Solvatochromic Studies of Chalcones in Alcohols

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ABSTRACT

The absorption and fluorescence spectra of substituted chalcones have been studied in various alcohols at room temperature. A reasonable agreement is observed with ground and excited state dipole moments which is determined using solvatochromic method based on the solvent properties f1(ε,n) and f2(ε,n). Change in dipole moment is also determined.

Chalcones are a class of compounds in which two aromatic planar rings are connected through α, β-unsaturated carbonyl system exerting strong electron donor-acceptor interactions depending on the substituent attached to the aromatic rings. Chalcones have found to be versatile synthetic intermediates in the synthesis of novel heterocycles with good pharmaceutical profile. These are main precursor of flavonoids and isoflavonoids which show a diverse range of pharmacological activities like cytotoxicity, anti-tumour, anti-inflammatory, anti-plasmodial and anti-oxidant.

Apart from very important biological and pharmaceutical applications, the photophysical properties of chalcones have attracted considerable research attention including metal sensing, optical materials, laser dyes, etc. These molecules usually show strong polarity-dependent Stokes shifts, large changes in dipole moments on excitation, and very high fluorescence quantum yields. Solvatochromismism dependence of absorption and emission maxima with the polarity of solvents. Excited state properties of the molecules are quite sensitive due to intermolecular solute-media interactions and in turn affect the energy of the electronic states thus gives rise to variation in the spectral shifts. The influence of the solvents on the absorption and emission spectra has been extensively used to determine the magnitude as well as direction of dipolemoment in ground and excited states.

Keywords: Solvatochromic, Alchols, Chalcones, Fluroescence

INTRODUCTION

Chalcone derivatives are prepared according to the literature methods [1]. Solvents used during the present investigation were methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol and octanol, these are of spectroscopic grade. The concentrations chosen were 10^{-5} M in all the cases. Ultraviolet-visible and fluorescence measurements are carried out at room temperature. The absorption spectra were recorded on a UV-visible spectrophotometer (U-3310 Spectrophotometer) and fluorescence spectrophotometer (Hitachi F-7000, Japan) [2].

Chalcone derivative of 3-(4′-dimethylaminophenyl)-1-(2-thienyl)prop-2-en-1-one

The absorption and fluorescence characteristics of 3-(4′-dimethylaminophenyl)-1-(2-thienyl)prop-2-en-1-one (DMATP) have been disquisitioned in different solvents. DMATP dye shows a large red shift in both absorption and emission spectra as solvent polarity induces and indicating a large change in the dipole moment of molecules upon excitation due to an intramolecular charge transfer interaction [3]. The fluorescence quantum yield depends strongly on the properties of the solvents, which was attributed to positive and negative solvatokinetic effects. A crystalline solid of DMATP gave an excimer like emission at 570 nm due to the excitation of molecular aggregates [4]. This is anticipated from the idealized crystal

structure of the dye that belongs to the B-type class of Steven's classification. A dye solution ca. 10^{-3} mol dm^{-3} in CHCl$_3$ gave a good laser emission in the range 480 nm-560 nm with emission maximum at 530 nm upon pumping by nitrogen laser (λex=337.1 nm) [5]. The excitation energy transfer from 7-Dimethylamino-4-Methyl Coumarine (DMC) to DMATP has been also studied in CHCl$_3$ and the values of energy transfer rate constant and critical transfer distance indicate a Forster-type mechanism.

The photo reactivity and net photochemical quantum yield of DMATP in chloromethane solvents are also determined. We applied semi empirical MO calculation using AMI and ZINO/S calculation to understand the geometric and electronic structure of DMATP molecule in both ground and excited states [6].

