

Solvatochromism of Indolino Spirobenzoxazine and Its Azo-Substituted Derivative: Comparison of Solvent Polarity Scales of Kamlet-Taft and Catalan

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Keywords

Solvatochromism, Kamlet-Taft, Catalan, Polarity scales, Azo, Spirobenzoxazine

The solvatochromic behavior of the electronic absorption spectra of indolino spirobenzoxazine and its azo derivative were investigated in polar and non-polar solvents. A bathochromic shift of about 10 nm in the electronic spectra of both compounds was observed as the solvent polarity increases from benzene to ethanol. The presence of an azo group substituted at oxazine fragment of indolino spirobenzoxazine exhibited a bathochromic shift of about 50 nm in all the solvents studied. The results obtained from single parametric regression analysis using both Kamlet-Taft and Catalan solvent parameters indicate that Kamlet-Taft scale is most suitable in describing hydrogen bond donor acidity and hydrogen bond acceptor basicity interactions whereas Catalan scale is a better descriptor of dipolarity and polarizability interactions. This shows that no one solvent polarity scale is adequate to describe all the solute-solvent interactions of molecular electronic absorption.

Introduction

Solvatochromism is a phenomena describing the shifting of absorption peak(s) position of the lowest energy, longest wavelength in solvent of varying polarities. The shift can be hypsochromic (blue shift, negative solvatochromism) when the shift is to lower wavelengths, or bathochromic (red shift, positive solvatochromism) when the shift is to longer wavelengths. The electronic absorption of organic molecules are usually modified when the molecules are dissolved in different solvents. This modification may be displayed as changes in the intensity, frequency or the shape of the absorption spectra [1]. These changes are a result of physical intermolecular solute-solvent interaction forces (such as ion-dipole, dipole-dipole, dipole-induced dipole, hydrogen bonding, etc.), which tend to alter the energy difference between the ground state and excited state of the absorbing species. The solvent-induced modification can offer useful information on the local electric field which acts on the spectrally active molecule [2-3], and the change in spectral position can be used as a probe for various types of interactions between the solute and the solvent.

Empirical parameters of solvent polarity have been developed to interpret and substantiate the solute-solvent interaction using spectroscopic data. Among the existing ones, solvent polarity scales according to Kamlet-Taft [4] and Catalan [5] are popular. Both scales attempt to evaluate behavior of solute-solvent interaction by looking at the dependence on specific and non-specific interactions. Specific interactions include hydrogen bond donor ability (acidity) and hydrogen bond acceptor ability (basicity) whereas non-specific interactions include polarity and polarizability interactions. The solvent parameters representing these interactions in the two solvent polarity scales are given as follows: acidity – S_A (Catalan) and α (Kamlet-Taft); basicity – S_B (Catalan) and β (Kamlet-Taft); dipolarity/polarizability – S_{PP} (Catalan) and π^* (Kamlet-Taft).

Quantitative assessment of solvents effects on electronic spectra employing these solvent scales have been achieved using the linear solvation energy relationship (LSER). The Kamlet-Taft approach is given in Eq. 1 [4].

$$\bar{\nu} = \bar{\nu}_0 + s\pi^* + b\beta + a\alpha \quad (1)$$

where α is a measure of the solvent hydrogen-bond donor (HBD) acidity, β is a measure of the solvent hydrogen-bond acceptor

(HBA) basicity, π^* is an index of solvent dipolarity/polarizability which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect, $\bar{\nu}_0$ is the regression value of the solute property in the reference solvent, cyclohexane and $\bar{\nu}$ is the solute property of interest such as wavenumber (or wavelength) of maximum absorption in the UV/Visible spectrum. The coefficients s , b and a in Eq. (1) measure the relative susceptibilities of the solvent-dependent solute property (absorption frequency) to the indicated solvent parameters. The Catalan approach uses a similar equation but the π^* , β and α parameters are replaced by S_{PP} , S_B and S_A respectively. The coefficients are determined in a multi-parametric regression analysis and thus, the contribution of the respective property of the solvents, i.e. the acidity (α or S_A), basicity (β or S_B) or the dipolarity/polarizability (π^* or S_{PP}), to the indicated spectral property of the molecule. The correlation coefficients obtained from both Kamlet-Taft and Catalan are usually compared, and when they are in good agreement with each other, both approaches are considered suitable for describing solute-solvent interactions. It may be difficult to say which approach is better since one approach may give better results for a particular compound and worst for other compounds. Good correlation with Kamlet-Taft parameter β was reported for non-symmetric viologen dye [6] whereas Catalan approach was found most suitable for describing the solvatochromic shift of a borondipyrromethene dye [7-8].

