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SOLVENT EFFECTS ON THE ELECTRONIC ABSORPTION SPECTRA OF SOME ANALYTICAL INDICATORS

Mamdouh S. Masoud
Professor, Faculty of Science, Alexandria University, Alexandria, Egypt, drmsmasoud@yahoo.com

Rabah H.A. Mohamed
Assistant Professor, Faculty of Science, Alexandria University, Alexandria, Egypt, rmohamed@sci.alex.edu.eg

Hesham M. Kamel
Assistant Professor, Faculty of Allied Medical Sciences, Pharos University, Alexandria, Egypt, esham.kamel@pua.edu.eg

Najat O. M. El-Ziani
Assistant Professor, Faculty of Science, Sirt University, Sirt, Libya, najatwer@yahoo.com

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SOLVENT EFFECTS ON THE ELECTRONIC ABSORPTION SPECTRA OF SOME ANALYTICAL INDICATORS

Abstract

Electronic absorption spectra of selected ligands (Alloxan, Carmine, Naphthol Yellow S, Hematoxylin and Cyanine) were recorded in presence of different solvents (H2O, Ethyl acetate, Ethanol, DMF, Isopropyl alcohol, Amyl alcohol and Butanol) of variable physical properties. The electronic transitions were assigned. The data are analyzed based on the multiple linear regression technique explained from the views of different solvent parameters. Statistical analyses of the effect of solvents on the electronic spectra of the present ligands have been investigated.

1. INTRODUCTION

Alloxan is an alterdentate ligand offering more than one equivalent coordination site, where always a rearrangement is possible in which the metal is transferred from one site to another. This can be either an inter - or intramolecular process (Refat, 2008)(Daul, 1983). In aqueous solution, the N–H bond is almost broken, while the O–H bond is only partially formed in the transition state (Kakkar, 2001). The stabilizing effect in aqueous solution is due to bulk solvent dielectric effects, which stabilize the transition state to a greater extent due to it has higher dipole moment. Although the transition states for proton transfer to the neighboring oxygen atoms on either side have comparable energies, as the mechanisms of proton transfer leading to the formation of the 2-hydroxy and 4-hydroxy tautomers are similar, bulk solvent effects are larger in the latter due to the higher dipole moment of the transition state (Kakkar, 2001). This is the almost complete separation of the two entities, i.e. the alloxan anion and the hydronium ion in the latter case, indicating that in this case a dissociative mechanism of the kind encountered in acid–base equilibria is operating. Hydrated alloxan can potentially exist in different tautomeric forms (Gupta, 1995).

Carmine is used for colorimetric determination for the analysis of Th in presence of Ce or UO_2 salts (Eswaranarayana, 1955). It is also used for the determination of trace amounts of osmium (VIII), based on its catalytic effect on the oxidation of carmine by hydrogen peroxide (Manzoori, 2000). Beside the determination of nitrite based on its effect on the oxidation of carmine with bromated in rain and river water (Manzoori, 1998).

The general protein stain Naphthol Yellow S has been studied with a model system of polyacrylamide films containing proteins to test the stoichiometry of the salt formation and the influence of some histochemical and histological conditions (Kiernan, 2006).

Haematein is the oxidized form of hematoxylin and forms strongly colored complexes with certain metal ions, notably Fe^{III} and Al^{III} salts. Metal-haematein complexes are used to stain cell nuclei prior to examination under a microscope. Structures that stain with iron- or aluminium-haematein are often called basophilic, even though the mechanism of the staining is different from that of staining with basic dyes (Abd El-Aal, 2002). The enthalpy and entropy changes of hematoxylin–Serum albumin interaction are important for confirming binding mode (Sioi, 2006).

It forms coordination compounds with mordant metals, such as aluminum, and the resulting lake attaches to cell nuclei ((Llewellyn, 2009)(Rastogi, 2019)). Aluminium was titrated directly with EDTA in presence of acetate buffer, lactic or glycolic acid being used as auxiliary complexing agent. Mixtures of two metal ions can be titrated if one is Bi^{3+} and the other Al^{3+}, Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+} or Er^{3+} (Ernst, 1989).