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MATERIALS AND METHODS

Series of ferrocenyl substituted chromophores were synthesized *via* a reaction of acetyl ferrocene and a variety of aldehyde under microwave irradiation. The structure of synthesized compounds were established by spectroscopic (FT-IR, 1H NMR, 13C NMR, ESI-MS) and elemental analysis. UV-Vis and fluorescence spectroscopy measurements provided that all compounds have good absorbent and fluorescent properties [9]. Fluorescence polarity studies demonstrated that these compounds were sensitive to the polarity of the microenvironment provided by different solvents. In addition, spectroscopic and physicochemical parameters, including singlet absorption, extinction coefficient, Stokes shift, oscillator strength and dipole moment, were investigated in order to explore the analytical potential of the synthesized compounds. The anti-bacterial activity of these compounds were first studied *in vitro* by the disk diffusion assay against two Gram-positive and two Gram-negative bacteria. The minimum inhibitory concentration was then determined with the reference of standard drug chloramphenicol. The results displayed that compound 3 was better inhibitors for both types of the bacteria (Gram-positive and Gram-negative) than chloramphenicol. Based on the density functional theory; total energy, the atomic orbital contribution to frontier orbitals: LUMO and HOMO, of all synthesized compounds were calculated to support the antibacterial activities (Figure 1) [10].

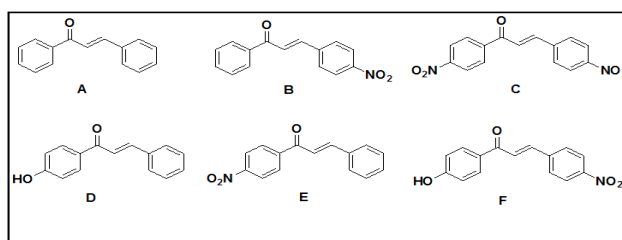**Determination of dipole moments**

Figure 1: Determination of dipole moments

Method 1: The method which employed depends on the internal electric field for studying the effect of substituted groups –NO$_2$ and -OH on the dipole moments of chalcones [11,12]. This method makes use of dependence of absorption and emission band maxima to estimate the excited state dipole moments of organic compounds. Knowing the excited-state dipole moment of organic molecules having large polarizability is important in designing efficient non-linear optical materials. For a chromophore, the tunablity range of the emission energy (as a function of the polarity of the medium) is also determined by excited-state dipole moment. Further, the experimental data on dipole moments are useful in parameterization in quantum chemical methods. Among the techniques available for the determination of the excited state dipole moments, the most popular is that based on the Bakshiev and Kawski-ChammaViallet equations which afford good results for the estimation of excited state dipole moments of organic compounds [13,14].

According to Bakhshiev;

$\bar{\upsilon}_a - \bar{\upsilon}_f = S_1\, f_1(\varepsilon,n) + \text{Constant}$ -----------(1)

According to Chamma and Viallet;

$(\bar{\upsilon}_a + \bar{\upsilon}_f)/2 = S_2\, f_2(\varepsilon,n) + \text{Constant}$ --------(2)

Where,

$\bar{v}_a$ is absorption maxima and $\bar{v}_e$ is emission maxima expressed in cm^{-1}

$$S_1 = 2(\mu_e - \mu_g)^2 / a_0{}^3 hc \quad \text{----------(3)}$$

$$f_1(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left(\frac{\varepsilon - 1}{\varepsilon - 2} - \frac{n^2 - 1}{n^2 - 2} \right) \text{----------(4)}$$

$$S_2 = -2(\mu_e{}^2 - \mu_g{}^2) / a_0{}^3 hc \quad \text{----------(5)}$$

$$f_2(\varepsilon, n) = \frac{2n^2 + 1}{2(n^2 + 2)} \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) + \frac{(n^4 - 1)}{2(n^2 + 2)^2} \quad \text{----------(6)}$$

Where 'n' is refractive index, 'ε' is dielectric constant of the solvents. Calculated values of solvents polarity parameter. The ground and excited state dipole moments are estimated by means of the following equations assuming that the symmetry of the investigated solute molecule remains unchanged upon electronic transitions and the ground and excited state dipole moments are parallel.

