http://www.e-journals.in
DOI:10.7598/cst2014.836

Chemical Science Transactions
2014, **3(3),** 919-928

RESEARCH ARTICLE

Solvatochromic Behaviour of Formazans and Contribution of Kamlet –Taft Coefficients towards Spectral Shifts of Formazans in Different Organic Solvents

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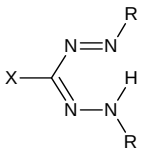
Received 10 February 2014/ Accepted 15 March 2014

Abstract: The electronic absorption profiles of 3-cyano-1,5-diarylformazans were recorded in different organic solvents having different polarities. Both macroscopic and microscopic aspects were contemplated to determine the influence of various solute-solvent interactions upon absorption spectral shifts. The effects of solvent polarity on the absorbance profiles of the compounds were evaluated. The multiple linear regression techniques were employed to evaluate Kamlet-Taft coefficients which proved to be instrumental in estimating the contribution of each type of interaction towards spectral shift profiles. It was deduced that the compounds under consideration possessed positive solvatochromism (Bathochromic shifts) owing to the non-specific solute –solvent interactions.

Keywords: Formazans**,** Solvatochromism**,** Linear regression method, Kamlet-Taft parameters

Introduction

Formazans fall under the category of azo compounds having the general formula R-N=N-C(X)=N-NH-R (Structure I) where R is an aryl or heterocyclic moiety and X=SH, OH, CN, NO_2, or substituted aryl group *etc.* form distinct class of organic compounds with characteristic properties.



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Formazan dyes are intensely colored artificial chromogenic products obtained by the reduction of tetrazolium salts by dehydrogenases and reductases. They exhibit a wide variety of colors from dark blue to deep red to orange. The reduction of tetrazolium salts in plant tissue at pH 7.2 was first demonstrated in 1941[1]. They have since been used in biochemistry, cytochemistry and histochemistry[2-5].The dehydrogenases essential for oxidation of organic

compounds and cellular metabolism reduce the tetrazolium salt to red TPF (1, 3, 5-triphenyl-formazan) while it remains as white TTC in areas of necrosis since these enzymes have been either denatured or degraded. Thus formazans have found utility in autopsy pathology. Formazans are also used to detect biological redox system in blood serum, in living cells, tissues, tumors and bacteria[6]. Many compounds of this type have also marked antiviral action, antimicrobial action, anti-cancer drugs and antineoplastic properties. The conversion of tetrazolium salts into metallizable formazan dyes can also be employed in photographic development processes[7,8]. Many metallized formazans are well suited as dyes for textile materials on the account of their coloring strength and good fastness. Another area of application is detection of bacterial capacity in industrial wastewater and determination of dehydrogenase activity in sludge[9]. They can also be effective in photographic emulsions as antifogging agents. Their bicyclic forms can be used as dyes in inks for ink-jet printing[10]. They find application as optic recording dyes to provide good light stability to optical recording layers and elements[11-13].

The properties of the solutes present in any chemical or biological system depend upon their interactions with the chemical entities prevailing in the environment. The quantitative aspects of these interactions based upon UV-Visible spectral probe help us to search for new frontiers of solute-solvent interactions. The UV-Visible spectral profiles are affected by non-specific interactions such as ion-dipole, dipole-dipole interactions, induced dipole- dipole Debye interactions or by specific interactions[14-18]. In the present study we have explored the influence of macroscopic continuum of different organic solvents on spectral profiles of compounds.

The solvent Induced absorption profile changes of compounds have been articulated quantitatively with the help of Kamlet-Taft equation (equation 1)[19-21]. This multi-parameter equation is one of the most important and relevant method of determining solvent effects such as the effect of acidity α (hydrogen bond donor capacity), the basicity β (hydrogen bond acceptor capacity) and π* the dipolarity/polrarizability which contribute towards spectral shifts.

$$\nu_{max}=\nu_{max,0} + a\alpha + b\beta + s\pi^* \quad (1)$$

The linear regression techniques are employed to infer about results of fitting coefficients which help us to estimate the type of interactions involved for absorption spectral shift in the molecule pertaining to electronic character of chemical nature of the substance. The nature of solute –solvent interactions have also been disentangled using plots between the experimentally determined ν_{max} *versus* f(D)-f(n^2), the orientation polarizations.

