Electronic Spectrum of different Bis-Schiff bases of Isatin and its Solvatochromism

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ABSTRACT

The influence of a series of organic solvents on the UV spectra on some selected bis-Schiff base derivatives has been studied in a number of organic solvents with diverse polarities. As a part of our efforts to interpret the effects of solvent polarity and hydrogen bonding on the absorption spectra of previously synthesized bis-Schiff base derivatives, the study design was based on the linear solvation energy relationship (LSER) concept using Kamlet-Taft solvatochromic parameters: π^*, α and β.

Correlation of spectroscopic data was carried out by means of multiple linear regression techniques. The fitting coefficient obtained from this analysis allows estimating the contribution of each type of interactions relative to total spectral shifts in solution. The dependence of (υ_{max}) on the solvent parameters indicated that the obtained bands were affected by specific and non-specific solute-solvent interactions.

Keywords: Bis-Schiff Bases, Solvatochromism, Multiple linear regressions, Solvent parameters

1. INTRODUCTION

Compounds containing azomethine group ($-$ C=N$-$) in their structures are known as Schiff bases that forms an important class of organic compounds with a wide range of biological applications. Literature review of these compounds revealed that many studies have been reported regarding the biological activities of these compounds but their solvatochromic comparisons, physiochemical properties and reactivity parameters have been studied considerably less so far. In order to characterize solute-solvent dipolar interactions, we chose to use the Kamlet-Taft π^* scale because this methodology is experimentally one of the most well founded scales of solvent strength[1].

In this paper we have reported the solvatochromic behavior of some carefully selected bis-Schiff base derivatives and the study is a continuation of our previous work[2]. Solvent-solute interactions were investigated using linear solvation energy relationships concept, proposed by Kamlet and Taft, i.e. $\upsilon = \upsilon_0 + s\pi^* + b\beta + a\alpha$ where α is solvent hydrogen-bond donor acidity, β is the scale of solvent hydrogen-bond acceptor basicity and π^* is measure of dipolarity/polarizability.

Solvation effects on the reactivity and the absorption spectra of organic molecules have been extensively studied for decades. Many workers have found that the absorption and emission spectra of organic molecule are frequently modified i.e. the intensity, shape and maximum absorption wavelength of the absorption band. This photo-physical of the molecule being studied is derived by the nature of its environment[3-4]. The UV–Visible spectrum is changed by nonspecific interactions like ion-dipole, dipole–dipole interaction, and induced dipole-dipole interactions or by interactions such as hydrogen bonding[5-6]. The modifications derived by the solvent in the spectra of molecule can render valuable evidences on the local electric field acting on the molecule[7].

It is obvious that polar solvents produce broad bands, non-polar solvents show more resolution, though completely removing the solvent gives the best resolution[8]. This is due to solvent-solute interactions, solvent interacts with the solute both in its ground state and excited state through intermolecular bonding changing the frequency of absorbed photon[9]. This phenomenon causes many different transition energies that average together in the spectra causing peak-broadening. This effect of peak broadening is more prominent for polar solvent, less so for non-polar solvents, and absent when the solute is in vapor phase[8,9,10].

Efforts were made to develop some empirical relations between the spectral characteristics and the microscopic or macroscopic parameters of the solutions, the interactions in the condensed phase were theoretically described in some kinetic and cell models[9-10]. However, multiparameter solvent polarity scale for quantitative valuation of the solvent-solute interaction and the absorption shifts can be used to study the effect of solvent polarity on the absorption spectra that is interpreted by means of linear solvation energy relationship (LSER) i.e. Kamlet–Taft Eq(1)[11] .

$$\upsilon = \upsilon_0 + s\pi^* + b\beta + a\alpha \ldots\ldots\ldots\ldots \text{ Eq(1)}$$

Where:

π^* is measure of dipolarity/polarizability[12]

α is solvent hydrogen-bond donor acidity[12]

β is the scale of solvent hydrogen-bond acceptor basicity[12]

A linear correlation was adopted to quantitatively evaluate the solvatochromic behavior between experimental spectral values υ_{max} and solvatochromic variables π^*, β and α to assess their contributions to the solute-solvent interactions[13]. Chemical structures of studied bases are shown in **Table-1**. Spectroscopic Solvent polarity parameters (*Kamlet–Taft Solvatochromic Parameters*) are given in **Table-2**.