$$\mu_g = \frac{s_1 + s_2}{2} \left[\frac{hca_0{}^3}{2s_1} \right]^{\frac{1}{2}}$$

$$\mu_e = \frac{s_1 - s_2}{2} \left[\frac{hca_0{}^3}{2s_1} \right]^{\frac{1}{2}}$$

Where μ_g and μ_e are ground and excited state dipole moments respectively, 'h' is Plank's constant, 'c' is the velocity of light, 'a_0' is Onsagar cavity radius, evaluated by calculating the Vander waal's volumes ($V = 4/3 \, \pi a^3$) according to Edwards method. The ratio of excited state dipole moment to the ground state dipole moment can be expressed as,

$$\Delta\mu = \frac{|s_1 - s_2|}{|s_1 + s_2|}$$

The slopes S1 and S2 have been determined by plotting the stoke's shifts ($\bar{v}_a - \bar{v}_f$) and $\frac{1}{2}(\bar{v}_a + \bar{v}_f)$ against the bulk solvent polarity functions f1(ε,n) and f2(ε,n) respectively for different solvents.

Method 2: For understanding polarization dependence or hydrogen bonding effects in solvents it is useful to use ET function, which is an empirical measure of solvent polarity and is based on solvatochromic behavior of betaine dye as a probe solute. On this scale each solvent gives a quantitative expression for polarity. However, to avoid dimensionality problems, normalized values of ET namely E_T^N are employed which includes not only solvent polarity but also the protic hydrogen bond effect.

The change in dipole moment can be determined by Eq. (10)

$$\Delta\mu = \sqrt{\frac{81m}{(6.2/a_0)^3 \, 11307.6}} \quad \text{--------(10)}$$

Where, m is the slope obtained from a linear plot of Stokes shift ($\bar{\upsilon}_a - \bar{\upsilon}_e$) against E_T^N.

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RESULTS AND DISCUSSION

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Electronic spectral properties

Electronic absorption spectra of chalcones exhibited a single band in the range 295-375 nm in the chosen alcohols. Solvent dependent absorption pattern has been observed and which is independent of alcohol polarity.

Solvent effects on the excited and ground states of chalcones investigated by absorption and fluorescence spectroscopy which have been correlated with the dipole moments by Kawski-ChammaVallet equations. In the present work we have demonstrated the application of solvatochromic shift method to the determination of the excited and ground state of chalcones (II to VI) in comparison with (I). Owing the applications of chalcones we carried the solvatochromic study of acetophenone- benzaldehyde chalcones and effect of electron withdrawing group –NO$_2$ On their absorption and emission spectra which was further confirmed by dipole moment calculation following I, II, III are the compounds which are under taken for the study.

The absorption and emission spectra of compounds 1–6 are recorded in various solvents of different solvent parameters of dielectric constant ($\mathcal{E}$) and refractive index (n). The values of Stokes shift and spectral shift are indicated in Tables 1-3. The absorption and maximum emission is indication of charge transfer during excitation. Larger magnitude of the Stoke shift indicates that the excited state geometry could be different from that of ground state. The general observation is that there is an increase in the stoke shift values when there is an increase in the solvent polarity, which shows that there is an increase in the dipole moment on excitation (Figures 2-13).The fluorescence emission peaks undergoes a red shift, confirming a π-π* transition (Tables 4 and 5).

Dipole moment studies

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Table 1: Absorption and Emission spectra of Compound 1-6

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Solvent	n	ε	f$_1$(ε,n)	f$_2$(ε,n)	$E\frac{N}{T}$
Methanol	1.329	33.7	0.857	0.652	0.762
Ethanol	1.361	24.3	0.811	0.651	0.654
Prapanol	1.385	20.6	0.778	0.6488	0.617
Butanol	1.399	17.4	0.754	0.6448	0.586
Pentanol	1.41	14.8	0.703	0.5779	0.568
Hexanol	1.418	13	0.69	0.628	0.559
Heptanol	1.424	11.3	0.6513	0.6135	0.549
Octanol	1.429	9.8	0.627	0.6045	0.537