Experimental

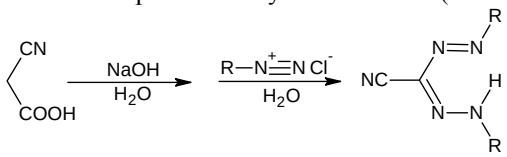
All absorption spectra were obtained using double beam UV-Vis Thermo Fischer Scientific 2600 spectrophotometer with 1.0 cm path length cells and matched dual silicon photodiode detectors. The data was analyzed using multiple linear regression technique with Mat Lab software.

All solvents including acetone, acetonitrile (ACN), chloroform, dichloromethane (DCM), *N,N´*-dimethyl formamide (DMF), *N,N´*-dimethylsulfoxide (DMSO), 1,4-dioxane, ethyl acetate, cyclohexane, ethanol(EtOH), methanol (MeOH) and tetrahydrofuran (THF) were of analytical grade. The stock solutions of all probes were prepared separately in each solvent and then diluted to the concentration 1.292×10^{-4} M. Each solution was scanned in the range of 330-600 nm. All the measurements were performed at the room temperature. The values of dielectric constant ε, refractive index n and solvatochromic parameters α, β and π* were taken from literature[22].

Synthesis of compounds

General procedure for synthesis of 3-cyanoformazans

3-Cyanoformazans were synthesized via reaction of two equivalents of the appropriate aryldiazonium chloride salt with deprotonated cyanoacetic acid (Scheme 1).



Scheme 1

The reaction proceeded upon attack of the diazonium cation by the *in situ* generated carbanion of cyanoacetic acid. The hydrazone-type intermediates are then deprotonated (by hydroxide or initial carbanion) and the resulting carbanion attacks a second equivalent of aryl-diazoniumcation, yielding a variety of highly coloured compounds[23].

Characterization data for the synthesized compounds

*3-Cyano-1,5-(4-methylphenyl)formazan (**3a**)*

Yield 58%,: m.p.= 198-200 ^{o}C, λ_{max} = 448.5 nm ($CHCl_3$), FTIR (KBr, cm^{-1}): 3215, 3023, 2915, 2219, 1594, 1507, 1392, 1259, 1182, 1037, 922, 811, 713 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.38 (s, 6H, $-CH_3$), 6.89-8.12 (m, 8H, aromatic), 13.21 (s, 1H, NH).

*3-Cyano-1,5-(4-methoxylphenyl)formazan (**3b**)*

Yield 62%,: m.p. = 150-154 ^{o}C, λ_{max} = 445.0 nm ($CHCl_3$), FTIR (KBr, cm^{-1}): 3207, 2937, 2218, 1592, 1502, 1459, 1299, 1229, 1170, 1137, 1022, 924, 819 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.85 (s, 6H, $-OCH_3$), 6.80-7.87(m, 8H, aromatic), 13.01 (s, 1H, N-H).

*3-Cyano-1,5-(4-chlorolphenyl)-formazan (**3c**)*

Yield 48%,: m.p. = 185-187 ^{o}C, λ_{max}= 419.0 nm ($CHCl_3$), FTIR (KBr, cm^{-1}): 3236, 2220, 1590, 1475, 1389, 1266, 1238, 1186, 1007, 926,804 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.83-8.35 (m, 8H, aromatic), 10.04 (s, 1H, N-H).

*3-Cyano-1,5-(4-bromophenyl)formazan (**3d**)*

Yield 50%,: m.p. = 218-220 ^{o}C, λ_{max}= 419.5 nm ($CHCl_3$), FTIR (KBr, cm^{-1}): 3232, 3091, 2220, 1575, 1478, 1391, 1266, 1181, 1067, 1004, 926, 808 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 6.83-8.35 (m, 8H, aromatic), 10.04 (s, 1H, N-H).

*3-Cyano-1,5-(3-chlorophenyl)formazan (**3e**)*

Yield 42%,: m.p. = 203-205 ^{o}C, λ_{max}= 409.5 nm ($CHCl_3$), FTIR (KBr, cm^{-1}): 3223, 2220, 1586, 1460, 1395, 1256, 1188, 1068, 994, 871, 763 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.83-8.35 (m, 8H, aromatic), 10.02 (s, 1H, N-H).

Results and Discussion

Electronic properties and solvatochromism of 3-cyanoformazans

The spectral profiles of the compounds under consideration were recorded in twelve organic solvents having wide variety of solvent parameters such as dielectric constantε, refractive index n and solvatochromic parameters α, β and π^*. The spectra of 3-cyanoformazans (**3a-3e)** in various organic solvents are presented in Figure 1-5 respectively. Their absorptions in the visible region are highly substrate dependent. These absorptions appearing at 377-492 nm

(Table 1) having significantly high values of extinction coefficients (10^3-10^4 dm^3 mol^{-1} cm^{-1}) advocate for typical π-π^* electronic transitions. The conjugation between rings and N=N bridges in the given compounds accounts for pronounced π-π^* electronic transitions.