The multi-parametric treatment using both solvent polarity scales incorporates all the parameters taken together. This may not give a better picture of the behavior of individual parameter since each parameter may be complemented by another. Although multi-parametric method with solvatochromic parameters have been reported [9-13], a single parametric treatment of each parameter is required to effectively compare each acidity, basicity or polarizability term for the Kamlet-Taft and Catalan solvent scales. This approach may offer more insight into the relevance of each solvent parameter with respect to solute-solvent interaction.

In order to investigate the two polarity scales by single parametric method, indolino spirobenzoxazine and its azo derivative were chosen. This is because the absorption bands of these spirooxazines strongly depend on the solvent used [14]. The solvatochromic behavior of electronic absorption spectra of some azo derivatives has been reported [15-16].

In this paper, the solvatochromic behavior of indolino spirobenzoxazine and its azo-derivative is investigated in different solvents including polar protic, polar aprotic and non-polar solvents. The spectroscopic properties of these compounds are correlated with solvent parameters of Kamlet-Taft and Catalan polarity scales. The two solvent scales are also compared.

Materials and Methods

General

All chemicals used were of analytical grade. The IR spectra were recorded on a Shimadzu FTIR-IR Prestige (200VCE) as KBr pellets. The C, H, N data were determined using a Perkin-Elmer Instrument (200B). The purity of the test compounds was determined by TLC. The appearance of a single spot confirmed the purity of compound. Electronic spectra were recorded on Unicam Helios Gamma UV-visible spectrophotometer. Single parametric regression analysis was performed using IBM SPSS Statistics version 21.

Synthesis of Indolino Spirobenzoxazine

Indolino spirobenzoxazine was synthesized according to the method reported earlier [17]. Resorcinol (0.2 mol) was dissolved in warm solution of 0.1 mol sodium hydroxide in 50 ml of water. The solution was cooled to 0°C. Sodium nitrite (0.2 mol) was added and the solution was stirred for one hour while maintaining the temperature at 0°C. 0.3 mol HCl was added and the product formed was filtered, washed with water and dried. The 4-nitrosoresorcinol obtained was purified by recrystallization from hot ethanol. The 4-nitrosoresorcinol (0.01 mol) was refluxed in 50 ml of 1,2-dichloroethane and to the hot solution, was added in drops over 15 minutes, a solution of 1,3,3-trimethyl-2-methylene indoline (0.01 mol). The mixture was refluxed for eight hours. The precipitated product was filtered by suction and washed with ethanol. The product was then dissolved in acetone and boiled with activated charcoal gently for five minutes. The solution was filtered while hot to remove the charcoal. The product was recrystallized from cyclohexane to obtain indolino spirobenzoxazine. Colour: light brown, Yield: 71%, IR (KBr cm^{-1}): 3798 (N-H, amine), 3397-3389 (C-H, benzene), 3370 (C-H, imine), 3320-3278 (C-H, methyl), 1855 (C-N), 1796-1777 (C-C, benzene), Analytical data: Cald. For $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2$: C 73.45, H 6.16, N 9.52; found C 73.23, H 5.81, N 9.27.