Table 2: Wave numbers (cm^{-1}) for the absorption and fluorescence emission maxima of Compounds A, B and C in different solvents and stokes shift

Compound	Solvent	λ$_a$ (nm)	λ$_f$ (nm)	$\bar{\upsilon}_a$ (cm^{-1})	$\bar{\upsilon}_f$ (cm^{-1})	($\bar{\upsilon}_a-\bar{\upsilon}_f$) (cm^{-1})	½($\bar{\upsilon}_a+\bar{\upsilon}_f$) (cm^{-1})
A	Methanol	316	410	31645	24390	7255	28010
	Ethanol	304	453	32894	22075	10819	27495

Compound	Solvent						
	Prapanol	306	406	32679	24630	8049	28654
	Butanol	307	456	32573	21929	10644	27251
	Pentanol	311	368	32154	27123	5031	29638
	Hexanol	312	402	32051	24875	7176	28463
	Heptanol	310	419	32258	23866	8392	28062
	Octanol	311	428	32154	23364	8790	27759
B	Methanol	362	431	27624	23201	4423	25412
	Ethanol	301	404	33222	24752	8470	28987
	Propanol	295	459	33898	2172	11726	28035
	Butanol	375	471	26666	21231	5435	23993
	Pentanol	295	471	33898	21231	12667	27564
	Hexanol	362	404	27624	24752	2872	26188
	Heptanol	301	431	33222	23201	10013	28211
	Octanol	298	453	33557	22075	11482	27816
C	Methanol	302	377	33112	26525	6587	29800
	Ethanol	303	450	33003	22222	10781	27600
	Propanol	309	335	32362	29850	2512	31106
	Butanol	300	375	33333	26666	6667	29999
	Pentanol	300	360	33333	27777	5556	30555
	Hexanol	299	476	33444	21008	12436	27226
	Heptanol	305	469	32786	21321	11465	27050
	Octanol	301	361	33222	27700	5522	30450

Table 3: Wave numbers (cm^{-1}) for the absorption and fluorescence emission maxima of Compounds D, E and F in different solvents and stokes shift

Compound	Solvent	λ_a (nm)	λ_f (nm)	$\bar{v}_a$ (cm^{-1})	$\bar{v}_f$ (cm^{-1})	$(\bar{v}_a-\bar{v}_f)$ (cm^{-1})	$\frac{1}{2}(\bar{v}_a+\bar{v}_f)$ (cm^{-1})
D	Methanol	315	487	31746	20503	11243	26124
	Ethanol	299	443	33444	22546	10898	27995
	Prapanol	300	442	33333	22624	10709	27978
	Butanol	306	442	32679	22624	10055	27651
	Pentanol	318	372	31446	26881	4565	29163
	Hexanol	341	406	29325	24630	4695	26977
	Heptanol	336	403	29761	24813	4948	27287
	Octanol	337	413	29673	24213	5460	26943
E	Methanol	306	329	32679	30379	2300	31529
	Ethanol	306	347	32679	28789	3890	30734
	Propanol	340	436	29411	22935	6476	26173
	Butanol	310	413	32258	24213	8045	28235
	Pentanol	318	387	31446	25839	5607	28642
	Hexanol	312	399	32051	25062	6989	28556
	Heptanol	310	411	32258	24330	7928	28294
	Octanol	312	498	32051	20080	11971	26065
F	Methanol	301	516	33222	19379	13843	26300
	Ethanol	301	509	33222	19646	13576	26435
	Propanol	332	403	30120	24813	5307	27466