Table-1: List of Bis-Schiff bases of isatin (Lu-01-Lu-08)

Compounds	Structures
Lu-01	
Lu-02	
Lu-03	
Lu-04	
Lu-05	
Lu-06	
Lu-07	
Lu-08	

Table-2: Kamlet–Taft Solvatochromic Parameters

Solvent	α	β	π^*
Methanol	0.98	0.66	0.60
Ethylacetate	0.00	0.45	0.55
Acetone	0.08	0.43	0.71
Tetrahydrofuran	0.00	0.55	0.58
Chloroform	0.20	0.10	0.58
Tetrachloromethane	0.00	0.10	0.59

2. EXPERIMENTAL

2.1 *Chemicals and Instruments*

Ultraviolet-Visible spectrums of these compounds were recorded on Perkin–Elmer Lambda-5 UV/Vis spectrometer. Pre-coated silica gel aluminum plates were used for thin layer chromatography (Kieselgel-60, 254 E. Merck-Germany). Chromatograms were visualized by UV at 254 and 365 nm.

2.2 *General Procedure for the Synthesis of Bis-Schiff bases (Lu-01 to Lu-08)*

The synthesis of bis-Schiff bases derivatives was carried out by refluxing a mixture of 1g isatin and 10ml hydrazine hydrate for 20 minutes. This yields a yellow colored precipitates of monohydrazones that were washed and filtered using methanol. The bis-Schiff base derivatives were synthesized by condensing monohydrazone with different substituted aromatic aldehydes in 1:1 molar ratio in methanol by refluxing for 3-4h. On cooling, the crystalline powder of bis-Schiff base derivatives were filtered and washed with methanol and dried in vacuum. Recrystallization of these compounds (Lu-01 to Lu-08) from methanol produced pure crystals [2-14].

