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# Spectral regression and correlation coefficients of some benzaldimines and salicylaldimines in different solvents

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### Abstract

Sixteen Schiff bases obtained from the condensation of benzaldehyde or salicylaldehyde with various amines (aniline, 4-carboxyaniline, phenylhydrazine, 2,4-dinitrophenylhydrazine, ethylenediamine, hydrazine, *o*-phenylenediamine and 2,6-pyridinediamine) are studied with UV–vis spectroscopy to observe the effect of solvents, substituents and other structural factors on the spectra. The bands involving different electronic transitions are interpreted. Computerized analysis and multiple regression techniques were applied to calculate the regression and correlation coefficients based on the equation that relates peak position  $\lambda_{max}$  to the solvent parameters that depend on the H-bonding ability, refractive index and dielectric constant of solvents.

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## 1. Introduction

The research on Schiff base compounds is growing because of their biological importance [1–3]. Recently, Co(III) complexes with Schiff bases were reported as a new anticancer agents with radio/thermosensitizing activities [4]. It was also found that Co–salen complexes bound to DNA in an intercalative model supported by fluorescence spectral studies (salen is bis(salicylidene)ethylenediamine) [5].

The study of solvent effects on the UV absorption spectra of Schiff bases has received great deal of attention. The benzaldimines studied are: substituted N-(R-benzylidene) benzidine and N-(R-furfurylidene)benzidine [6], N-benzylidene and N-naphthylbenzylidene-2-aminopyrimidine [7] bis(X-benzylidene-o-phenylenediamine [8]. Salicylaldimines show important photochromism where light absorption causes interconversion between enol-imine and keto-amine tautomers through intramolecular hydrogen transfer. Several spectroscopic studies on the photochromisms of salicylaldimines of different structures were undertaken: N,N'-bis(salicylidene)-1,2-diaminoethane and N,N'bis(salicylidene)-1,6-hexanediamine [9], N-salicylidene-1hexadecylamine [10], N,N'-bis(salicylidene)-1,2-cyclohexanediamine [11] and N-salicylidene- $\alpha$ -methylbenzylamine [12]. The tautomeric equilibrium of salicylidene Schiff bases is the subject of considerable interest from both theoretical and practical point of view [13–15]. The position of proton transfer equilibrium in solution is affected by interactions with the solvent molecules. The tendency of interconversion to ketoamine has been observed in polar solvents for N-(R-salicylidene)-benzylamine [16], N-(R-salicylidene)-methylamines [17,18] and N,N'bis(salicylidene)-2,6-pyridinediamine [19].

Although UV–vis spectral behavior of Schiff bases have been extensively investigated in recent years, only spare information is available about the effect of different solvent parameters on the position of observed absorption peak [17]. In a continuation of our previous studies of computerized correlation data for the solvent effects on the electronic spectra of organic compounds (barbiturate and azo compounds) [20–25], the present work was undertaken. This paper deals with solvent and structural effects on the UV–vis absorption spectra of 16 Schiff bases derived from benzaldehydes or

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Numbers and n	ames of Schill bases		
IA	N-Benzylideneaniline	IB	N-Salicylideneaniline
IIA	N-(4-Carboxyphenyl)benzylideneimine	IIB	N-(4-Carboxyphenyl)salicylideneimine
IIIA	Benzaldehydephenylhydrazone	IIIB	Salicylaldehydephenylhydrazone
IVA	2,4-Dinitrobenzaldehydephenylhydrazone	IVB	2,4-Dinitrosalicylaldehydephenylhydrazone
VA	N, N'-bis(Benzylidene)ethylenediamine	VB	N, N'-bis(Salicylidene)ethylenediamine
VIA	N, N'-bis(Benzylidene)hydrazine	VIB	N,N'-bis(Salicylidene)hydrazine
VIIA	N,N'-bis(Benzylidene)-o-phenylenediamine	VIIB	N,N'-bis(Salicylidene)-o-phenylenediamine
VIIIA	N,N'-bis(Benzylidene)-2,6-pyridinediamine	VIIIB	N,N'-bis(Salicylidene)-2,6-pyridinediamine

Table 1Numbers and names of Schiff bases

salicylaldehydes and various amines (Table 1; Figs. 1–4). Correlation data was computed in order to evaluate the solvent–solute interaction effects on the electronic absorption spectra of Schiff bases. Several absorption peaks in a single

compound was studied independently by regression analysis and high positive correlation coefficients were obtained. The effect of molecular structures of the compounds on their spectral behavior is also discussed.



Fig. 1. Structure of Schiff bases IA, IB, IIA and IIB.





Fig. 2. Structure of Schiff bases IIIA, IIIB, IVA and IVB.



Fig. 3. Structure of Schiff bases VA, VB, VIA and VIB.



Fig. 4. Structure of Schiff bases VIIA, VIIB, VIIIA and VIIIB.