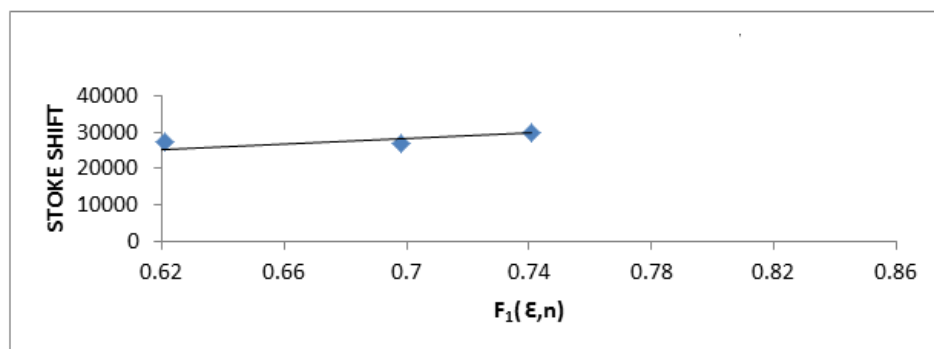|						
Butanol	301	513	33225	19493	13732	26359
Pentanol	314	364	31847	27472	4375	29659
Hexanol	346	392	28901	25510	3391	27205
Heptanol	335	427	29850	23419	6431	26634
Octanol	310	447	32258	22371	9887	27314

Figure 2: Variation of stoke shift with $F1(\varepsilon,n)$ by using Bakhshiev'sequation in different solvents for compound 1. Note: $Y=38274+1446.2$ $R^2=0.8578$
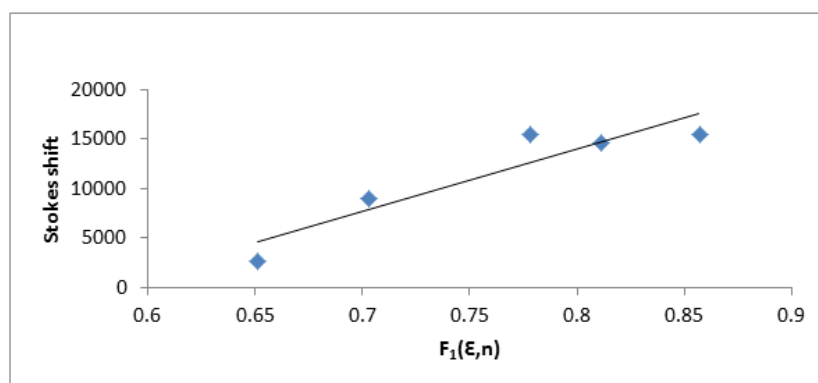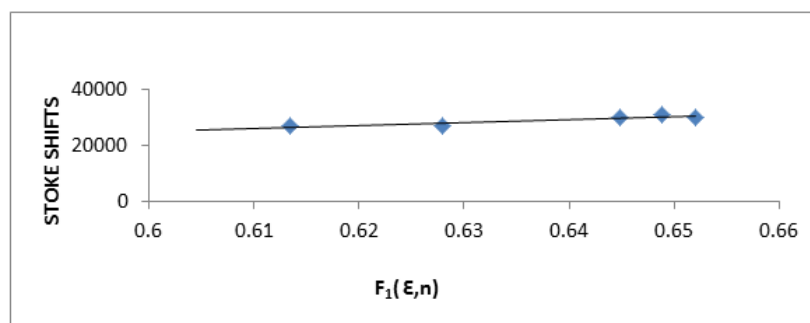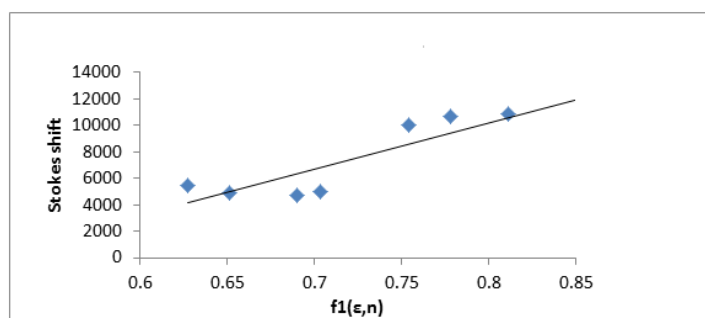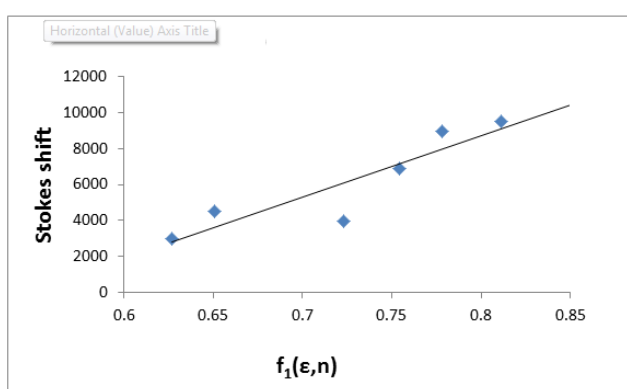