Lu-01-Lu-08
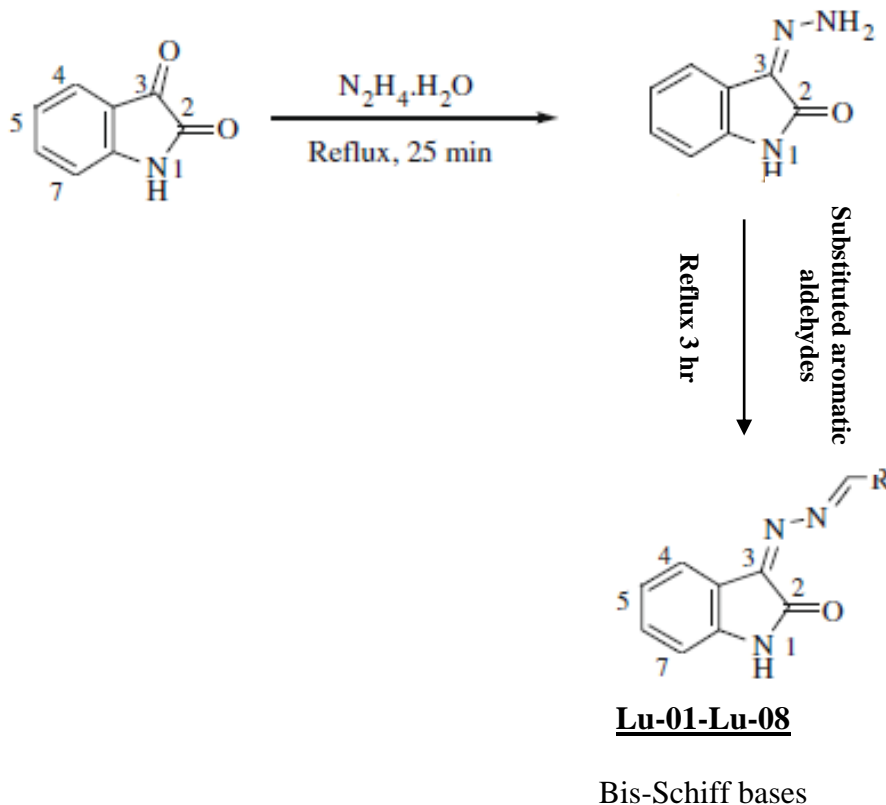
Bis-Schiff bases

Eq.2: Diagramatic representation of different substituted Bis-Schiff bases of isatin

2.3 *UV-Visible Spectroscopy*

Solvation was done by preparing solutions of each compound in a series of organic solvents. Accurately $1.0 \exp^{-3}$ molar solution of each ligand from Lu-01 to Lu-08 was prepared first in 25.0 ml volumetric flask and were further diluted to made solutions up to 1.0×10^{-5} M. UV-Vis spectrums were recorded and peaks were observed over a wavelength range of 300–800 nm. Quartz cuvettes (b = 1.0 cm) were used to record the UV-Vis Spectra of all solutions.

3. RESULTS AND DISCUSSION

3.1 *Uv-Visible Spectrums*

Nearly all compounds showed significant solvatochromic behavior associated with large dipole moment changes during electronic transitions. The shift in the absorption maxima is resulted from the interaction between solute and solvent molecules which is in turn derived by the polarity of specific solvent. Visible spectrum of each compound was recorded at ambient room temperature using various organic solvents. The spectral data is summarized in **Table-IV**.

The bathochromic shift in Lu-01, Lu-06 and Lu-07 was observed in CCl$_4$, in case of Lu-02 and Lu-04 the shift was observed in chloroform. In case of Lu-03 and Lu-05 this shift was observed in methanol while in Lu-08 it was observe in acetone. Strong bathochromic were observed for all compounds which is a clear indication of intense guest-host interactions between solvent and (-N=N-) of the molecule. Similarly hypsochromic shifts in Lu-01 and Lu-05