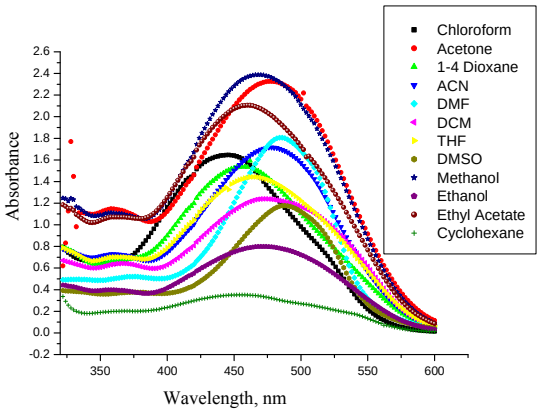


Figure 1. UV-Visible spectrum of compound **3a**

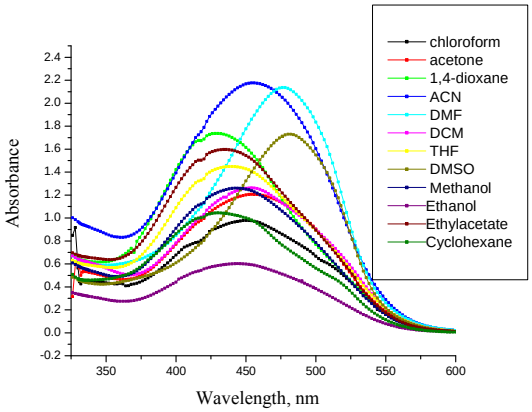


Figure 2. UV-Visible spectrum of compound **3b**

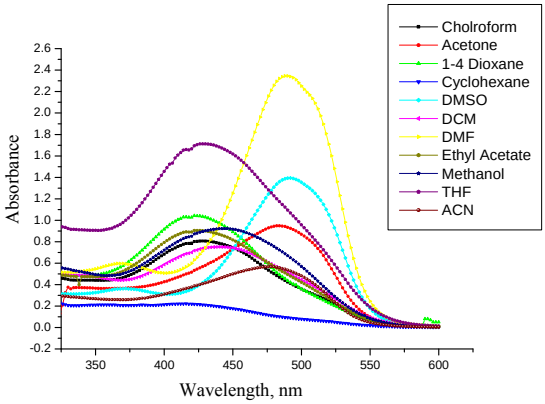


Figure 3. UV-Visible spectrum of compound **3c**

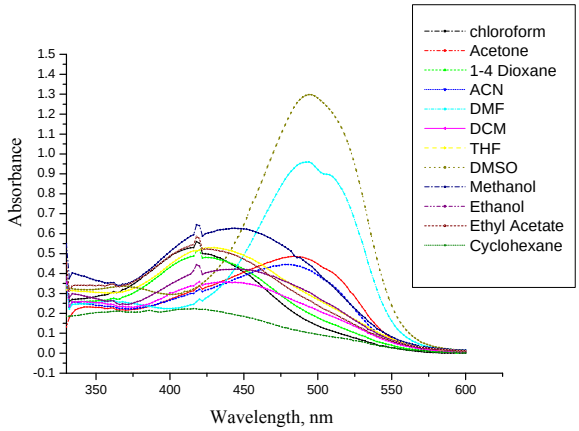


Figure 4. UV-Visible spectrum of compound **3d**

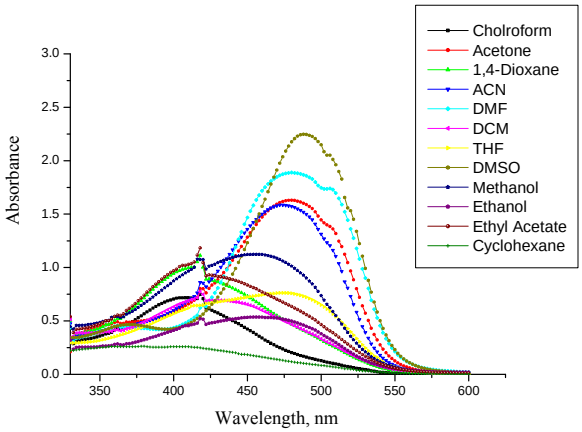


Figure 5. UV-Visible spectrum of compound **3e**

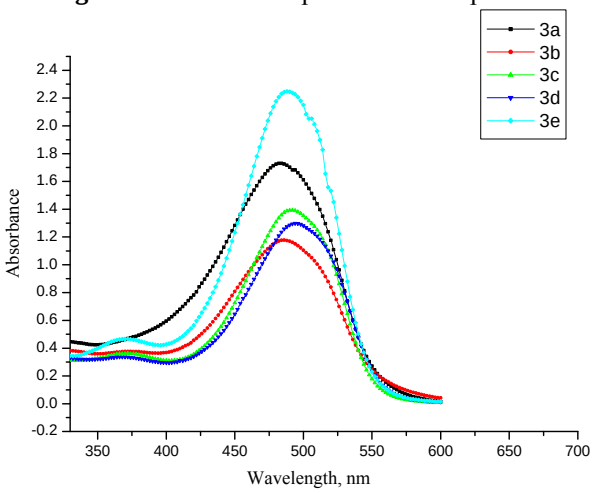


Figure 6. UV-Visible spectrum of compound **3a-3e** in DMSO

Table 1. λ_{max}(nm) values of the given compounds **a-e** in different organic solvents.

Compound	Cyclohexane	1,4-Dioxane	Chloroform	Methanol	Ethanol	CAN	DMF	THF	Acetone	EtOAc	DCM	DMSO
3a	418.5	428.5	448.5	442.5	446.0	454.0	476.5	438.5	454.0	434.5	453.5	481.0
3b	416.0	427.0	445.0	469.5	474.0	473.0	485.0	464.0	477.0	460.0	473.0	487.5
3c	415.5	423.5	419.0	442.5	452.0	478.5	489.0	430.0	483.5	423.5	439.5	492.0
3d	386.0	419.0	419.5	443.0	444.0	480.5	493.5	428.0	483.0	424.0	436.5	495.0
3e	377.0	418.0	409.5	453.5	457.0	473.0	480.0	474.5	480.0	418.0	424.0	488.0

It is obvious that there is considerable change in absorption profile of the molecules with variation in polarity of the medium. The given compounds 3**a-3e** possess bathochromic spectral shifts (positive solvatochromism) while moving from least polar solvent (cyclohexane) to the most polar solvent (DMSO). This is attributed to the fact that molecule in the ground state and excited state possesses different polarities. The compounds with non-polarized ground state are strongly polarized in protic solvents since the high energy polar structure of excitation state is stabilized. The excited state is lowered and ground state is hardly altered which leads to suppression in energy difference and hence molar electronic transition energy is decreased.