Figure 3: Variation of stoke shift with $F1(\varepsilon,n)$ by using Bakhshiev'sequation in different solvents for compound 2. **Note:** $Y=63010x-36460$ $R^2=0.8588$
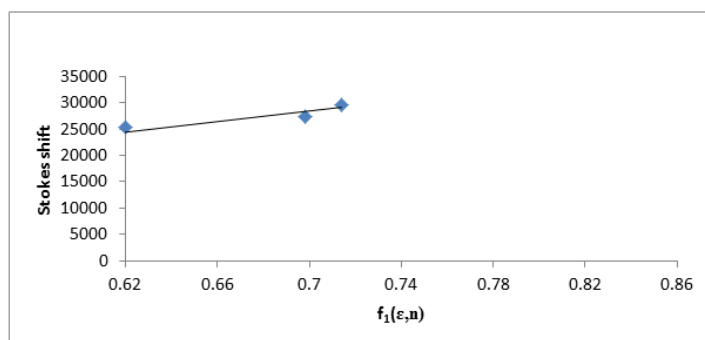

Figure 4: Variation of stoke shift with $F1(\varepsilon,n)$ by using Bakhshiev'sequation in different solvents for compound 3. **Note:** $Y=100580x-35075$ $R^2=0.8219$

Figure 5: Variation of stoke shift with F1(ε,n) by using Bakhshiev'sequation in different solvents for compound 4. **Note:** Y=34641x–17547 R^2=0.8103

Figure 6: Variation of stoke shift with F1(ε,n) by using Bakhshiev'sequation in different solvents for compound 5. **Note:** Y=34201x–18627 R^2=0.8236

Figure 7: Variation of stoke shift with F1(ε,n) by using Bakhshiev'sequation in different solvents for compound 6. **Note:** Y=50875x–7093.9 R^2=0.9576
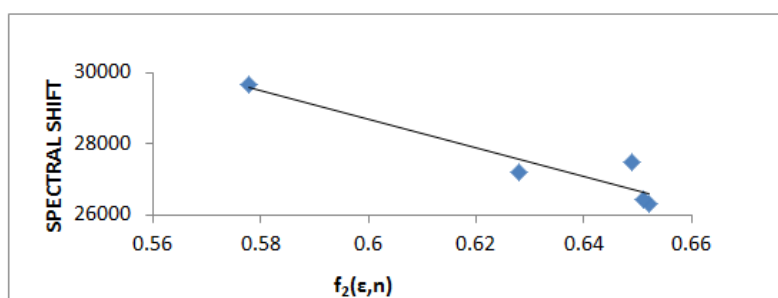
Figure 8: The Variation of the arithmetic mean $\vee$a and $\vee$f with F2(ε,n) by Kawaski-Chamma-Viallet's equation in different solvents for compounds 1. **Note:** Y= -40308x+52869 R^2=0.8887
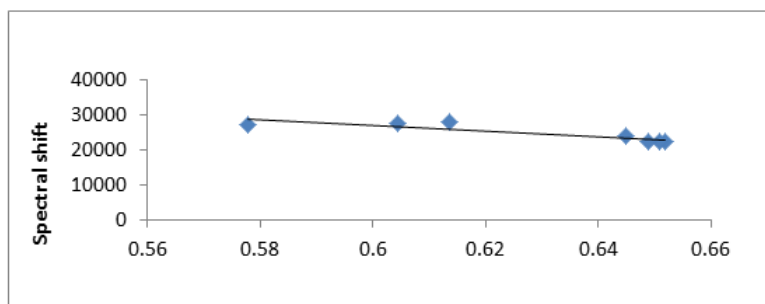
Figure 9: The Variation of the arithmetic mean ∨a and ∨f with F2(Ɛ,n) by Kawaski-Chamma-Viallet's equation in different solvents for compounds 2. **Note:** Y= -81861x+76398 R^2=0.7952