were observed in chloroform, in case of Lu-02, Lu-06, Lu-07 and Lu-08 it was observed in THF, while in case of Lu-03 and Lu-04 it was observed in CCl$_4$. Sometime the peaks doesn't appear like Lu-01 and Lu-08 in chloroform, this may be due to dissociation of bases in chloroform.
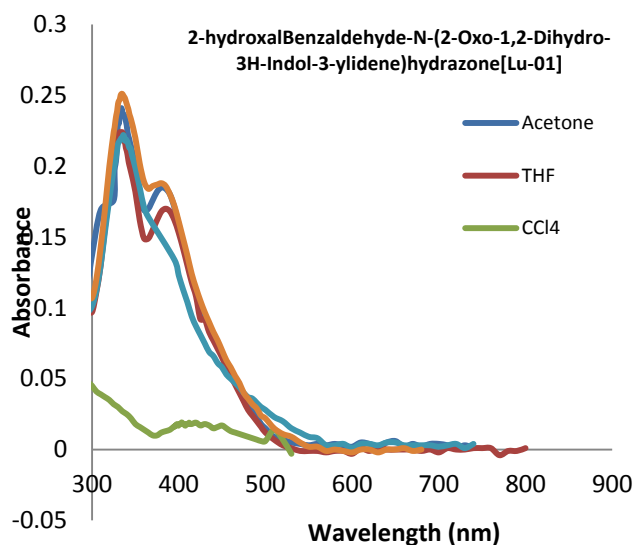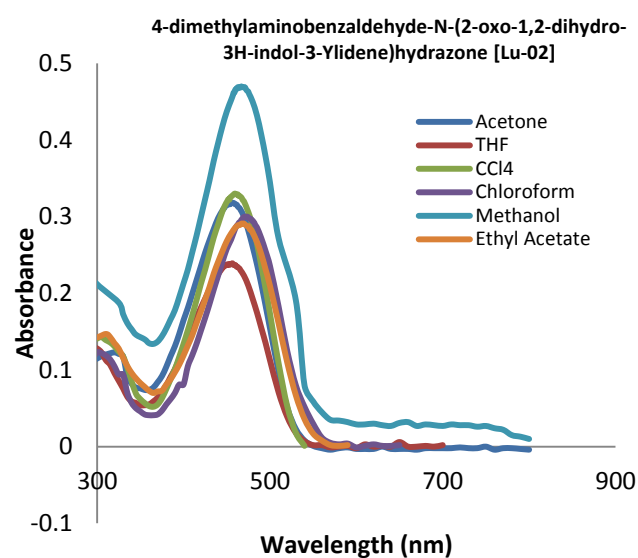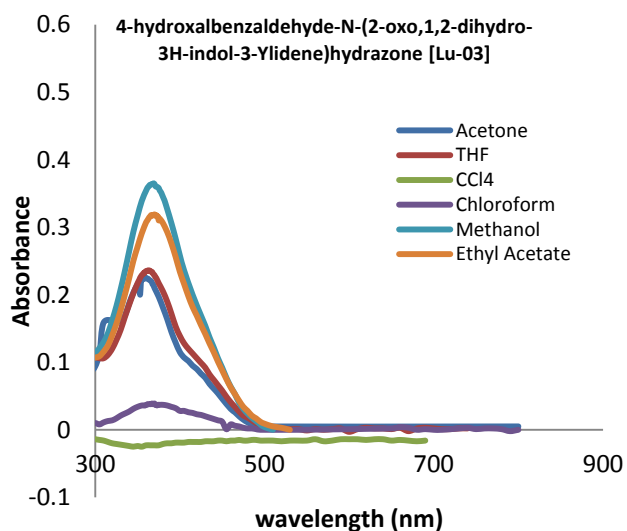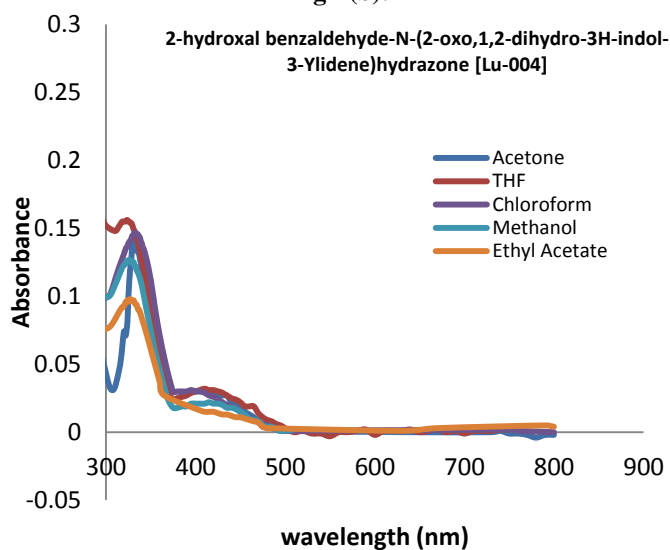

Fig-1(a):

Fig-1(b):

Fig-1(c):