The π-π^* electronic transition ranges from 66.19 kcal mol^{-1} in cyclohexane to 59.24 kcal mol^{-1} in DMSO, from 62.56 kcal mol^{-1} in cyclohexane to 58.45 kcal mol^{-1} in DMSO, from 68.58 kcal mol^{-1} in cyclohexane to 57.92 kcal mol^{-1} in DMSO, from 73.82 kcal mol^{-1} in cyclohexane to 57.57 kcal mol^{-1} in DMSO and from 75.19 kcal mol^{-1} in cyclohexane to 58.39 kcal mol^{-1} in DMSO in conjunction with ΔE_{max} = +6.95 kcal mol^{-1}, ΔE_{max} = +4.11 kcal mol^{-1} , ΔE_{max} = +10.66 kcal mol^{-1}, ΔE_{max} = +16.25 kcal mol^{-1} and ΔE_{max} = +16.80 kcal mol^{-1}for the compounds 3a-e respectively, positive values of $\Delta E_{max} = \Delta E_{max}^{non\ polar} - \Delta E_{max}^{polar}$ indicate that molecules under consideration possess positive solvatochromism.

The bathochromic shifts can also be described by hydrogen donor ability of the compounds and hydrogen acceptor ability of some solvents like DMF and DMSO. The given compounds are more polar in excited states than in ground states.The absorption maxima of compounds exhibit maximum bathochromic shifts with substituent in para position in contrast ortho and meta positions. Moreover amongst halogen substituted compounds, the absorption maxima varies inversely with electronegativity of atoms. The λ_{max} values for various substituted formazans in DMSO (Figure 6) follow the order:

p-Br> p-Cl> m-Cl> p-OCH_3>p-CH_3

This trend is attributed to the maximum delocalization of electrons in p-Br substituted compound which enhances the conjugation of the system. DMSO being highly polar induces maximum dipole-dipole interactions in p-Br substituted formazan which stabilizes the excited state to higher extent. Further in case of p-Cl substituted compound, due to higher electronegativity of Cl group and decrease in +R effect, thedelocalization is decreased which further denouncesthe dipole –dipole interactions. The λ_{max} values of the compounds under discussion are in conformity with their structures.