Cyanine has many uses as fluorescent dyes, particularly in biomedical imaging. Depending on the structure, they cover the spectrum from IR to UV (Meloan, 1987). These can be divided into two groups, i.e., symmetrical and asymmetrical dyes. Since, the addition of transition metal chelate compounds as quenchers to cyanine dyes enhances their photo stability and essentially inhibits their decolorization by lighting. The stabilized cyanine dyes complex has a much higher resistance to light, heat and moisture than the mixture of the cation and the anion (Zhang, 2009).

The present paper is aimed to study the effect of solvents on the electronic absorption spectra of Alloxan, Carmine, Naphthol Yellow S, Hematoxylin and Cyanine. The data will be analyzed from the different solvent parameters with the view of structural configuration of the compounds. The solvent-solute interactions are of major importance for explaining the spectral properties.

2. MATERIALS AND METHODS

Alloxan   Carmine   Naphthol yellow S   Hematoxylin   Cyanine
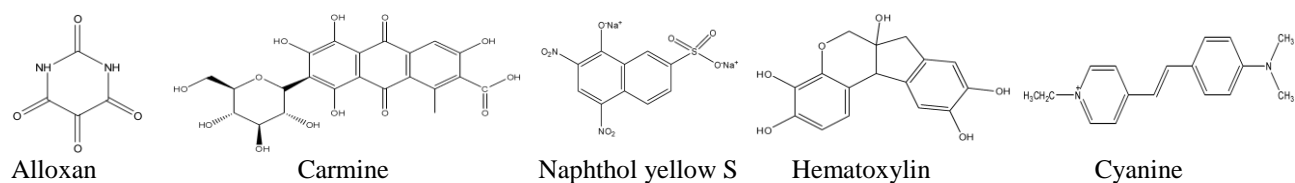
The selected ligands [Alloxan (H2L1), Carmine (H9L2), Naphthol Yellow S (L3), Hematoxylin (H5L4) and Cyanine (L5)] were purchased from Fluka, Sigma and Lobachemie companies and used without further purification. (All solvents (H2O, Ethyl acetate, Ethanol, DMF, Isopropyl alcohol, Amyl alcohol and Butanol) were of spectroquality grade).

The spectral studies in solution were measured using UV- visible spectrophotometer (Jasco-V. 530) and Perkin Elmer (Lambda 4B) covering the wavelength range 190-900 nm. Measurements were carried out at the central laboratory, Faculty of Science, Alexandria University.

The spectrophotometer absorbance data in the presence of different solvents have been analyzed by the multiple linear regression technique using statistical package of social science program, SPSS version 20. The physical properties of the ligands are given in Table (1).

Table 1: Physical properties for the ligands.

Compound	M.wt	Color	Formula	m.p (^{o}C)	Abbreviation
Alloxan	160.09	Golden yellow	$C_4H_2N_2O_4$-H_2O	250	H_2L^1
Carmine	492.40	Red	$C_{22}H_{20}O_{13}$	>300	H_9L^2
Naphthol yellow S	358.19	Brown	$C_{10}H_4N_2O_8SNa_2$	230	L^3
Hematoxylin	356.28	Brown	$C_{16}H_{14}O_6$-$3H_2O$	>300	H_5L^4
Cyanine	253	Dark blue	$C_{17}H_{21}N_2$	164	L^5

3. RESULTS AND DISCUSSION

Table (2) represents the electronic absorption spectra of the ligands in presence of different solvents of different polarities, leading to change the position and the intensity, due to many factors:

a) The physical properties of the solvent mainly its polarity. The non - polar solutes can interact with non polar solvent through temporary dipole - induced dipole forces (London-dispersion forces).
b) The difference in solvation energy from one solvent to another, and on going from the ground to the excited states in the same solvent.
c) The change in the polarity or dipole moment of the solvent during excitation.