Fig-1(d):
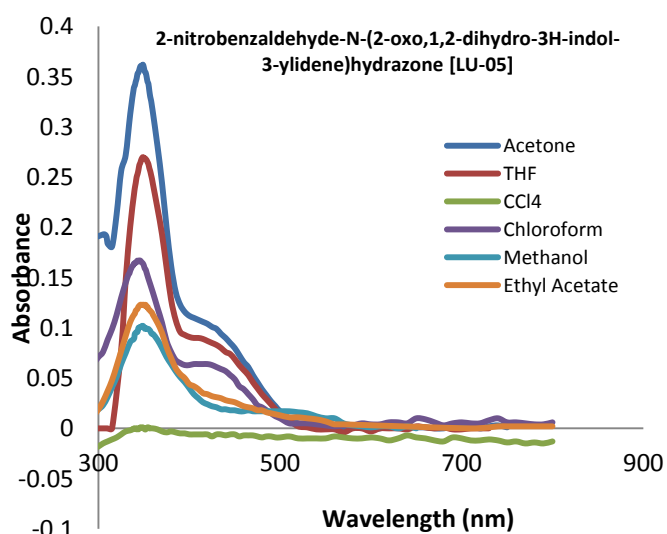
Fig-1(e):
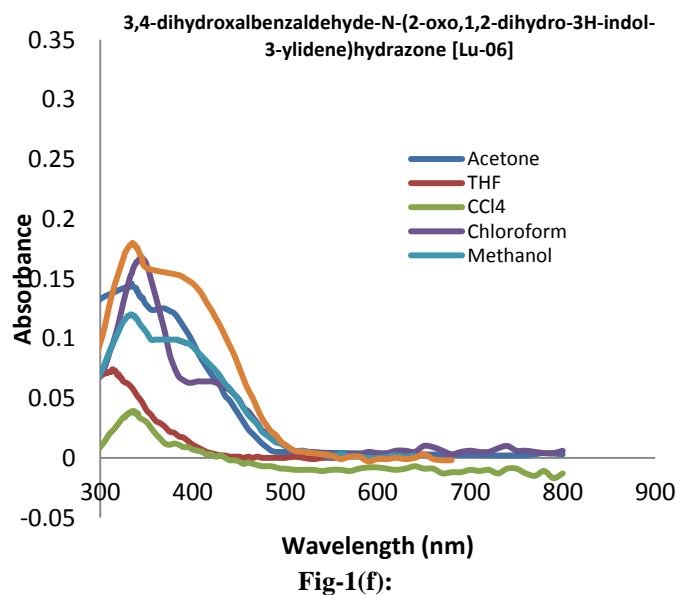
Fig-1(f):
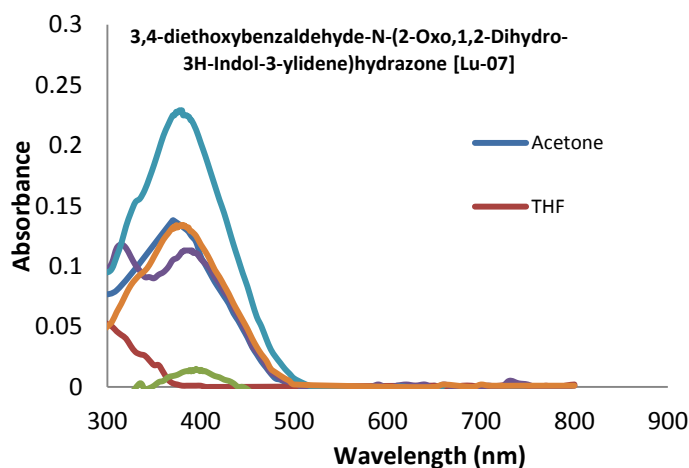
Fig-1(g):
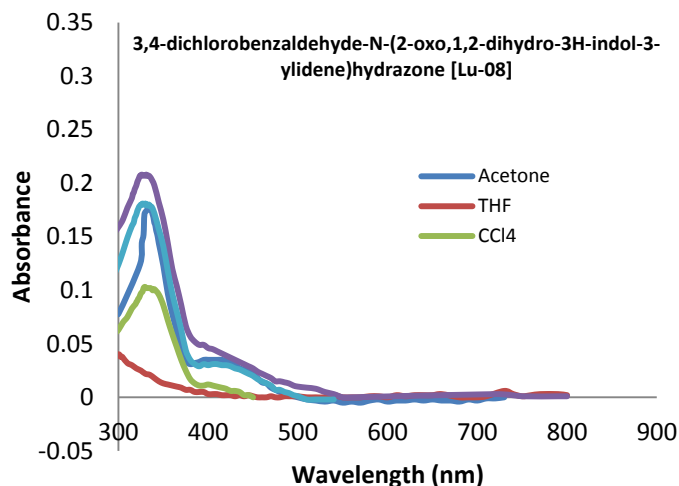
Fig-1(h):