Multiple linear regression analysis

The parameters governing the contribution of the influence of wide solvent parameters upon spectral shifts in terms of specific and non-specific interactions have been evaluated using Kamlet-Taft equation.

$$\nu_{max}=\nu_{max,0} +a\alpha +b\beta +s\pi^* \quad (2)$$

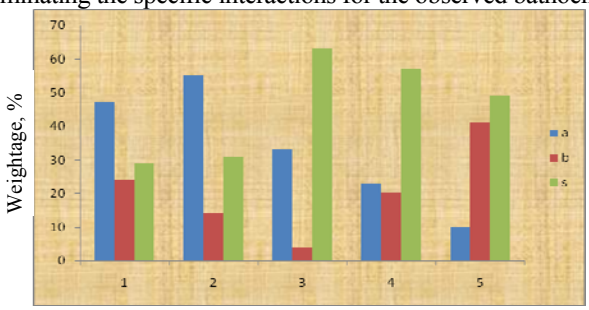
Where ν_{max} is maximum absorption wavenumber of the given compound processed experimentally, $\nu_{max,0}$ was calculated by the regression method, the other parameters *i.e.* the Kamlet-Taft coefficients a, b and s were also calculated using regression analysis method. These coefficients on their percentage basis as evaluated on the basis of values of regression coefficients contributed differently, predicted the type of solute-solvent interactions and solvatochromic behavior.

Negative values of both s and b (Table 2) indicate that there is positive solvatochromism which means bathochromic shift with increase in solvent polarizability and solvent bond basicity.

Table 2. The values of Kamlet-Taft coefficients a, b and **s** for the compounds **3a-3e**

Compound	$\nu_{0,}$ x10^4	a, x10^2	b, x10^3	s, x10^3
3a	2.2297	+1.6721	-0.8558	-1.0258
3b	2.5039	+ 6.0779	-1.4919	-3.4430
3c	2.3908	+1.3125	-0.1665	-2.4941
3d	2.6480	+2.0526	-1.7630	-5.1629
3e	2.6441	+0.8629	-3.4154	-3.9552

These coefficients (Figure 7 and Table 3) further signify the fact that non-specific interactions are dominating the specific interactions for the observed bathochromic spectral shifts.



Compounds **3a-3e**

Figure 7. Depiction of contribution of Kamlet-Taft parameters

Table 3: Type of characteristic solvatochromism and contribution weightage for solvatochromic parameters

Compound	ΔE_{max}, kcal mol^{-1}	Solvatochromism	W_α, %	W_β, %	W_π, %
3a	+6.95	Positive	47	24	29
3b	+4.11	Positive	55	14	31
3c	+10.66	Positive	33	4	63
3d	+16.25	Positive	23	20	57
3e	+16.80	Positive	10	41	49

These non-specific dipole-dipole interactions for the given compounds follow the following sequence depending upon the substituent attached to aryl group. These interactions are working comprehensively for the *p*-Cl substituted compound because C–Cl bond being highly polar promotes orientation polarizations to greater extent than other substituents possessing different inductive and resonance effects. In the case of *m*-substituted compound, resonance effect disappears and so does the extent of dipole-dipole interactions. In *p*-CH_3substituted compound, C–CH_3being non-polarhas the least degree of orientation polarizations.

$$p\text{-Cl} > p\text{-Br} > m\text{-Cl} > p\text{-OCH}_3 > p\text{-CH}_3 \quad (3)$$

Solvent-solute interactions

Plots of $\pi \rightarrow \pi^*$ absorption band wavenumbers as a function off (D)-f (n^2), where f (D)-f (n^2) is the measure of non-specific dipole –dipole interactions, show a correlation between ν_{max} and f(D)-f(n^2). The plots of **3a** and **3b** possess less degree of linearity than plots of **3c, 3d** and **3e** (Figures 8-12). The negative slopes of plots reveal positive solvation energies.

$$E_{solvation} = -\frac{\mu m}{am^3}\ [f(D)\text{-}f(n^2)] \quad (4)$$

Negative slopes and positive solvation energies support dispersive nature of interactions. It is obvious that these non-specific interactions are weak Vander Waals like interactions.