Synthesis of Azo-Substituted Indolino Spirobenzoxazine

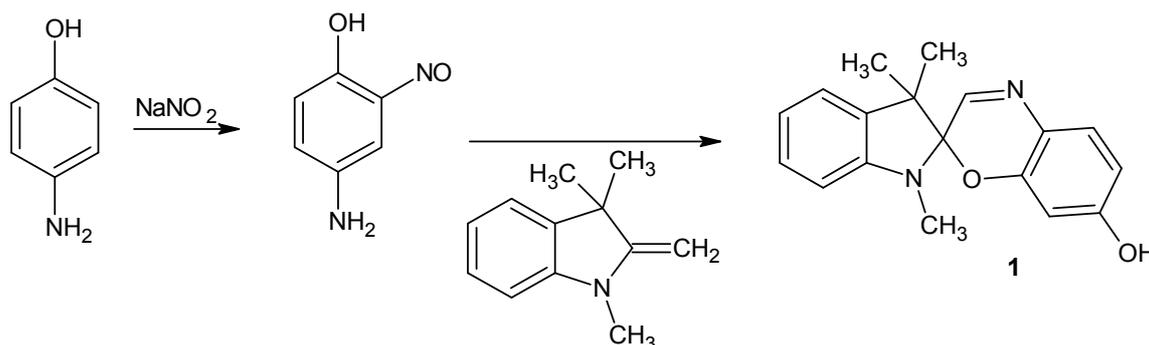
The azo compound was prepared according to the method reported earlier [18]. Concentrated HCl (2 ml) was diluted in 20 ml of water and to it was added 10 mmol of p-toluidine, stirred to dissolve and cooled to 0°C. To the cooled solution was added in drops, 8 ml of sodium nitrite, NaNO₂ (10.88 mmol) while maintaining the temperature between 0-5°C. The diazonium ion formed was consecutively coupled with 10 mmol of indolino spirobenzoxazine previously dissolved in 15 ml of 10 % sodium hydroxide, NaOH. The reaction mixture was stirred at 0°C for one hour. The product formed was filtered, washed with water and recrystallized twice from ethanol. Colour: orange, Yield: 76%, IR (KBr cm⁻¹): 3798 (N-H, amine), 3397-3389 (C-H, benzene), 3370 (C-H, imine), 3320-3278 (C-H, methyl), 1855 (C-N), 1796-1777 (C-C, benzene), 1451 (N=N). Analytical data: Cald. For C₂₅H₂₄N₄O₂: C 72.80, H 5.86, N 13.58; found C 72.51, H 5.52, N 13.34.

UV-Visible Absorption Spectrum

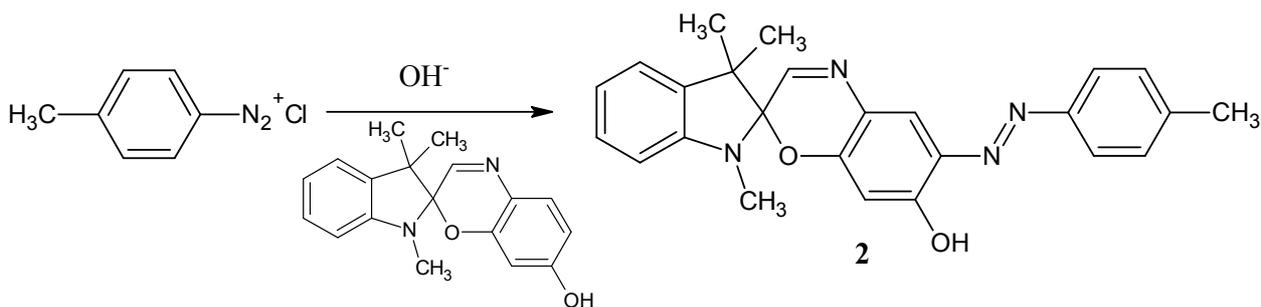
Indolino spirobenzoxazine (SPO) and azo-substituted indolino spirobenzoxazine (ASPO) were dissolved in appropriate solvent (ethanol, acetone and benzene) to give a concentration of 5.0x10⁻³ mol/L. The absorption spectra of 3 ml aliquot were taken between 200-700 nm wavelengths on the UV-visible spectrophotometer with the cell path length of 1 cm.

Results and Discussion

Indolino spirobenzoxazine (**1**) was synthesized as shown in scheme 1 whereas the azo-substituted indolino spirobenzoxazine (**2**) was prepared as shown in scheme 2.



Scheme 1. Preparation of indolino spirobenzoxazine.



Scheme 2. Preparation of azo-substituted indolino spirobenzoxazine

The Uv-visible absorption spectra of SPO and ASPO were recorded using polar protic solvent, ethanol, polar aprotic solvent, acetone and non-polar solvent, benzene. SPO and ASPO showed two absorption bands in all the solvents used. These bands are presented in Table 1. The two absorption bands observed at 300 nm and 380 – 440 nm represent characteristic π - π^* absorption bands from indoline fragment and oxazine fragment, respectively. The absorption maxima, λ_{max} due to absorption from indoline fragment remains unmodified at 300 nm in ASPO, since no substitution was made and it is also solvent insensitive. Bands that are insensitive to solvent interactions are due to local transitions [19]. The absorption band emanating from the oxazine fragment is solvent sensitive and also shows modification in shape, size and intensity due to the functionalization of the oxazine fragment by an azo group.