Table-3: υ_{max} of Electronic Absorption Spectra (cm^{-1}) in different solvents.

Solvents	υ_{max} (cm^{-1})							
	Lu-01	Lu-02	Lu-03	Lu-04	Lu-05	Lu-06	Lu-07	Lu-08
Methanol	29761.9	21413.2	26881.7	30674.8	28653.2	29440.1	26315.7	30674.8
Ethylacetate	29850.7	21276.5	27027.0	30581.0	28653.2	29850.7	26315.7	30581.0
Acetone	29940.1	21929.8	27855.1	30303.0	28653.2	29940.1	27027.0	29940.1
Tetrahydrofuran	30030.0	21929.8	27624.3	30864.1	28653.2	31948.8	----	34129.6
Chloroform	----	21141.6	27247.9	30120.4	29154.5	30120.4	25706.9	----
Tetrachloromethane	----	21786.4	----	30864.1	28848.4	29761.9	25380.7	30395.1

3.2 *Multiparameter of Solvent Polarity and Solvatochromic Behavior*

The effects of solvent polarity and hydrogen bonding on the bis-Schiff base derivatives were interpreted by means of the linear solvation energy relationship using Kamlet–Taft Equation i.e. **Eq. (1)**. The correlations of the spectroscopic data were carried out by means of multiple linear regression analysis using a software SPSS [15]. It was found that absorption frequencies for bis-Schiff base derivatives in solvents showed acceptable correlation with π^*, β and α parameters. The results of the multiple regressions parameters and υ_{max} are presented in **Table-4** and coefficients υ_o, s, b and a have confidence intervals at a level of significance of 95%.

Table-4: Solvent Independent Correlation Coefficient a, b, s of the Kamlet–Taft Parameters.

| Compound	υ_0	s	b	a	R-square	F-statistic
Lu-01	28640	977.2	1500	-461.9	0.99	0
Lu-02	19490	3269	581	-484.4	0.55	0.80
Lu-03	24720	4437	198	-636.5	0.84	1.74
Lu-04	31680	-2163	608.7	-180.8	0.28	0.26
Lu-05	29360	-490.3	870.9	198.3	0.80	2.68
Lu-06	29630	680	-418.4	-281.6	0.61	0.54
Lu-07	22400	5111	2348	-664	0.91	3.65
Lu-08	32800	-4146	57.32	295	0.99	0

Bis-Schiff derivatives showed moderate to strong solvatochromic behavior with large dipole moment changes during transitions between two electronic states i.e. π to π^*. The negative sign of b and s coefficient for Lu-04, Lu-05, Lu-06 and Lu-08 indicates a bathochromic shifts with both increasing solvent hydrogen bond acceptor basicities and solvent dipolarity/polarizability. The negative sign of (a) coefficient for Lu-01, Lu-02, Lu-03, Lu-04, Lu-06 and Lu-07 shows a positive solvatochromism with increasing solvent dipolarity/polarizability (π^*). The positive sign of a coefficient for Lu-04 and Lu-08 indicates a hypsochromic shifts with increasing solvent hydrogen bond donor acidities. This suggests stabilization of the ground state relative to the electronic excited state.

The Percentage contribution of the solvatochromic parameter was calculated from the values of regression coefficients and given in **Table-5**.