The electronic absorption spectra of alloxan in different solvents, Table (2), gave two bands in butanol and amyl alcohol while one band is detected in presence DMF, ethyl acetate, isopropyl alcohol, ethanol and water. The absorption spectrum of alloxan exhibits bands in the range of 228–274 nm due to the π-π* transitions of conjugated multiple bands, and the band at 310 nm can be assigned to the n-π* transition of the ketone groups. These bands point to the presence of lactam forms of the molecule in solution (Shebaldina, 2004). However, carmine, Table (2), pointed the existence of three bands in water, while two bands are detected in butanol, ethanol and amyl alcohol, and only one band is appearing in DMF, isopropanol and ethyl acetate solvents. The main bands of carmine compound are located in the spectral range of 236–258 nm, 281-291 nm and 350-399 nm, exhibit an apparent blue shift in presence of different solvents according to the sequence: H2O > ethanol = butanol > ethyl acetate for the first band. The shifts agree with the change in the polarity of the organic solvents and can be considered a result of combination of several solvent characteristics such as polarity and H-bond-accepting ability.

This trend was observed with the second band except with DMF. The displacements of absorption bands, which occur without affecting the basic electronic process, imply that the environment of simple chromophores (C=O, C=C) polarizes the valence electrons. This includes, (a) intramolecular forces such as those arising from conjugation of double bonds, substitution in the benzene ring and hydrogen bond formation, (b) intermolecular forces such as association in all its aspects with mainly solvent–solute interactions. Meanwhile, naphthol yellow S, Table (2), gave four bands in butanol, DMF, ethyl acetate and ethanol. While in presence of amyl alcohol, two bands are appeared. However, only one band is detected in isopropyl alcohol. The bands at the wavelength range 233-297 nm are due to π-π* electronic transition. The bands appeared in the wavelength range 310-343 nm are due to n-π* electronic transitions. Aryl group part of the molecules and the naphthalene moiety contain different substitute's containing nitrogen, oxygen or sulphur atoms (e.g. SO3H, NO2 and OH groups). Thus, many n-π* transitions are expected to take place from these non-bonding orbitals to different π* molecular orbital's. The structure of naphthol yellow S contains SO3Na group, is ionized easily. However, hematoxylin, Table (2), gave four bands in water and ethanol, two bands in butanol, and one band in the remain solvents. The bands are due to π-π* transition at wavelength range 225- 294 nm and the other bands at the wavelength range 391-565 nm are due to n-π* transition. The blue shift of n-π* transition by increasing the solvent polarity, due to hydrogen bond formation takes place between the solute and the solvent through the hydroxyl group. The π-π* system is stabilized and lower the energy of the ground state and thus blue shift occurs. The lower part of absorbance curve indicates the equilibrium between the protonated and the neutral forms of compound. Shifting to cyanine in presence of different solvents, Table (2), gave one band except in water two bands are appeared. These spectral bands are mainly due to n-π* transitions.

Table 2: Electronic absorption spectra of the ligands in different solvents (λ_{max}nm).

Compound	Butanol	Amyl alcohol	Isopropyl alcohol	DMF	Ethanol	Ethyl acetate	H$_2$O
Alloxan	250*	228*	-	-	248*	-	230*
	274**	289**	310**	268**	-	254**	-
Carmine	248*	-	-	-	248*	258*	236*
	283**	287**	-	291**	279**	-	281**
	-	398***	350***	-	-	-	399***
Naphthol yellow S	249*	-	-	-	246*	257*	233*
	284**	-	-	270**	-	-	275**
	296***a	293***a	-	296***a	297***a	295***a	-
	-	-	-	310***b	310***b	310***b	-
	341****	343****	341****	340****	340****	337****	-
Hematoxylin	247*	-	-	-	242*	-	225*
	291**	291**	-	294**	291**	284**	284**
	400***	400***	410***	400***	400***	400***	400***
	450****a	-	444****a	442****a	446****a	-	435****a
	-	-	-	-	565****b	-	564****b
Cyanine	-	-	-	-	-	-	402*
	589**	589**	616**	604**	604**	594**	624**