Effect of Solvent

The absorption maxima of both SPO and ASPO are affected by the type of solvent used. The absorption pattern of SPO shows a bathochromic shift of 10 nm in the longest wavelength as the solvent polarity increases from benzene to ethanol. Similar bathochromic shift of 10 nm was also exhibited by ASPO as shown in Fig 1. It is well known that absorption bands arising from π - π^* transitions are shifted bathochromically [20].

Table 1. Absorption maxima, observed E_T and E_T^N of indolino spirobenzoxazine and solvent parameters.

Solvent	Absorption maxima, λ_{max} (nm)				E_T^N	E_T^N (ISPO)		$E_T(30)$	E_T (ISPO) (kcal/mole)		Solvent parameter					
	SPO		ASPO			SPO	ASPO		SPO	ASPO	Kamlet-Taft			Catalan		
	α	β	π^*	S_A							S_B	S_{PP}				
Ethanol	300	390	300	440	0.65	1.32	1.06	51.90	73.31	64.98	0.86	0.75	0.54	0.40	0.66	0.85
Acetone	300	385	300	435	0.35	1.34	1.08	42.20	74.26	65.73	0.80	0.48	0.62	0	0.47	0.88
Benzene	300	380	300	430	0.11	1.37	1.10	32.30	75.24	66.4	0	0.10	0.55	0	0.12	0.67

ISPO: Indolino spirobenzoxazine; $E_T(30)$: transition energy of reference dye; E_T^N : normalized $E_T(30)$