It was observed that the transitions are sensitive to the solvent polarity and the transition (π-π^*) are shifted bathochromically as the solvent polarity increases. These changes were attributed to hydrogen-bonding interaction between the solute molecule and the solvent molecule which is a clear indication that most of the solavochromism of bis-Schiff base derivatives is due to the basicity and dipolarity/polarizability **i.e β and π** respectively, rather than acidity.

Table-5: Percentage Contribution of the Solvatochromic Parameter

Compound	Pπ (%)	Pβ(%)	Pα(%)
Lu-01	33.2	51.0	15.7
Lu-02	75.4	13.4	11.2
Lu-03	84.2	3.8	12.1
Lu-04	73.3	20.6	6.1
Lu-05	31.4	55.8	12.7
Lu-06	49.3	30.3	20.4
Lu-07	62.9	28.9	8.2
Lu-08	92.2	1.3	6.6
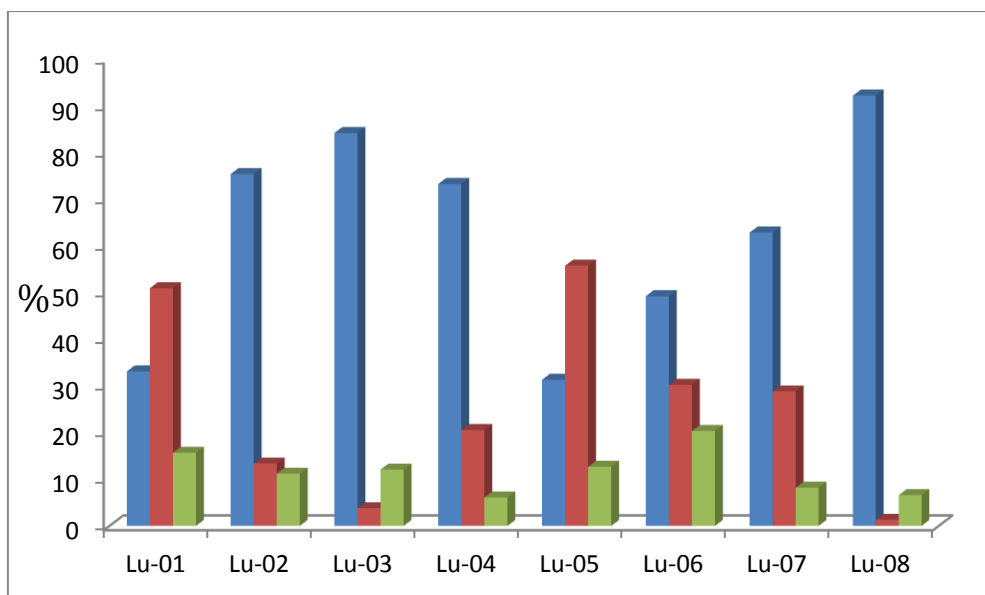
Fig-2: Percentage Contribution of the Solvatochromic Effects;
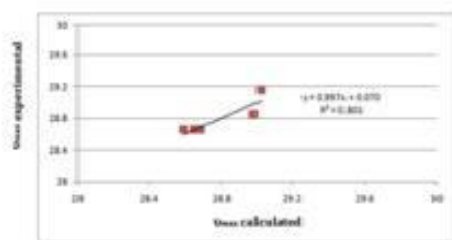(1)Lu-01 (2)Lu-02 (3)Lu-03 (4)Lu-04 (5)Lu-05 (6)Lu-06 (7)Lu-07 (8)Lu-08
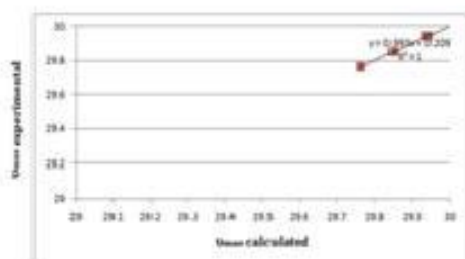
Figure: 03-A
Plot of υ max verses υ experimental for Lu-01
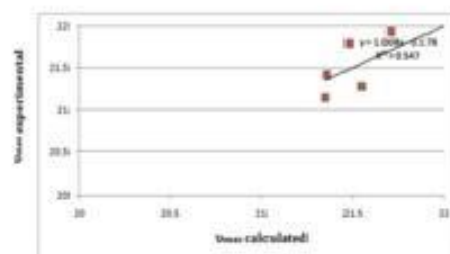
Figure: 03-B
Plot of υ max verses υ experimental for Lu-02
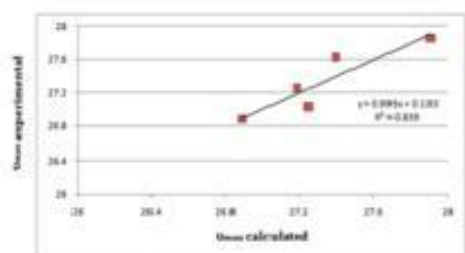
Figure: 03-C
Plot of υ max verses υ experimental for Lu-03
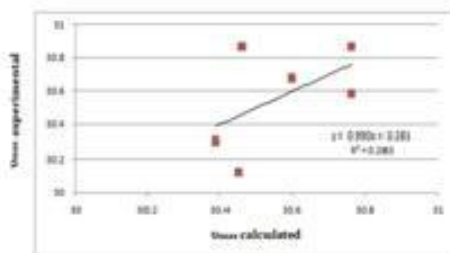
Figure: 03-D
Plot of υ max verses υ experimental for Lu-04