Where * = λ_1, ** = λ_2 ,*** =λ_3 , and **** =λ_4

(Masoud et al., 1984, 2001, 2002, 2005, 2006, 2007, 2008, 2011, 2012, 2014, 2015, 2016, 2017) published a series of papers to throw light on the solvent effects on the chemistry of some biologically active organic compounds. The solvents are selected to show a wide variety of solvent parameters such as dielectric constant, D, refractive index, n, and hydrogen bonding capacity to permit a good understanding of solvent-induced spectral shifts. Different one-, two- three- and four -parameters equations are applied using suitable combinations between the solvent polarity parameters (E, K, M, J, H and N) (Eqs. (1-6)).

Eq. (1) $E = 2.895 \times 10^{-3}\upsilon^{-}$

Eq. (2) $K = (D-1) / (2D+1)$

Eq. (3) $M = (n^2 - 1)/ (2n^2 + 1)$

Eq. (4) $J = (D - 1) / (D + 2)$

Eq. (5) $H = (n^2 - 1) / (n^2 + 2)$

Eq. (6) $N = J - H$

The observed peak position of an absorption band Y of any of the investigated compounds in a given solvent has been expressed as a linear function of different solvent polarity parameters Xn (Eq. (7)), as follows:

Eq. (7) $Y = a_o + a_1X_1 + a_2X_2 + ... + a_nX_n$

Where ao is the regression intercept. It has been assumed (Masoud, 2017) to be an estimate of the peak position for gas phase spectra. (a1, a2, ... an) are the solvent polarity parameter`s coefficients.

E is related to $\upsilon-$, which is the wavenumber of the absorption maximum in a given solvent (Reichardt, 1965). The function is sensitive to both solvent–solute hydrogen bonging and dipolar interactions. The Kirkwood's dielectric function K represents the dipolar interaction and is related to the dielectric constant (D) of the solvent. The functions J and H have been introduced (Kirkwood, 1934) to account for the non–specific solute – solvent interactions such as dispersion and dipolar effects. These are related to the dielectric constant (D) and refractive index (n) of the solvents.

The functions M and N have been introduced (McRae, 1957)(Masoud, 1981) to account for the solute permanent dipole–solvent induced dipole and solute permanent dipole-solvent interaction, respectively. The values of the solvent parameters (E, M, N, K, D, n, X1 and X2) in different solvents are collected in Table (3).

Table 3: Solvent parameters and X_1 and X_2 for solvents.

Solvent	D	n	E	M	N	K	X_1	X_2
Butanol	17	1.399	50.20	0.20	0.60	0.46	0.888	0.389
Amyl alcohol	14.7	1.405	47.00	0.20	0.57	0.45	0.872	0.393
Isopropyl alcohol	18.3	1.377	48.60	0.19	0.62	0.46	0.896	0.373
DMF	36.7	1.427	43.80	0.20	0.67	0.48	0.946	0.408
Ethanol	24.3	1.361	51.90	0.18	0.67	0.47	0.920	0.362
Ethyl acetate	6	1.372	38.10	0.19	0.40	0.39	0.714	0.370
H_2O	78.5	1.33	63.1	0.17	076	0.49	0.794	0.337

$X_1 = 2(D - 1)/ 2D + 1$ $X_2 = 2(n^2 - 1)/ (2n^2 + 1)$

The regression intercept ao has been considered the peak position in the gas spectra (Hasanein, 1985)(Masoud, 2004)(Taft, 1976). The intercept a0 and the coefficients (a1, a2, a3 and an) have been calculated by multiple regression analysis using a micro static program (SPPS) and the calculation have been carried out on a PC computer. The results for the alloxan, Table (4), assigned of the electronic transition peaks, the multiple correlation coefficient (MCC) value is considered a measure of the goodness of the fit. The high value of MCC (~1) is of a good correlation to the spectral shifts. Alternatively, the small value (~ zero) of the probability of variation parameter (P) means the correlation is good. The spectral shifts of the electronic absorption spectra of investigated compound as following:

1. Based on one parameter regression equation, all MCC values for all solvent parameters are very poor indicating difficulty of correlation for the studied spectral region λ1, λ2, λ3 and λ4. But (M) parameter is more effective than K, N and E. However, the parameter (M) give moderate correlation (MCC= 0.620) for the carmine in the region λ1.
2. Based on two parameters equation, the higher values of multiple regression (MCC) and probability of variation (P) are shown for cyanine at λ2 and naphthol yellow S at λ4 for the combination (M, E). But on the combination (M, N), the MCC value is the highest and P value is the lowest for cyanine at λ2. They are of opposed trend for hematoxylin λ2.

3. The solvent–solute hydrogen bonding combined with the solute permanent dipole-solvent induced dipole interactions are major factors for determining the spectral shifts in this case. The effect of the intermolecular hydrogen bonding is of major importunacy. Such effect, is absent on one parameter correlation. The combination (K, N) and (K, M) give best values correlation for cyanine at $\lambda 2$, while in other compounds are very poor.

4. The combination (M, N, E) gives higher values of correlations for cyanine at $\lambda 2$ and naphthol yellow s at $\lambda 4$ as shown by its multiple regression coefficient (MCC) and probability of variation (P). The addition of E to M and K leads to better results for cyanine at $\lambda 2$ and naphthol yellow S at $\lambda 4$. The interamoleculer hydrogen bonding combined with solute permanent dipole-solvent induced dipole and solute permanent parameter to explain the spectral shifts. The combination (K, N, E) gives higher values of correlations for cyanine at $\lambda 2$, hematoxylin at $\lambda 2$, naphthol yellow s at $\lambda 4$ and carmine at $\lambda 2$. The dielectric constants are effective parameters to explain the spectral shifts.

Table 4: Regression analysis for alloxan in different solvents at (λ_2)

Parameter	a0	a1	a2	a3	a4	MCC	P
K	302.6	-76.62	-	-	-	0.01	0.835
M	5.585	1390.082	-	-	-	0.324	0.182
N	30.62	-53.78	-	-	-	0.49	0.633
E	335.0	-1.375	-	-	-	0.155	0.382
K,M	29.93	-49.484	1380.67	-	-	0.328	0.45
K,N	-459.04	2809.721	-907.31	-	-	0.480	0.271
K,E	231.48	352.911	-2.594	-	-	0.244	0.571
M,N	29.205	1336.938	-22.22	-	-	0.332	0.446
M,E	35.015	1292.203	-0.224	-	-	0.326	0.454
N,E	332.96	86.373	-2.413	-	-	0.194	0.650
K,M,N	-1468.4	9664.413	-4156.9	-3087.7	-	0.651	0.311
K,M,E	-79.13	1455.687	0.185	-79.13	-	0.328	0.714
K,N,E	-631.62	3388.845	-1152.6	1.194	-	0.497	0.504
M,N,E	-28.547	1572.188	-59.976	0.745	-	0.337	0.704
K,M,N,E	-1483.3	10500.32	-5099.1	-3277.9	-1.48	0.668	0.554

K1, K2, vvapour, r2 (v, D), r2 (v, n) and MCC values are computed and listed in Table (5). The (D) and the (n) values of solvents affect the electronic absorption spectra of these compounds, and the following equation (Eq. (8)) is applied (Taft, 1976)(Abu-Eittah, 2009)

Eq. (8) $\quad v_{solution} = v_{vapour} + K_1 \dfrac{2E-2}{2E+1} + K_2 \dfrac{2n^2-2}{2n^2+1}$

The vvapour values and the coefficients K1, K2 are determined. Based on linear regression, the function v solution is linear in both D and n (Eq. (9)), so:

Eq. (9) $\quad v_{solution} = v_{vapour} + K_1 X_1 + K_2 X_2$

Table 5: K_1, K_2, v_{vap} and correlation analysis data for ligands.