## 2. Experimental

All chemicals used in the present work were Merck products. The organic solvents used were spectroscopic grade products (>99.8%). The mono-benzylidenimines and - salicylidenimines Schiff bases were synthesized in ethanol by the condensation of equimolar amounts of benzalde-

hyde or salicylaldehyde with the amine, (aniline) giving IA [26] or IB [27]; (4-carboxyaniline), IIA or IIB; (phenylhydrazine), IIIA or IIIB [28]; (2,4-dinitrophenylhydrazine), IVA or IVB (Table 1; Figs. 1 and 2). The bis-benzylidenimines and -salicylidenimines Schiff bases were also synthesized in ethanol by the condensation of 2–1 molar amounts of the benzaldehyde or salicylaldehyde with the amine,

(ethylenediamine) giving VA or VB [29,30]; (hydrazine) VIA or VIB; (*o*-phenylenediamine) VIIA or VIIB [28,31]; (2,6-pyridinediamine) VIIIA or VIIIB [19,28,32] (Table 1; Figs. 3 and 4). The crude products were purified by recrystallization from ethanol. The structures (Figs. 1–4) and purity of the compounds were checked by mp, elemental analysis, IR and NMR spectra [33].

The electronic spectra of the solution (concentration  $1 \times 10^{-5}$  to  $1 \times 10^{-6}$  mol/L) were investigated in various organic solvents of different polarities: carbon tetrachloride (CCl<sub>4</sub>), diethylether, dioxane, chloroform (CHCl<sub>3</sub>), acetone, *N*,*N'*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), acetonitrile, ethanol (EtOH) and methanol (MeOH). The electronic spectra were recorded on a Ciba Corning 2800 Spectrophotometer using 1 cm quartz cell at 25 °C. The electronic absorption spectra were recorded immediately after preparing the solutions in order to obtain the spectra of mainly the enolimine tautomer and avoiding interference from the second ketoamine tautomer in the case of salicylaldimines.

#### 3. Results and discussion

## 3.1. Method of calculations and results

The absorption maximum  $(\lambda_{max})$  of Schiff bases molecules is shifted due to solvent effects (Tables 2–4). The absorption spectra of Shiff bases in a single solvent are shown in Figs. 5–8. While Fig. 9 shows the influence of different solvents on the UV–vis absorption spectra of compound IVB and VB.

An empirical expression (1) have been developed for the evaluation of solvent effects [20,23–25]:

$$Y = a_0 + a_1 X_1 + a_2 X_2 + a_3 X_3 + \ldots + a_n X_n \tag{1}$$

The observed peak location  $\lambda_{\text{max}}(Y)$  is considered as the dependent variable while the independent variables have been selected to be the solvent interaction mechanisms *E*, *K*, *M*, *N* (Tables 2–4). The constant  $a_1$ ,  $a_2$  and  $a_3$  are the different regression coefficients and the constant  $a_0$  is the regression intercept.

Table 2

Solvent dielectric constant, refractive index and parameters used in spectral correlation equations

Solvent	D	n	E	K	М	N
Carbon tetrachloride	2	1.426	32.5	0.2	0.22	0.01
Diethylether	4.2	1.353	34.6	0.34	0.18	0.3
Dioxane	2.2	1.422	36	0.22	0.2	0.03
Chloroform	4.7	1.443	39.1	0.36	0.21	0.29
Acetone	20.7	1.359	42.2	0.46	0.18	0.65
Dimethyl formamide	36.7	1.427	43.8	0.48	0.2	0.67
Dimethyl sufoxide	48.9	1.478	45	0.49	0.22	0.66
Acetonitrile	37.5	1.344	46	0.48	0.18	0.71
Ethanol	24.3	1.361	51.9	0.47	0.18	0.67
Methanol	32.6	1.329	55.5	0.48	0.17	0.71

Table 3

 $\lambda_{max}$  (nm) values for the Schiff bases IA–IVB compounds in different solvents

Solvents	IA	IB	IIA	IIB	IIIA	IIIB	IVA	IVB
Carbontetrachloride	315 263	343 323	271	347 325 307 277	345	350 304	367	373 297
Diethylether	328	340 316 300 268		344	344 321 275	350	380	389
Dioxane	320 263	339 320	267	344 322 306 277	345 303 246	348 302 245	376 296	381
Chloroform	315 264	340 319 268	272	345 321 307 278	341 303 245	345 302 246	379 297	382 297
Acetone	327	339		341	345	346	380	387
Dimethylformamide	308 268	340 318	272	345 322 306 278	349 305 257	353 303	390 298	400
Dimethylsulfoxide	312 268	340 320 271	274	344 324 306 280	353 306 260	356 304 260	395 299	408
Acetonitrile	319 260	336 316	268	342 320 305 275	341		380 296	383 294
Ethanol	312 263	338 316 301 268	274	344 321 305 277	346 303 242	348 302 245	378 295	388 295
Methanol	310 261	336 315 300 268	275	341 320 304 275	344 303 240	346 300 243	376 293	387 294

The parameter *E* is an empirical solvent polarity parameter sensitive to both solvent–solute hydrogen bonding and dipolar interactions,  $E = 2.859 \times 10^{-3} \nu$ , where  $\nu$  is the wavenumber of the absorption maximum in the given solvent.

