprotic → nonpolar aprotic solvents we have recorded the uv absorption spectra of the chalcone derived from acetyl benzooxazinone in solvents like Benzene, Ethyl acetate, Hexane, Acetone, DMF, DMSO and the λmax values are given in Table-.5

TABLE-5 λ_{max} of chalcone in various solvents

SOLVENT	λmax(nm)
Benzene	280
Ethyl acetate	293
Hexane	270
Acetone	295
DMF	299
DMSO	304

From the above investigation and λmax values obtained in the various solvent given in the above table it is inferred that the compound shows bathochromic shift (RED shift)by changing the polarity from non-polar to polar aprotic solvent(Hexane→DMSO).

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