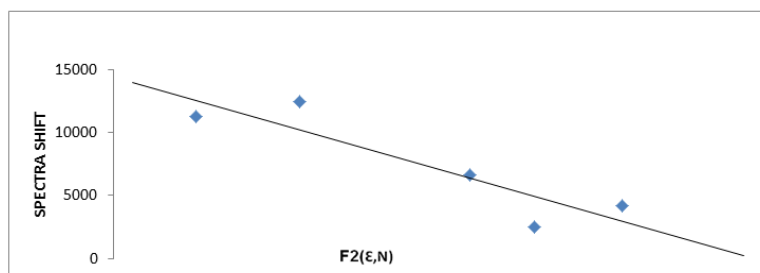**Figure 10:** The Variation of the arithmetic mean ∨a and ∨f with F2(Ɛ,n) by Kawaski-Chamma-Viallet's equation in different solvents for compounds 3. **Note:** Y= -59793+51484 R^2=0.8123
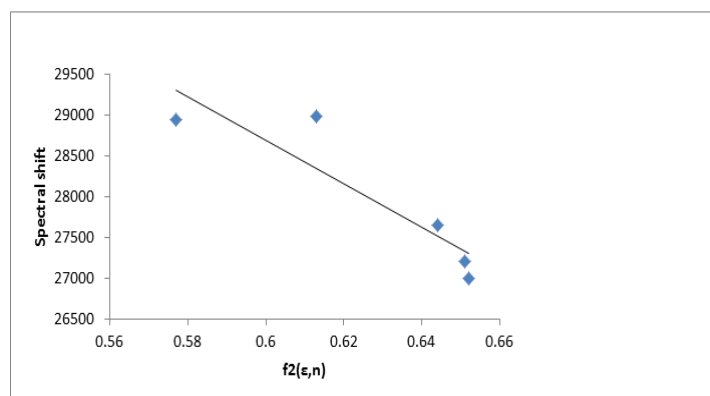

Figure 11: The Variation of the arithmetic mean ∨a and ∨f with F2(Ɛ,n) by Kawaski-Chamma-Viallet's equation in different solvents for compounds 4. **Note:** Y= -26679+44694 R^2 = 0.815, ◆ Spectral shift, ◆ Linear (Spectal shift)
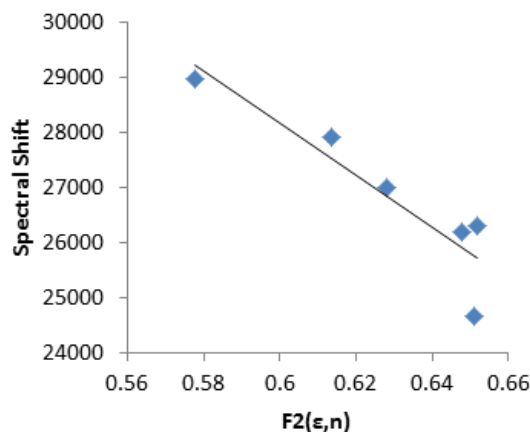