Figure: 03-E
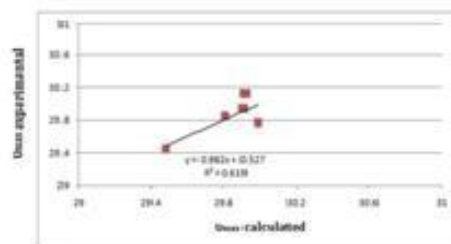Plot of ʋ max verses ʋ experimental for Lu-05

Figure: 03-F
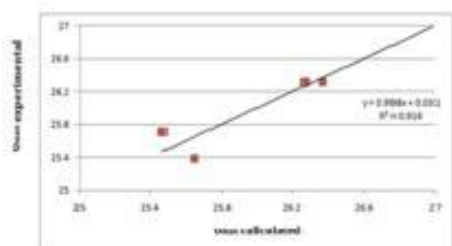Plot of ʋ max verses ʋ experimental for Lu-06

Figure: 03-G
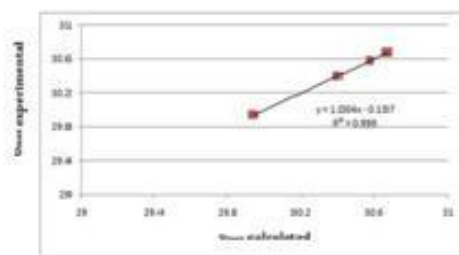Plot of ʋ max verses ʋ experimental for Lu-07

Figure: 03-H
Plot of ʋ max verses ʋ experimental for Lu-08

The degree of success of Eq. (1) is shown in **Figure-03-A to Figure-03-H** by means of a plot of v_{exp} calculated versus v_{calc} observed in different solvents.

4. CONCLUSION

These results showed that the effects of solvent on electronic spectra of bis-Schiff base derivatives were strongly dependent on the nature of the substituent. This conclusion implies electron-donating substituents in the azo group i.e. difference in the conjugational or migrating ability of the electron lone pairs on nitrogen atoms and azo-hydrazo tautomerism shows most of the solvatochromism. These results are in accordance with structure of these bis-Schiff base derivatives. We can express this effect quantitatively by applying multiple regressions using Kamlet–Taft equation.

5. ACKNOWLEDGEMENT

6. REFERENCES

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