*K* depends on the solvent dielectric constant *D* and is a measure of the polarity of the solvent:

$$K = \left[ \left( \frac{D-1}{2D+1} \right) \right]$$

*M* depends on the solvent refractive index *n* and is a measure of solute permanent dipole–solvent induced dipole interactions:

$$M = \left[ \left( \frac{n^2 - 1}{2n^2 + 1} \right) \right]$$

Table 4  $\lambda_{max}$  (nm) values for the Schiff bases VA–VIIIB compounds in different solvents

Solvents	VA	VB	VIA	VIB	VIIA	VIIB	VIIIA	VIIIE
Carbon tetrachloride	256	323	302	363 295	298	340 273	320	373 278
Diethylether	245	331		355	291	335	241	
Dioxane	245	320 257	302	358 293	299	335 271	320 247	372 278
Chloroform	249	318 258	304	360 295	298	337 270	319 247	374 279
Acetone		328		355		336		373
Dimethyl- formamide	261	316	303	356 296	295	335 273	322	379 279
Dimethyl- sulfoxide	262	316 264	305	358 296	298	334 272	325	380 278
Acetonitrile	244	315 255	298	355	301	331 268	319 244	374 280
Ethanol	245	318 256	300	356 294	291	332 269	321 248	376 277
Methanol	249	316 255	298	355 293	290	330 270	320 248	373 276



Fig. 5. Absorption spectra of Schiff bases IA, IB and IIA, IIB in ethanol.



Fig. 6. Absorption spectra of Schiff bases IIIA, IIIB and IVA, IVB in ethanol.

*N* is a measure of permanent dipole–permanent dipole interactions:

$$N = \left[ \left( \frac{D-1}{D+2} \right) \right] - \left[ \left( \frac{n^2-1}{n^2+2} \right) \right]$$

A multiple regression analysis has been performed. In each case, fits are obtained as a function of one, two or three parameters. The results are listed in Tables 5 and 6.

In a complementary study, the coefficients  $K_1$ ,  $K_2$ ,  $\nu$  vapor (cm<sup>-1</sup>) were calculated using multiple regression technique based on Equation (2) [22,25]:

$$\nu$$
 (solution) =  $\nu$  (vapor)+ $K_1\left(\frac{2D-2}{2D+2}\right) + K_2\left(\frac{2n^2-2}{2n^2+1}\right)$  (2)

v (vapor) is the wavenumber of the maximum in absence of solvents. *D* is the dielectric constant and *n* is the refractive index of the solvents. As an indication of the goodness of the fit, the multiple correlation coefficient and the square of correlation were calculated for each  $r^2$  (v,  $n^2$ ) and  $r^2$  (v, *D*). The results are summarized in Table 7.

## 3.2. Discussion

The present work study the roles played by different solvents on the spectral properties of benzylaldimines and



Fig. 7. Absorption spectra of Schiff bases VA, VB and VIA, VIB in ace-tonitrile.

salicylaldimines and compare their spectra according to difference in structures.

#### 3.2.1. Electronic absorption spectral peaks

The absorption spectra of the investigated Schiff bases in different solvents are composed of several bands in the 200–500 nm region (Figs. 5–9). It is evident that the molecular structure of the compound and the polarity of the medium both are of great importance to affect the spectral behavior of Schiff bases. The longest  $\lambda_{max}$  is  $\lambda_1$  followed by  $\lambda_2$ ,  $\lambda_3$ and  $\lambda_4$  (Tables 3 and 4). Those bands indicate that different electronic transitions are involved. The first one or two bands in the wavelength range 230-280 nm (Bands A and B) could be assigned to the excitation of the  $\pi$ -electrons of the aromatic system. These bands are sensitive to substitution at the aromatic rings and their positions are little influenced by changing the solvent polarity confirming the local  $\pi - \pi^*$  nature of the electronic transition [34]. The third band observed within the wavelength range 270-310 nm (Band C) can be due to transition between the  $\pi$ -orbital localized on the central bond of azomethine group (>CH=N-) [6,35]. The fourth band located within the wavelength 320-400 nm (Band D) can be the effect of an intramolecular charge transfer (CT) transistion within the whole Schiff base molecule



Fig. 8. Absorption spectra of Schiff bases VIIA, VIIB and VIIIA, VIIIB in dioxane.

[6,36]. This band is more important in salicylaldimines compounds due to the presence of strong intramolecular hydrogen bond between the hydroxyl group and the azomethine nitrogen [37] that causes planarity of the molecules and facilitates the charge transfer to take place within the whole molecule. These charge transfer bands are more sensitive to solvent changes than bands resulting from local transition [6].

The effect of solvents on the shift of  $\lambda_{max}$  for the enolimine tautomer of salicylaldimines has been studied with minimum interference from the other ketoamine tautomer by running the absorption spectra of freshly prepared solutions in a minimum time. This decreases the proton transfer of hydroxyl group to the imine nitrogen of enolimine tautomer in H-bonding solvent and thus reduces subsequent formation of ketoamine tautomer [9,17,38]. Hence, no intense new peaks appear in the spectrum of salicylaldimines in H-bonding solvent compared to non-polar solvents (Tables 3 and 4; Fig. 9).

