



Solvatochromic behavior of the electronic absorption spectra of gallic acid and some of its azo derivatives

Mamdouh S. Masoud^{a,*}, Sawsan S. Hagagg^a, Alaa E. Ali^b, Nessma M. Nasr^c

^a Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt

^b Chemistry Department, Faculty of Science, Damanhour University, Damanhour, Egypt

^c Faculty of Pharmacy, Alexandria University, Alexandria, Egypt

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ABSTRACT

The electronic absorption spectra of gallic acid and its azo derivatives have been studied in various solvents of different polarities. Multiple regression techniques were applied to calculate the regression and correlation coefficients based on an equation that relates the wavenumbers of the absorption band maxima (ν_{\max}^-) to the solvent parameters; refractive index (n), dielectric constant (D), empirical Kamlet–Taft solvent parameters, π^* (dipolarity/polarizability), α (solvent hydrogen-bond donor acidity) and β (solvent hydrogen-bond acceptor basicity). The fitting coefficient obtained from this analysis allows estimating the contribution of each type of interactions relative to total spectral shifts in solution. The dependence of ν_{\max}^- on the solvent parameters indicates that the obtained bands are affected by specific and non-specific solute-solvent interactions.

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1. Introduction

Gallic acid (3, 4, 5 trihydroxy benzoic acid) is one of the most abundant plant phenolic acid [1] it is especially found in tea [2]. It can be isolated from wood [3], fruits, wine [4–8], different alcoholic beverages and various medicinal plants such as traditional Chinese medicine [9]. The isolation of gallic acid from plant source is more preferable than the synthetic methods [8,10]. Ultra-high pure gallic acid has been used as a friendly environment processing to replace catechol (1, 2 dihydroxybenzene) in removing photo resist [11]. It is prepared by combining resin adsorption, crystallization, membrane filtration with industrial grade gallic acid as a raw material [11]. It is a basic structure unit of hydrolysis tannin that has been chosen as a model compound to investigate solute-solvent interaction in polar media [12].

It is known by its antioxidant, antiallergic, anticarcinogenic [13,14], anti mutagenic [15] and displaying fungicidal, fungi static properties [16]. Gallic acid and gallates possess a scavenger activity against several types of free radicals, such as 145 DUL prostate cancer cells [17] and L1210 leukemia cells [18], which could cause aberrance of normal tissue and protect cells from danger induced by ionizing irradiation [13]. Gallic acid is used as a non toxic corrosion inhibitor for steel structures in place of toxic lead oxide.

Possibility of steel surface covered by insoluble gallic acid ferric complex can be one of the reasons for corrosion inhibitor [19] that is due to its strong potential reduction. It was found that, it's adsorbed on metal surface and acts as a corrosion inhibitor. The iron gall inks were one of the most impotent writing materials used to prepare documents, drawings, and other written materials photography, and they were used in cosmetic industry [20]. The UV–vis absorption spectra can be influenced by non specific interactions such as ion-dipole, dipole-dipole interaction, induced dipole-permanent dipole interactions (Debye interaction) or by specific interaction such as hydrogen bonding solvents [21]. The aim of this work is to investigate the solvent effects on electronic absorption spectra of gallic acid and its azo derivatives. A linear correlation was adopted to indicate the solvatochromic behavior between experimental spectral values ν_{\max}^- and solvent parameters: $f(D) = 2n^2 - 2/2n^2 + 1$, and $f(n^2) = 2n^2 - 2/2n^2 + 1$, or solvatochromic variables π^* , α , and β and to evaluate their contributions to the solute-solvent interactions. Chemical structures of investigated compounds are illustrated in Fig. 1.

2. Experimental

Substituted phenyl azo gallic acid was synthesized by diazotizing, with substituted anilines as reported [22]. The UV–vis spectra were measured with a PerkinElmer Lambda 4B spectrophotometer. The solvents used were of spectrophotometric quality grade. Gallic

* Corresponding author. Tel.: +201223431922.

E-mail address: drmsmasoud@yahoo.com (M.S. Masoud).

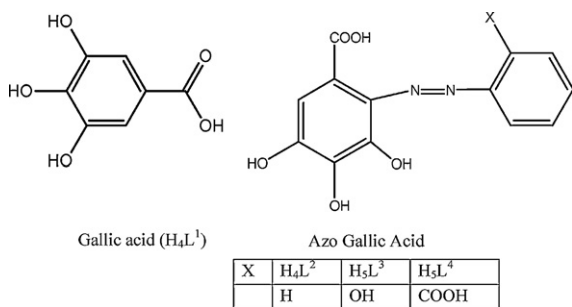


Fig. 1. Structures of the investigated compounds.

acid and solvents were purchased from Sigma and Aldrich and were used as received.

3. Results and discussion

3.1. Electronic absorption spectral peaks

The electronic absorption spectral of gallic acid, Fig. 2, represents an example for illustration, where two bands are appeared for all solvents. The high energy bands are due to π - π^* transition at wavelength range 216–228 nm, and the other one is due to low lying n - π^* electronic transition at wavelength range 259–296 nm, except in DMSO and dioxan, only one band is observed at 277 and 296 nm, respectively [23] (Figs. 3–5).