Compound	$v_{vap}(cm^{-1})$	K_1	K_2	MCC	$r^2(v, D)$	$r^2(v, n)$
Alloxan	72562.98	-5693.618	-91167.3	0.557	0.226	0.737
Carmine	47489.19	-15040.8	-24203.4	0.843	0.841	0.397
Naphthol yellow S	33275.10	-2270.79	-9531.21	0.813	0.631	0.766
Hematoxylin	39641.74	-2238.54	-13762.9	0.875	0.485	0.875
Cyanine	13988.82	-264.69	7698.49	0.766	0.073	0.614

From Table (5), the following points are documented:

a) The v_{vapour} of alloxan is located at 72562.98 cm^{-1}, due to the presence of C=O and NH groups.

b) The K_1 values related to dielectric constant of the solvents for all ligands are of high negative sign and while cyanine is of smaller value.

c) The K_2 values (related to the refractive index of the solvents) are with negative sign except that of the cyanine. This assumes that forces of solute- solvent interactions for all the ligands are in the same direction while that for Cyanine is of opposite trend.

d) The data favored argue that both E and n parameters are comparative to affect the spectral data.

e) Solvation energy can be defined quantitatively as the energy of interaction between a solute and a solvent (Dwiecki, 2006). The two important and commonly used formulations for solvent-solute interactions are the Born (point charge model) and Onsager (point dipole dielectric continuum model) formulations (Eqs. (10,11)). In both models electric charges and lengths are combined to obtain the physical dimension of energy.

Eq. (10) $\quad E_{solv}^{ion} = \frac{-q^2}{2a} F(D)$ $\qquad$ Born equation

Eq. (11) $\quad E_{solv}^{dipol} = \frac{-\mu^2}{2a^3} f(D)$ $\qquad$ Onsager equation

The solvent polarity function (Ebead, 2010) F(D) and f(D) represent the relative strength of the electric field experienced by the ion or dipole where a neutral dipolar molecule is a sphere with center point dipole moment μ and has two separate effects on the surrounding solvent molecules:

a. Induction polarization.
b. Orientation of polarization.

In case induction polarization, the solute-solvent interaction is given by (Eq. (12)):

Eq. (12) $\quad E_{slov} = \frac{-\mu_M}{2a^3} [f(D) - f(n^2)]$

Eq. (13), is a measure of the permanent dipole - induced dipole interactions, the correlation of vmax and f(n2), gives a straight line with a negative slope, which equals to - μM/a3M, where n is refractive index and a3M is the radius of the spherical cavity which contains the solvent molecule. For orientation polarization of the solvent dipoles, the total solvation energy Eqs. (14,15):

Eq. (13) $\quad (n^2) = \frac{2(n^2 - !)}{2n^2 + 1}$

Eq. (14) $\quad E_{slov} = \frac{-\mu_m}{a_M^3} [f(D) - f(n^2)]$

Eq. (15) $\quad (D) = \frac{2(D - !)}{2D + 1}$

Where, D is the dielectric constant and [f (D) –f (n2)] is a measure of the interactions between the permanent dipoles. The solvatochromic shifts are often used to assign the transition as π-π*, n-π* or charge transfer. However, the relation between the wavenumber (cm-1) of highest energy electronic transition for alloxan, carmine, naphthol yellow s, hematoxylin and cyanine with dielectric constant f (D) for a number of polar solvents are given. Also, the relation between the wavenumber (cm-1) against [f (D)-f (n2)] for polar and non polar solvents are given as follows:

1- The slopes for all compounds are negative except in case hematoxylin.
2- Such relation with refractive index is controlled by the function $f(n^2)$.
3- The linearity with a negative slope and of small value except in case cyanine has positive value.
4- This reflects a weak solvent- solute interaction controlled by the variation of the solvent refractive index.

The influence of non-specific chemical interactions, including electrostatic effects (dipolarity ∕ polarizability), from specific interaction that is hydrogen bonding, related to the molecular structure of a compound Eq. (16) (Taft, 1979)(Kamlet, 1983)(Thomas, 2019).