Figure 12: The Variation of the arithmetic mean ∨a and ∨f with F2(Ɛ,n) by Kawaski-Chamma-Viallet's equation in different solvents for compounds 5. **Note:** Y=-47060+56410 R^2 =0.8366, ◆ Spectral shift , ◆ linear shift.
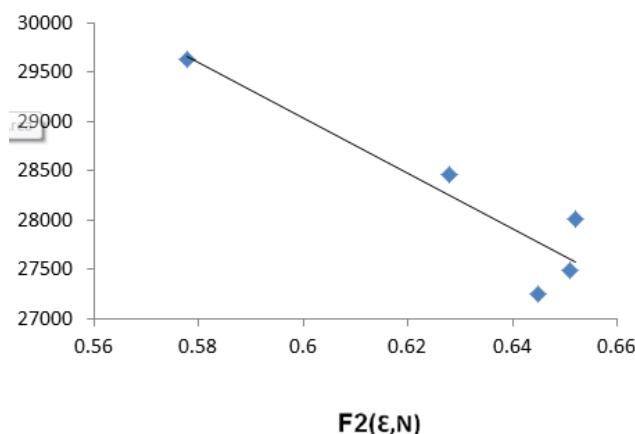
Figure 13: The Variation of the arithmetic mean $\vee a$ and $\vee f$ with $F2(\mathcal{E},n)$ by Kawaski-Chamma-Viallet's equation in different solvents for compounds 6. **Note:** $Y=-28077x+4588$ $R^2=0.8531$

Table 4: The slopes obtained by plotting stoke's shift($\sqrt{a}-\sqrt{f}$) versus bulk solvent polarity function $f1(\mathcal{E},n)(S1)$ and spectral shift $\frac{1}{2}(\sqrt{a}+\sqrt{f})$ versus bulk solvent polarity function $f2(\mathcal{E},n)(S2)$

Compound	S_1	S_2
1	38274	-40308
2	63010	-81861
3	10058	-59793
4	34641	-26679
5	34201	-47060
6	50875	-28077

Table 5: Onsagarcavity(a_0),ground state(μ_g),excited state(μ_e) and change in dipole moment($\Delta \mu$) of compounds

Compound	a_0 (Onsagar radius)	μ_g(exp)	μ_e(exp)	μ_e/μ_g	$\Delta \mu (\mu_e - \mu_g)$
1	3.513	0.5	1.31	0.38	0.81
2	4.78	0.25	1.98	0.126	1.73
3	3.789	1.6	2.28	0.7	0.68
4	4.3	0.14	1.07	0.129	0.93
5	4.92	0.23	1.53	0.15	1.3
6	3.707	0.16	1.43	0.11	1.27

CONCLUSION

The sufficient difference in the ground and excited state dipole moments of compound I shows that α,β- unsaturated ketone is resonance stable and due to which the excited state is little stable compared to ground state. Thus the higher value of dipole moment is observed in excited state. Introduction of nitro group on carbonyl side ring in case of compound 2 increases the excited state dipole moment indicating the increase of α,β-unsaturation conjugation extent with the carbonyl as $-NO_2$ withdraws the π-electron density from the ring than from C=O which is further supported by the decrease in the ground state dipole moment.

But in case of compound 3 ground state as well as excited state dipole moments have been increased which is attributed to the introduction of $-NO_2$ group on alkenyl side ring that results in the more stable charge separated structures by withdrawing the π-electrons of alkenyl bond into the ring. The difference of around 1 Debye ground and excited state dipole moment of compound 5 indicates that there is a resonance stable excited state as the μ_e is higher compared to μ_g .

When the $-OH$ group is replaced by $-NO_2$ group carbonyl side ring, μ_e again increases which indicates the more contribution of the α-β unsaturated charge separated systems to the excited state stability. But in case of compound 6, where $-OH$ introduced on carbonyl side ring and $-NO_2$ is introduced on alkenyl side ring did not show much variation in μ_g and μ_e which may be because of electron donating and withdrawing

groups compensation nature.

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