These interactions emerging from the phenomenon of orientation polarizations lead to dispositions of transient cavities withholding the solute molecules paving the way for augmentation of non-specific solute-solvent interactions.

Equation 4 was used to calculate the radii of cavities emerging from this cavitation process which are tabulated in the Table 4 and it clearly shows that augmentation is higher in protic solvents like DMSO, DMF *etc*.

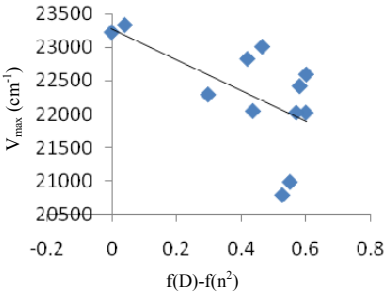


Figure 8. Compound **3a**

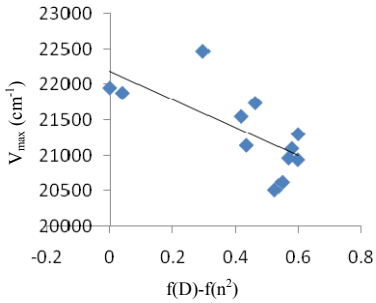


Figure 9. Compound **3b**

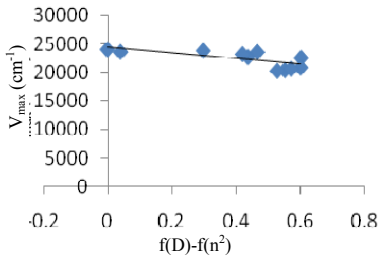


Figure 10. Compound **3c**

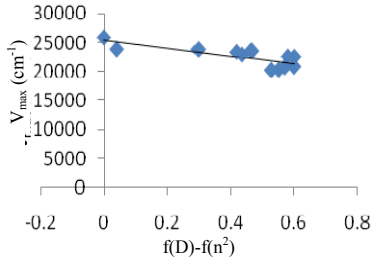


Figure 11. Compound **3d**

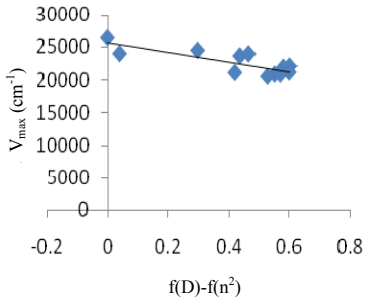


Figure 12. Compound **3e**

Table 4. Radii of cavities (Å, Angstrom) of the different organic solvents accommodating compounds (**3a-e**) as calculated from equation 4.

Solvent	Compd. **3a**	Compd. **3b**	Compd. **3c**	Compd. **3d**	Compd. **3e**
Methanol	0.09041	0.09528	0.06986	0.06373	0.06192
Ethanol	0.09024	0.09510	0.06972	0.06360	0.06180
Chloroform	0.07675	0.08089	0.05930	0.05409	0.05257
THF	0.09129	0.09621	0.07054	0.06435	0.06253
DCM	0.08860	0.09338	0.06846	0.06245	0.06069
DMF	0.11842	0.12480	0.09149	0.08347	0.08111
DMSO	0.11986	0.50173	0.09259	0.08448	0.08210
Cyclohexane	0.05235	0.05516	0.04045	0.03690	0.03585
1-4Dioxane	0.05804	0.06118	0.04486	0.04088	0.03971
Ethyl Acetate	0.09181	0.09675	0.07094	0.06471	0.06288
Acetone	0.10777	0.11359	0.08328	0.07597	0.07383
ACN	0.11945	0.12558	0.09228	0.08420	0.08182

Conclusion

- The compounds under consideration undergo bathochromic shift (positive solvatochromism). The magnitude of bathochromic shift increases with increase in solvent polarizability/basicity.
- Multiple regression analysis unfurls the contribution of various solvent parameters *i.e.* Kamlet-Taft coefficients which affect the absorption profiles.
- The contribution due to polarizability of solvents is found to be dominating which supports the fact that interactions are of non-specific type.
- The non-specific solute-solvent interactions due to orientation polarizations lead to augmented cavities withholding the network of solute-solvent interactions.

Acknowledgement

Authors are thankful to the college management for providing research facilities. Authors are also thankful to University Grants Commission (UGC), New Delhi for financial support.

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