Eq. (16) $\nu_{max} = \nu_o + s\pi^* + b\beta + a\alpha$

Where, vmax is the wavenumber (cm-1) of the maximum absorption band of the investigated compounds in pure solvents, vo is the regression intercept corresponds to the gaseous of the spectrally active compounds, π^* is a measure of the solvent dipolarity / ploarizability, β is the scale of the solvent hydrogen-bond acceptor (HBA) basicities, α is the scale of the solvent hydrogen-bond donor (HBD) acidities and (vo, a, b, s) are solvents independent constants, their magnitudes and sign provide measures of the influence of the corresponding solute-solvent interactions on the wavenumber of the maximum of the electronic absorption band, this which have been determined by multiple regression analysis, using SPSS statistics program. The solvent parameters (Yazdanbakhsh, 2009)(Raposo, 2008)(Divijak, 2009) and vmax values for alloxan, carmine, naphthol yellow S, hematoxylin and cyanine ligands are given in Tables (6,7). The results of the multiple regressions are presented in Table (8). Fig. (1) and Table (8) shows the percentage contribution to the solvatochromic effects (π^*, β, α). The quality of the multilinear regressions analysis, where the correlation between the predicted absorption maxima (vcal calculated) versus (vexp experimental) as shown in Fig. (2). This gives good results due to its accounts both universal interactions and specific interaction. Universal interactions are expressed by F (n) and F (D, n).

Table 6: ν_{max} of electronic absorption spectra (cm^{-1}) in different solvents.

Solvent/ Compound	ν_{max} x 10^{-3}(cm^{-1})				
	Alloxan	Carmine	Naphthol yellow S	Hematoxylin	Cyanine
Butanol	36496	35335	29325	34364	16722
Amyl alcohol	34602	34843	29154	34364	16722
Isopropyl alcohol	32258	-----	29325	------	16233
DMF	37313	34364	29411	34013	16556
Ethanol	40322	35842	29411	34364	16556
Ethyl acetate	39370	38759	29673	34364	16835
H$_2$O	43478	35587	36363	35211	16025

Table 7: Solvatochomic parameters.

Solvent	π^*	α	β
Butanol	0.47	0.79	0.88
Isopropyl alcohol	0.48	0.76	0.95
DMF	0.87	0.0	0.69
Ethanol	0.54	0.83	0.77
Ethyl acetate	0.54	0.0	0.45
H$_2$O	1.09	1.17	0.47

Table 8: Solvent independent correlation coefficients a,b,s based on Kamlet-Taft parameters and Percentage contribution of the solvatochromic parameter.

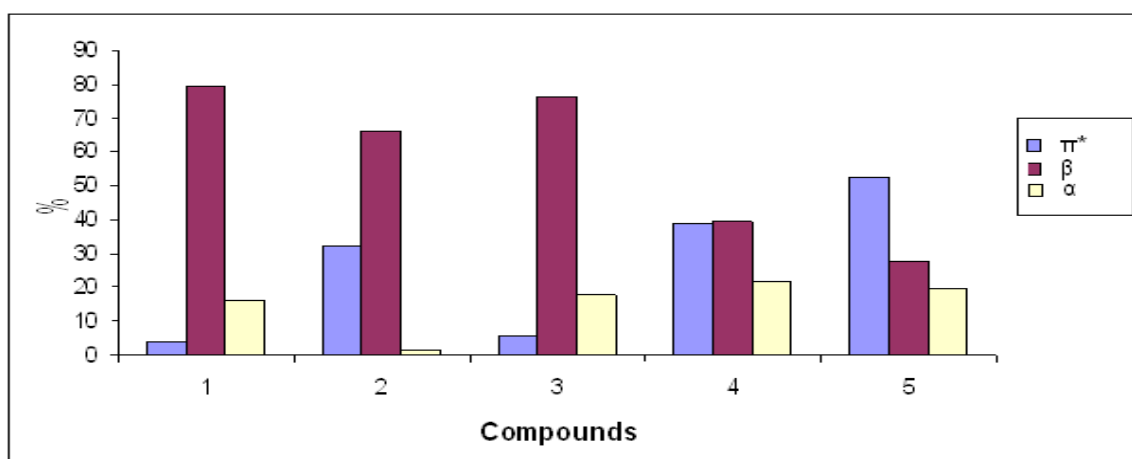| Compound	s	a	b	intercept	MCC	p_{π^*} (%)	p_β (%)	p_α (%)
Alloxan	794.234	3267.058	-15875.214	46867.107	0.803	3.9	79.62	16.36
Carmine	-6061.174	256.156	-12452.349	47939.921	0.860	32.29	66.34	1.36
Naphthlol yellow S	-1220.986	3897.625	-16667.0	48367.647	0.493	5.60	76.50	17.89
Haematoxylin	-7255.123	4033.303	7330.046	35142.779	0.958	38.96	39.36	21.66
Cyanine	-832.588	-311.074	-436.216	17532.037	0.748	52.69	27.61	19.68