The previous studies absorption spectrum of *N*-benzylideneaniline IA in 95% ethanol contained three peaks (not well resolved) and interpreted to be at 260 and 300 nm ( $\pi$ – $\pi^*$ ) and 360 nm (n– $\pi^*$ ), relatively very small in absorbency [26]. Fig. 5 shows the absorption spectra of IA in absolute ethanol. The peaks are at 263 nm (Band B) due to  $\pi$ – $\pi^*$  localized on the phenyl rings, 312 nm (Band C) due



Fig. 9. Absorption spectra of Schiff bases IVB and VB in different solvents.

to  $\pi - \pi^*$  localized on the azomethine (>CH=N-) group and the expected third peak at 360  $(n-\pi^*)$  is submerged under the more intense C band [26] (Table 3; Fig. 5). The peak at  $\lambda_2$  (Band B) of IA shifts to longer wavelengths 268 nm in highly polar solvent DMF (D = 36.7) and DMSO (D = 48.9) compared to 263 nm in non-polar solvent  $CCl_4$  (D=2.0) and dioxane (D=2.2) (Tables 2 and 3). This confirms that the absorption peak at  $\lambda_2$  is due to  $\pi - \pi^*$  electronic transition. The shift to longer wavelength on going to more polar solvents is due to more stabilization of the excited state  $\pi^*$  than that of the ground state  $\pi$ . The spectrum of the related compound IIA in absolute ethanol (Fig. 5) indicates the presence of one peak at  $\lambda_1 = 271$  nm (Band B) (Table 3) and two unresolved peaks at  $\lambda = 290$  and 325 nm. The solvent effect has been studied for only  $\lambda_1$  (Table 3). There has been a small red shift of  $\lambda_1$  to longer wavelength in DMSO, ethanol and methanol also confirming  $\pi - \pi^*$  transition. The presence of -COOH auxochrome in the structure of IIA causes red shift of Band B at  $\sim$ 270 nm by 7–10 nm with respect to those for IA at  $\sim$ 263 nm. Fig. 5 indicates that four peaks appear in the spectrum of salicylaldimines IB and IIB with intensification of longest wavelength peaks compared to the corresponding peaks of benzaldimines IA and IIA. Both Band A ( $\lambda_4$ ) and Band B ( $\lambda_3$ ) of compounds IB and IIB are little affected by change in solvent polarity and involve  $\pi - \pi^*$  transition of aromatic rings [6], while Band C ( $\lambda_2$ ) and Band D ( $\lambda_1$ ) slightly shift to shorter wavelength with increasing H-bonding ability of solvent (solvent parameter E) (Tables 2 and 3). The presence of -COOH in IIB caused a red shift of all four peaks by about 2–5 nm with respect to those of IB (Table 3). The electronic-withdrawing nature of –COOH group seems to stabilize the excited state of the involved electronic transitions.

The absorption spectra of benzaldehydephenylhydrazone IIIA and salicylaldehydephenylhydrazone IIIB shows three peaks corresponding to Bands B–D at  $\lambda \sim 245$ , 303 and 347 nm, respectively, in ethanol (Fig. 6). Band D ( $\lambda_1$ ) of compound IIIB shows a bathochromic shift of 2–6 nm with respect to IIIA in different solvents (Fig. 6; Table 3). Also, the peak at  $\lambda_1$  (Band D) of 2,4-dinitrosalicyl-aldehydephenylhydrazone IVB is red shifted of 3–13 nm with respect to 2,4-dinitrobenzaldehydephenylhydrazone IVA in various solvents (Fig. 6; Table 3). The H-bond between hydroxyl O–H and imine (>CH=N–) groups forces planarity of the whole molecule in the case of IIIB and IVB. This action stabilizes  $\pi^*$  orbital and decreases its energy, thus facilitating intramolecular charge transfer and causing red shift [17].

It is also observed that the charge transfer of IVA and IVB at  $\lambda_1$  is red shifted in all solvents by an average  $\Delta\lambda_1 = 35$ and 39 nm relative to the CT band of the other compounds IIIA and IIIB, respectively (Fig. 6; Table 3). The red shift is attributed to the presence of electron-withdrawing  $-NO_2$ substituents in IVA and IVB supporting the CT nature of the band at  $\lambda_1$  [36]. The high electron-withdrawing power of the  $-NO_2$  group makes it behave as a good CT acceptor center with the n-orbital of azomethine group being the main participant of the electron donor group.