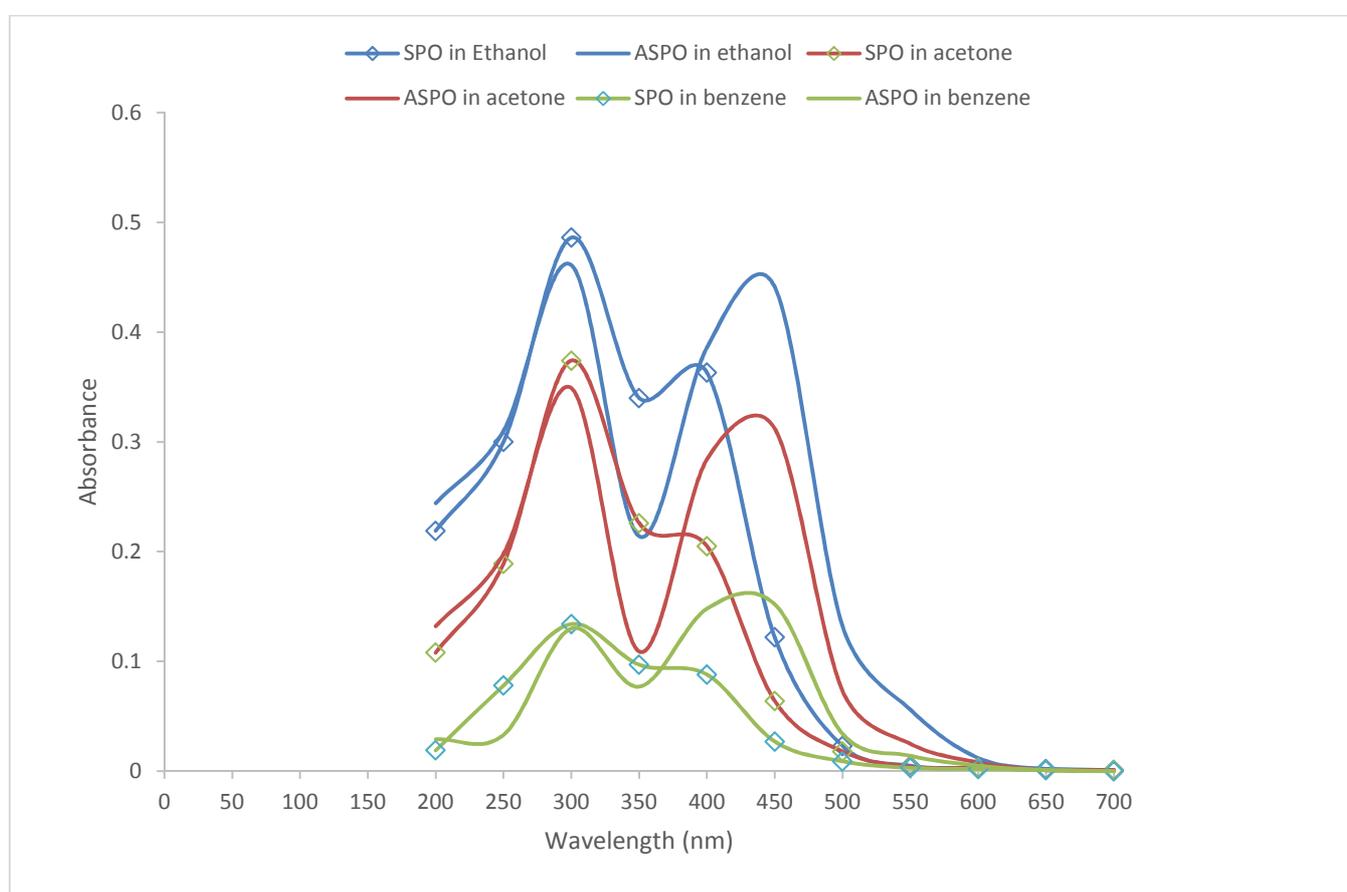


Figure 1. UV-Visible spectra of indolino spirobenzoxazine (SPO) and azo-substituted indolino spirobenzoxazine (ASPO) in polar and non-polar solvents.

Effect of Azo Group

Indolino spirobenzoxazine, being a heterocyclic system comprises of two parts. The two parts, indoline fragment and oxazine fragment are joined by a spiro carbon which separates the two fragments with no continuous conjugation [21]. The oxazine fragment of spirobenzoxazine was modified by substituting an azo group derived from p-toluidine. By comparing the electronic spectra of SPO and ASPO in polar and non-polar solvents, the evaluation of the effect of the substituted azo group on the electronic spectral properties could be determined. The presence of an azo group is observed to cause a shift in the absorption maxima towards longer wavelength (bathochromic) in both polar and non-polar solvents. A shift in absorption maxima of 50 nm was observed in ethanol, acetone and benzene as a result of electronic modification by azo group. The azo group also caused a

much intense absorption and an increase in size of the absorption peak as shown in Fig 1. A bathochromic shift from π - π^* transitions indicate better stabilization of the excited state of the molecule compared to the ground state [22].

Correlation of Solvent Parameters

In order to quantitatively assess the solvatochromic behavior of SPO and ASPO, solvent polarity parameters according to Kamlet-Taft (α , β and π^*) and Catalan (S_A , S_B and S_{PP}) were correlated with spectroscopic properties and compared, to investigate the solvent polarity scale that best describe the solute-solvent interaction of indolino spirobenzoxazine. To achieve this purpose, the absorption data of the longest wavelength were converted to corresponding transition energies, $E_T(\text{SPO})$ and $E_T(\text{ASPO})$ using Eq. (2) and the data are given in Table 1. Eq. (1) is an expression for $E_T(30)$ [23] whose values are based on the negatively solvatochromic pyridinium-N-phenolate betaine dye which exhibits one of the largest solvatochromic effects ever observed and is simply defined as the transition energy measured in kilocalories per mole (kcal/mol) [24].

$$E_T(30) = 28591.5/\lambda_{\max} \text{ (nm)} \quad (2)$$

where λ_{\max} is the longest wavelength of $\pi \rightarrow \pi^*$ absorption band of betaine dye.

Although $E_T(30)$ values have been used to interpret solute-solvent interaction [25], the most successful treatment involves the use of normalized $E_T(30)$ values represented as E_T^N [26]. E_T^N values are dimensionless and is determined according to Eq. (3).

$$E_T^N = [E_T(\text{solvent}) - 30.7] / 32.4 \quad (3)$$

The E_T values of SPO and ASPO were normalized to $E_T^N(\text{SPO})$ and $E_T^N(\text{ASPO})$ using Eq. (3), and the normalized values are also presented in Table 1. Successful correlation of E_T^N values with solvent parameters have been reported in literature [27-28],

A single parameter regression model for the evaluation of solute-solvent interaction was employed. The essence of using this single parameter (variable) regression model was to test each variable individually and exclude any possible multiple variable effect. These solvents parameters were subjected to regression analysis using LSER (Eq. 4)

$$E_T^N(\text{SPO}) = E_{T_0}^N + aX_1 \quad (4)$$

where $E_{T_0}^N$ is the regression constant. The regression coefficient, a , measures the sensitivity of the solvent parameter (X_1) toward the solute property, E_T^N . The solvent parameters (X_1) used for the regression analysis were obtained from literature [22] and these are given in Table 1. The results of the single parameter regression analysis is presented in Table 2.