Fig.1: Percentage contribution of the solvatochromic effects.
1- Alloxan   2- Carmine   3- Hematoxylin   4- Naphthol yellow S   5- Cyanine
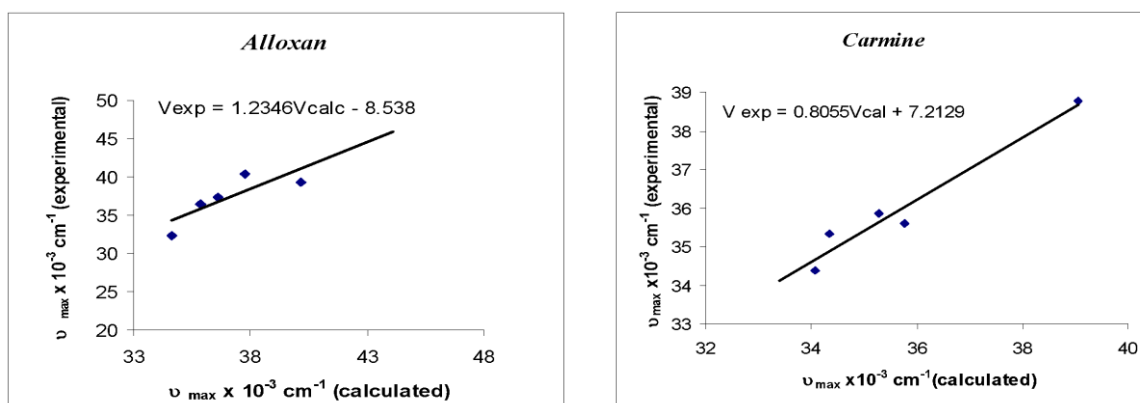
Fig.2: Plot of ν_{max} experimental versus ν_{max} calculated

4. CONCLUSIONS

A. The electronic absorption spectra of the ligands in presence of different solvents of different polarities, leading to change the position and the intensity.

B. The absorption spectra of the ligands in different solvents give exhibits bands in different ranges due to the π-π* transitions of conjugated multiple bands, as well as the band at 310 nm which can be assigned to the n-π* transition of the ketone groups. These bands point to the presence of lactam forms of the molecule in solution.

C. The results of calculations based on regression analysis of the electronic transition peaks of the investigated compounds, the multiple correlation coefficient (MCC) value is considered a measure of the goodness of the fit. The high value of MCC (~1) is of a good correlation to the spectral shifts. Alternatively, the small value (~ zero) of the probability of variation parameter (P) means the correlation is good. The spectral shifts of the electronic absorption spectra of investigated compound.

D. The dielectric constant D, [f (D) − f (n²)] is a measure of the interactions between the permanent dipoles. The solvatochromic shifts are often used to assign the transition as π- π*, n- π*or charge transfer.

E. The quality of the multilinear regressions analysis, where the correlation between the predicted absorption maxima (v_{cal} calculated) versus (v_{exp} experimental). This gives good results due to its accounts both universal interactions and specific interaction. Universal interactions are expressed by F (n) and F (D, n).

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