New peak at the longer wavelength region appears in the electronic absorption spectra of N,N'bis(salicylidene)ethylenediamine (salen) VB and N,N'-bis-(salicylidene)hyrazine VIB compared to N,N'-bis(benzylidene)ethylenediamine VA and N,N'-bis(benzylidene)hydrazine VIA, respectively (Figs. 3 and 7; Table 4). The peaks observed in different solvents are: Band A ( $\lambda_2$  at 225 nm) and Band B ( $\lambda_1$  at 244–262 nm) for compound VA compared to Band A ( $\lambda_3$  at 230 nm), B ( $\lambda_2 = 255-264$  nm) and C ( $\lambda_1 = 315 - 328$  nm) for compound VB. Band A ( $\lambda_2$  at 225 nm) and Band C ( $\lambda_1 = 298-305$  nm) for VIA compared to Band A ( $\lambda_4$  at 230 nm), B ( $\lambda_3$  at 240 nm), C ( $\lambda_2 = 293-296$  nm) and D ( $\lambda_1 = 355-363$  nm) for VIB (Table 4). The peaks of salen VB at  $\sim$ 257 and 318 nm observed in different solvents are due to the enolimine tautomer, the other peaks at  $\sim$ 290 nm and 370 nm due to the ketoamine tautomer are negligible (Figs. 7 and 9; Table 4). The ketoamine tautomer become important when salen VB was irradiated at  $\lambda_{ex}$  276 nm in chloroform where spectral changes resulted in intensification of the peaks at 291 and 369 nm and reduction of 259 and 320 nm [9].

Fig. 4 shows the structures of N,N'-bis(benzylidene)o-phenylenediamine VIIA, N,N'-bis(salicylidene)-ophenylenediamine (salophen) VIIB, N,N'-bis(benzylidene)-2,6-pyridinediamine VIIIA and N,N'-bis(salicylidene)-2,6pyridinediamine VIIIB. The structure of VIIB has been confirmed by mass spectra and <sup>1</sup>HNMR [31]. The crystal structure of VIIIB was studied by X-ray diffraction revealing Table 5

Regression analysis values of multiple correlation coefficients MCC for solvent parameters at different  $\lambda_{max}$  of Schiff bases

Parameters	IA	IB	IIA	IIB	IIIA	IIIB	IVA	IVB	VA	VB	VIA	VIB	VIIA	VIIB	VIIIA	VIIIB
Ε	0.521 0.179	0.758 0.672	0.708	0.609 0.516 0.889 0.109	0.204 0.049 0.309	0.024 0.651 0.162	0.264	0.366	0.093	0.674 0.306	0.605	0.546 0.349	0.617	0.818 0.613	0.159 0.57	0.2 0.766
Κ	0.297 0.169	0.666 0.667	0.462	0.601 0.454 0.622 0.064	0.413 0.519 0.068	0.245 0.287 0.334	0.643	0.66	0.02	0.565 0.049	0.322	0.682 0.159	0.631	0.706 0.365	0.383 0.145	0.019 0.514
М	0.295 0.629	0.758 0.926	0.422	0.775 0.858 0.904 0.809	0.388 0.569 0.787	0.545 0.927 0.755	0.159	0.091	0.749	0.04 0.873	0.908	0.817 0.791	0.681	0.722 0.853	0.397 0.175	0.49 0.578
Ν	0.289 0.092	0.698 0.684	0.478	0.64 0.457 0.698 0.013	0.419 0.468 0.018	0.226 0.325 0.249	0.572	0.604	0.012	0.577 0.062	0.428	0.709 0.086	0.612	0.739 0.445	0.349 0.154	0.051 0.504
EK	0.564 0.625	0.763 0.699	0.752	0.636 0.518 0.921 0.299	0.465 0.866 0.552	0.459 0.824 0.86	0.78	0.721	0.214	0.647 0.582	0.7	0.682 0.933	0.652	0.821 0.676	0.492 0.845	0.317 0.805
EM	0.858 0.803	0.865 0.944	0.738	0.808 0.858 0.911	0.613 0.789 0.859	0.761 0.939 0.766	0.444	0.501	0.853	0.845 0.972 0.95	0.923	0.827 0.921	0.737	0.884 0.857	0.848 0.902	0.736 0.903
EN	0.588 0.543	0.767 0.702	0.766	0.654 0.517 0.197	0.5 0.918 0.499	0.462 0.854 0.839	0.697	0.658	0.18	0.674 0.493 0.904	0.64	0.715 0.933	0.636	0.824 0.641	0.463 0.908	0.294 0.858
KM	0.558 0.833	0.844 0.979	0.514	0.828 0.865 0.927 0.917	0.732 0.864 0.839	0.79 0.936 0.924	0.808	0.783	0.851	0.638 0.937	0.918	0.893 0.969	0.784	0.842 0.855	0.772 0.393	0.555 0.635
KN	0.299 0.572	0.72 0.688	0.485	0.683 0.458 0.855 0.548	0.419 0.592 0.541	0.27 0.416 0.598	0.791	0.747	0.225	0.579 0.678	0.845	0.724 0.545	0.638	0.761 0.705	0.442 0.161	0.231 0.515
MN	0.582 0.828	0.844 0.969	0.513	0.829 0.86 0.932 0.907	0.772 0.896 0.848	0.831 0.942 0.945	0.767	0.754	0.865	0.674 0.943	0.913	0.889 0.971	0.758	0.844 0.854	0.797 0.454	0.596 0.617
EKM	0.884 0.836	0.869 0.986	0.849	0.828 0.869 0.954 0.925	0.732 0.877 0.859	0.802 0.939 0.993	0.858	0.798	0.862	0.847 0.974	0.923	0.922 0.977	0.785	0.887 0.857	0.85 0.998	0.776 0.827
EKN	0.626 0.682	0.773 0.702	0.775	0.687 0.527 0.961 0.919	0.503 0.939 0.609	0.464 0.865 0.979	0.835	0.763	0.247	0.68 0.703	0.882	0.735 0.938	0.689	0.829 0.767	0.497 0.936	0.333 0.906
EMN	0.883 0.832	0.868 0.974	0.845	0.829 0.86 0.951 0.548	0.777 0.928 0.861	0.834 0.942 0.957	0.816	0.768	0.869	0.846 0.972	0.926	0.919 0.984	0.758	0.886 0.859	0.855 0.996	0.751 0.86
KMN	0.606 0.834	0.844 0.999	0.514	0.829 0.93 0.946 0.924	0.827 0.981 0.883	0.92 0.981 0.998	0.845	0.799	0.881	0.709 0.956	0.966	0.895 0.971	0.865	0.844 0.866	0.819 0.616	0.812 0.728