Table 2. Regression fits to solvatochromic parameters with single parameter regression model.

Compound	Parameter	R ²	F	Significance	SE
SPO	α	0.8849	7.689	0.2203	0.0121
SPO	β	0.9997	3240	0.0112 ^{se}	0.0006
SPO	π^*	1.71E-16	1.71E-16	1.0000	0.0356
SPO	S_A	0.6447	1.8148	0.4065	0.0212
SPO	S_B	0.9970	336.4	0.0347 ^{se}	0.0019
SPO	S_{PP}	0.7347	2.763	0.3445	0.0183
ASPO	α	0.8021	4.051	0.2935	0.0126
ASPO	β	0.9905	104.8	0.0620	0.0275
ASPO	π^*	0.0132	0.0133	0.9268	0.0281
ASPO	S_A	0.7500	3.000	0.3333	0.0478
ASPO	S_B	0.9716	34.17	0.1078	0.0048
ASPO	S_{PP}	0.6279	1.6875	0.4176	0.2558

SE: Standard error; F: Fisher number; ^{se}Statistically significant at 95% confidence level.

Six parameters were investigated. Three parameters were taken from each polarity scale respectively (Kamlet-Taft and Catalan) representing similar measurement: α and S_A (acidity); β and S_B (basicity); π^* and S_{PP} (dipolarity/polarizability). By comparing the R^2 (coefficient of determination) values, the parameter and of course, the solvent scale which best described the solute-solvent interaction can be determined.

For SPO, Kamlet-Taft scale seems to be more accurate in predicting acidity and basicity of solute-solvent interactions (Table 2) while Catalan seems more effective in predicting dipolarity and polarizability interactions. At 95 % confidence level used, β and S_B gave statistically significant correlation with R^2 of 0.9997 and 0.9970 respectively. Comparing the two R^2 values, β has a

higher value than S_B indicating more accuracy and predictability for the regression model. Also, the “F” number could be also used to compare two models describing the same experimental data: the higher “F”, the more adequate the corresponding model. The F number for Kamlet-Taft β parameter is 3240 while that of Catalan S_B parameter is 336.4. Comparing R^2 obtained for α and S_A , the value for α is higher than that of S_A even though both were statistically insignificant at the level of confidence used. This also indicate that measurement of acidity of solute-solvent interaction can be effectively explained by Kamlet-Taft scale. Comparing π^* and S_{PP} , it can be seen that Kamlet-Taft parameter, π^* showed very poor correlation ($R^2 = 1.71E^{-16}$) whereas Catalan parameter, S_{PP} showed a better correlation ($R^2 = 0.7347$). Therefore, Catalan solvent scale present a better determination of dipolarity and polarizability interactions than Kamlet-Taft scale.

For ASPO, a similar trend in R^2 values previously seen in SPO was observed, although statistically significant correlations were not obtained at the level of confidence used. It is therefore evidence from the results that Kamlet-Taft solvent scale is more effective in determining the acidity (HBD) and basicity (HBA) of solute-solvent interactions whereas Catalan solvent scale is more effective in determining dipolarity and polarizability interactions.

Conclusion

Electronic absorption properties of indolino spirobenzoxazine and its azo derivative are influenced by solvent polarity. A bathochromic shift in the wavelength of absorption maxima was exhibited as the solvent polarity increases. The solvent scales according to Kamlet-Taft and Catalan were investigated and compared on individual parameter basis. Single parametric regression analysis using the spectroscopic property of the compounds shows that Kamlet-Taft scale for estimating the solvent effect on the absorption properties is more adopted for hydrogen bond donor acidity and hydrogen bond acceptor basicity interactions whereas Catalan scale is most suitable for dipolarity and polarizability interactions. ■



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