using three parameters equation F = K M or (K = M N)

	$a_0$	$a_1$	$a_2$	$a_3$
IA	415.36 (355.04)	-1.16 (82.6)	22.33 (-253.07)	-300.62 (-47.27)
	224.46 (229.25)	0.077 (20.94)	11.91 (138.66)	157.97 (-2.58)
IB	334.11 (329.58)	-0.104 (-5.67)	-2.68 (63.66)	55.16 (-0.788)
29	296.13 (303.75)	0.079 (-43.52)	-11.63 (126.52)	118.36 (14.76)
IIA	185.82 (281.51)	1.42 (13.01)	-39.78 (-71.21)	206.29 (0.686)
IIB	333.47 (332.63)	0.005 (0.346)	-5.2 (62.14)	64.56 (-2.39)
	306.37 (312.56)	0.0376 (-41.35)	-3.66 (92.59)	77.92 (16.31)
	304.2 (297.25)	-0.091 (12.13)	1.49 (32.84)	24.96 (-5.98)
	254.08 (255.09)	0.055 (20.13)	4.19 (83.83)	96.35 (-5.49)
IIIA	315.29 (326.34)	0.004 (-69.16)	18.99 (152.47)	115.78 (36.78)
	297.68 (293.42)	-0.111 (-54.83)	13.54 (101.98)	26.32 (25.4)
	111.66 (166.9)	0.607 (-230.6)	1.8 (632.2)	547.69 (102.58)
IIIB	297.89 (316.12)	0.156 (-110.1)	14.16 (256.78)	195.8 (55.36)
	283.29 (289.55)	0.058 (-25.84)	-0.814 (88.05)	83.71 (11.64)
IVA	335.03 (298.16)	-0.544 (193.19)	85.47 (159.16)	176.6 (-54.95)
IVB	325.76 (299.01)	-0.363 (183.35)	91.46 (191.6)	213.26 (-44.92)
VA	171.04 (189.86)	0.22 (-66.82)	12.89 (353.33)	328.68 (37.89)
VB	391.46 (348.33)	-0.84 (46.61)	10.79 (-165.74)	-204.51 (31.13)
	201.65 (222.8)	0.278 (-60.84)	0.094 (232.73)	223.2 (29.41)
VIA	266.59 (269.52)	0.094 (60.13)	-0.17 (96.8)	155.1 (-24.02)
VIB	337.09 (344.25)	0.145 (-20.06)	-16.04 (95.54)	103.25 (4.46)
	283.59 (277.08)	-0.094 (0.161)	10.46 (80.41)	54.54 (2.76)
VIIA	271.06 (290.49)	0.07 (-166.87)	-24.79 (229.42)	167.67 (60.05)
VIIB	331.92 (322.48)	-0.197 (-0.648)	-3.14 (74.05)	62.06 (-4.85)
	250.29 (252.3)	0.046 (19.6)	-0.75 (72.81)	94.95 (-7.87)
	-59.99 (189.55)	3.4 (-200.31)	-135 (483.32)	1061.18 (94.16)
VIIIA	281.59 (302.491)	0.276 (-26.75)	1.66 (107.11)	133.84 (16.51)
	204.94 (224.6)	0.56 (-99.53)	-22.25 (211.67)	134.31 (45.85)
VIIIB	206.75 (334.53)	1.7 (-501.87)	-47.32 (694.16)	580.41 (220.32)
	297.99 (275.08)	-0.38 (-51.69)	10.1 (74.6)	-33.55 (19.97)

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coplanarity of whole molecule because of intramolecular Hbond between hydroxyl and imino groups [19]. There is large shift to longer wavelength in  $\lambda_{max1(av)}$  (av: average in all solvents) in the spectra of salicylaldehyde derived Schiff bases relative to the corresponding benzaldehyde derived Schiff bases ( $\lambda_{1(av)} = 334$  nm for VIIB compared to  $\lambda_{1(av)} = 296$  nm for VIIA,  $\Delta \lambda = 38 \text{ nm}$ ) and  $(\lambda_{1(av)} = 377 \text{ nm}$  for VIIIB compared to  $\lambda_{1(av)} = 321$  nm for VIIIA  $\Delta \lambda = 56$  nm) (Fig. 8; Table 4). The expected peak  $(n-\pi^*)$  at  $\lambda_1 = 370$  nm of VIIB is submerged under the peak  $(\pi - \pi^*)$  at  $\lambda_{1(av)} = 335$  nm (Fig. 8) [31]. Replacement of the central phenyl ring of VIIA and VIIB with a pyridine ring causes a red shift of  $\lambda_{1(av)}$  by  $\Delta \lambda = 25$  nm for VIIIA with respect to VIIA and a red shift of  $\lambda_{1(av)}$  by  $\Delta \lambda = 43$  nm for VIIIB with respect to VIIB (Fig. 8; Table 4). There is a reduced tendency to tautomeric interconversion in the case of Schiff bases of aminopyridine VIIIB. The tautomeric constant  $K_t = [\text{ketoamine}]/[\text{enolimine}] = 0.02$ in methanol. The electron delocalization causes a decrease in imino nitrogen basicity, followed by a weakening of the

Table 6

Pagrassion analysis coefficients for Schiff bases at different )

intramolecular H bond OH…N=C and reduced tendency to tauomeric interconversion [19].

#### 3.2.2. Correlation studies

The electronic absorption spectra of the investigated Schiff bases show shift in  $\lambda_{max}$  in different solvents (Tables 3 and 4). Such behavior is depicted in Fig. 9, where  $\lambda_{max1}$  shifts to longer wavelengths in the order dioxane, ethanol and DMSO for compound IVB and ethanol, dioxane and CCl<sub>4</sub> for compound VB.

The value of  $\lambda_{max1}$  of the studied benzaldimine and salicylaldimine (except IA, IIA and VB) is slightly red shifted with changing the solvent physical parameters according to the following order: MeOH < EtOH < DMF < DMSO (Tables 3 and 4). This suggests that this band is the effect of an intramolecular charge transfer transition within the whole molecule, where azomethine group is the primary center contributing to CT. In ethanol and methanol, the electron charge transfer is difficult through the solute molecule because of for-

Table 7	
$K_1, K_2, \nu$ (vapor) and correlation analysis data for Schiff bases at different $\nu$	cm <sup>-1</sup>

	$\nu$ (vap) cm <sup>-1</sup>	$K_1$	<i>K</i> <sub>2</sub>	MCC	$r^2(v,D)$	$r^2(v,n)$
IA	27980.69	1456.64	6817.21	0.634	0.254	0.055
	42851.88	-771.11	-11101.2	0.923	0.025	0.636
IB	417091.7	43156.3	-1022	0.473	0.065	0.209
	32739.94	505.9	-4336.53	0.92	0.482	0.592
IIA	35501.86	-975.33	4831.78	0.516	0.211	0.144
IIB	29861.93	282.48	-2547.37	0.803	0.368	0.475
	32138.41	168.12	-3055.71	0.773	0.193	0.534
	33412.67	162.98	-2119.91	0.912	0.405	0.695
	38715.93	-282.64	-6155.78	0.961	0.003	0.825
IIIA	31274.9	-632.28	-4786.68	0.539	0.193	0.218
	34520.11	-453.72	-3039.06	0.913	0.284	0.357
	54473.83	-2492.23	-30735.3	0.918	0.062	0.642
IIIB	31014.57	-435.3	-5232.63	0.647	0.284	0.053
	34465.34	37.44	-3539.82	0.85	0.718	0.079
	51985.28	-2654.54	-24330.4	0.946	0.107	0.554
IVA	31373.77	-1785.51	-9419.21	0.875	0.414	0.133
IVB	31179.09	-2137.5	-9775.83	0.84	0.443	0.078
VA	49542.45	-1192.01	-22182.5	0.754	0	0.487
VB	28882.89	1278.76	3885.96	0.649	0.347	0.01
	44553.11	-935.75	-12800.5	0.962	0.001	0.763
VIA	36267.51	4.74	-7860.22	0.983	0.966	0.119
VIB	28780.04	438.18	-2838.86	0.831	0.474	0.432
	35771.93	-219.89	-4141.36	0.894	0.023	0.662
VIIA	35419.36	1311.47	-7030.74	0.705	0.366	0.263
VIIB	30704.31	596.66	-3231.99	0.82	0.499	0.377
	39130.02	85.72	-5781.98	0.87	0.749	0.145
VIIIA	33049.08	-461.68	-3881.66	0.796	0.152	0.515
	45852.33	-1450.19	-10985.2	0.526	0.023	0.048
VIIIB	27815.48	333.87	-3945.12	0.6	0.192	0.298
	36090.92	385.12	-1257.58	0.534	0.252	0.119

mation of intermolecular hydrogen bond between the hydrogen bond donor solvent and the solute molecule [37]. This results in blocking the n-electrons of the azoethine nitrogen atom and a small blue shift is observed compared to DMF and DMSO.

The peaks due to  $\pi - \pi^*$  transitions show bathochromic shift in going to more polar solvent due to the stabilization of the excited state more than that of the ground state. Red shift in  $\lambda_{max}$  values is observed in solvents in the following increasing order: dioxane < chloroform < DMF < DMSO for peaks at  $\lambda_2$  of IA, IVA, IIIB, VIB, VIIB and VB;  $\lambda_3$  of IB;  $\lambda_2$  and  $\lambda_4$  of IIB; and  $\lambda_2$  and  $\lambda_3$  of IIIA.

The spectral data are good evidence for the presence of solute–solvent interactions between the active solvent and Schiff bases. The absorption spectra are influenced by the physical properties of the solvent (dipole moment, dielectric constant and refractive index), the change in the polarity and dipole moment of the solute through excitation and the difference in solvation energy from one solvent to another. The solvent effects and the effect of specific interaction between solute and solvent molecules (hydrogen bonding) are major factors to explain the spectral behavior of compounds. The shift in  $\lambda_{max1}$  due to differences in solvents range from  $\Delta\lambda_1 = 6$  to 28 nm for benzaldimines and from  $\Delta\lambda_1 = 6$  to 35 nm for salicyladlimines, with 2,4-dinitrobenzaldehydephenylhydrazone IVA and 2,4dinitrosalicylaldehydephenylhydrazone IVB showing the maximum ranges, respectively.

The influence of empirical solvent polarity on the position of  $\lambda_{\text{max}}$  is evident by the high correlation coefficients MCC (greater than 0.5) computed with *E* parameter for absorption peaks of salicylaldimines:  $\lambda_1$  of VB and VIB;  $\lambda_2$  of IIIB and VIIIB;  $\lambda_1$  and  $\lambda_2$  of IB and VIIB;  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$ of IIB. Also, high correlations with *E* parameter are found for benzaldimines absorption peaks:  $\lambda_1$  of IA, IIA, VIA and VIIA and  $\lambda_2$  of VIIIA (Table 5). The high correlation values obtained using the parameter *K* indicates high influence of the dielectric constant on the position of absorption peak at  $\lambda_1$  of IVA, IVB, VB, VIB, VIIA and VIIB;  $\lambda_2$  of IIIA and VIIIB;  $\lambda_1$  and  $\lambda_2$  of IB; and  $\lambda_1$  and  $\lambda_3$  of IIB (Table 5). The solute permanent dipole–solvent induced dipole interactions (parameter *M* that depends on refractive index) plays a major role in the spectra of Schiff bases:  $\lambda_2$  of IA;  $\lambda_1$  and  $\lambda_2$  of IB;  $\lambda_1$ ,  $\lambda_2$ ,  $\lambda_3$  and  $\lambda_4$  of IIB;  $\lambda_2$  and  $\lambda_3$  of IIIA;  $\lambda_1$ ,  $\lambda_2$ and  $\lambda_3$  of IIIB;  $\lambda_1$  of VA;  $\lambda_2$  of VB;  $\lambda_1$  of VIA;  $\lambda_1$  of VIIA;  $\lambda_1$  and  $\lambda_2$  of VIIB and  $\lambda_2$  of VIIB. The permanent dipolepermanent dipole interactions (parameter *N*) has important effect on  $\lambda_1$  of IVA, IVB, VIB, VIIA and VIIB;  $\lambda_2$  of VIIIB;  $\lambda_1$  and  $\lambda_2$  of IB;  $\lambda_1$  and  $\lambda_3$  of IIB. Table 5 also indicates improvement of the fits when using three-parameters equation over two-parameters and one-parameter equations, since higher correlation coefficients are obtained.

Table 6 lists the coefficients for the regression analysis when using three-parameter equations E, K, M or K, M, N. The value of  $a_0$  is the intercept. The solvent effects due to E, Kand M or K, M and N parameters produce bathochromic shift for positive values of coefficients  $a_1$ ,  $a_2$  and  $a_3$ , respectively, and hypsochromic shift for negative values of the coefficients.

The values of  $K_1$ ,  $K_2$ ,  $\nu$  (vapor),  $r^2$  ( $\nu$ , D),  $r^2$  ( $\nu$ , n) and MCC for the Schiff bases are computed and listed in Table 7. The data indicates that both the dielectric constant and the refractive index of solvents affect the electronic absorption spectra of compounds but with varying degrees. The negative values for  $K_1$  and  $K_2$  indicate the occurrence of strong solute–solvent interaction and causes decrease in energy of electronic transition from LUMO to HOMO in comparison with the vapor phase. The correlation data between ( $\nu$ , D) is good for VIA at  $\lambda_1$  and IIIB and VIIB at  $\lambda_2$ . The correlation data between ( $\nu$ ,  $n^2$ ) is good for IA, VB and VIB at  $\lambda_2$ ; IIIA at  $\lambda_3$ ; IIB at  $\lambda_3$  and  $\lambda_4$ .

The multi-parameter Equations (1) and (2) gave high multiple correlation coefficients values. This indicates that the used empirical expressions are successful in the evaluation of solvent effects on the electronic absorption spectra of Schiff bases.

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