Blue shift of n - π^* transition by increasing the solvent polarity is happened due to hydrogen bond formation that probably takes place between the solute and the solvent through the hydroxyl group, which leads to the existence of some chromophoric groups. Thus, the π -system is stabilized and tends to lower the energy of

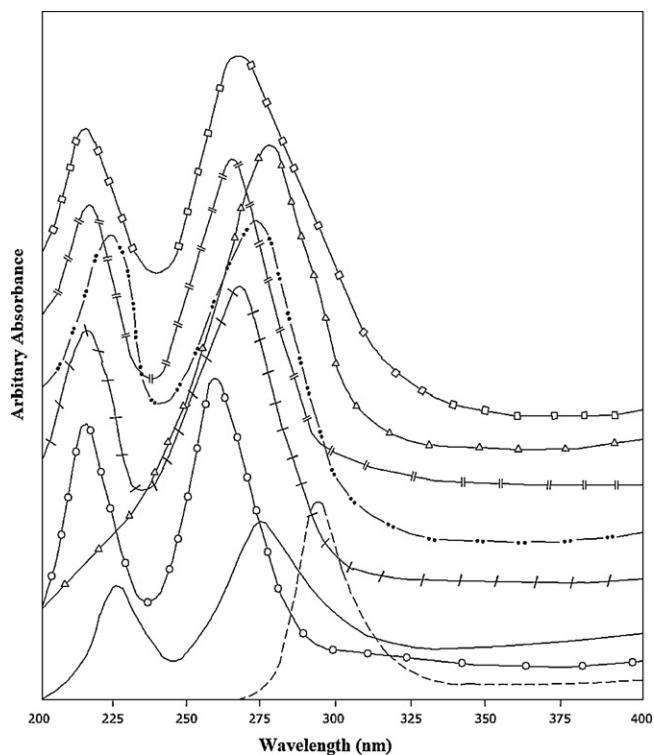


Fig. 2. Effect of solvents on the electronic spectra of H₄L¹, — CCl₄, - - - DMF, — — — CHCl₃, || || || Acetonitrile, ○—○ Ethanol, △—△—△ DMSO, + + + + Methanol, □—□—□ H₂O.

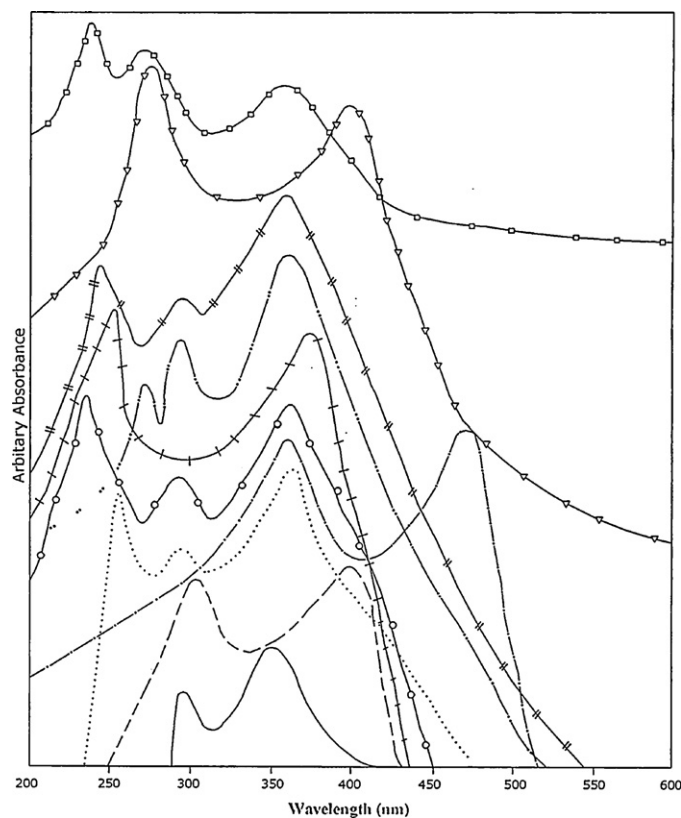


Fig. 3. Effect of solvents on the electronic absorption spectra of H₄L², — CCl₄, + + + + Methanol, - - - Dioxane, - - - - - DMF, CHCl₃, || || || Acetonitrile, - - - - - Acetone, △—△—△ DMSO, ○—○ Ethanol, □—□—□ H₂O.

the ground state and thus blue shift occurs and the changes can be represented as in Fig. 6.

However, H₄L², points to the existence of three bands in the presence of chloroform, DMF, acetonitrile, and water, while only two bands are appeared in the presence of CCl₄, dioxane, acetone, methanol and DMSO. It seems that blue-shift of λ_{\max} occurs as the dielectric constant of the solvent increased, (i.e. in the presence of water). This points to that the compound is strongly accumulated by water solvent molecules through hydrogen bond. The first and second bands are appeared in the wavelength range 233–265 nm and 272–294 nm, and that is due to different types of π - π^* electronic transitions. However, the third band appeared in wavelength range of 350–382 nm, which is assigned to the n - π^* electronic transition probably in a hydrazo form [24,25]. The observed broadening nature of the band is due to mixing the ground state of the hydrogen bonded complex with different electronic states. This verified the presence of hydrazone tautomer to exist and the changes are represented as in Fig. 7.

In case of H₅L³, two bands are appeared in the presence of acetone, while three bands are appeared in the presence of CCl₄, dioxan, chloroform, ethanol, DMF, acetonitrile, DMSO and H₂O. However, four spectral bands are appeared in methanol. The spectral bands appeared in the wavelength range 232–256 nm and 272–300 nm, which are due to different types of π - π^* electronic transitions. The bands are located in the wavelength range 336–364 and 426–475 nm and that are due to n - π^* electronic transitions, where different species are existing, irrespective of the solvents used. An internal hydrogen-bond is depicted from the blue shift which is observed during changing the solvent from ethanol to water in n - π^* band. It was suggested that a substance containing hydrogen bond should be represented as resonance of hybrids,

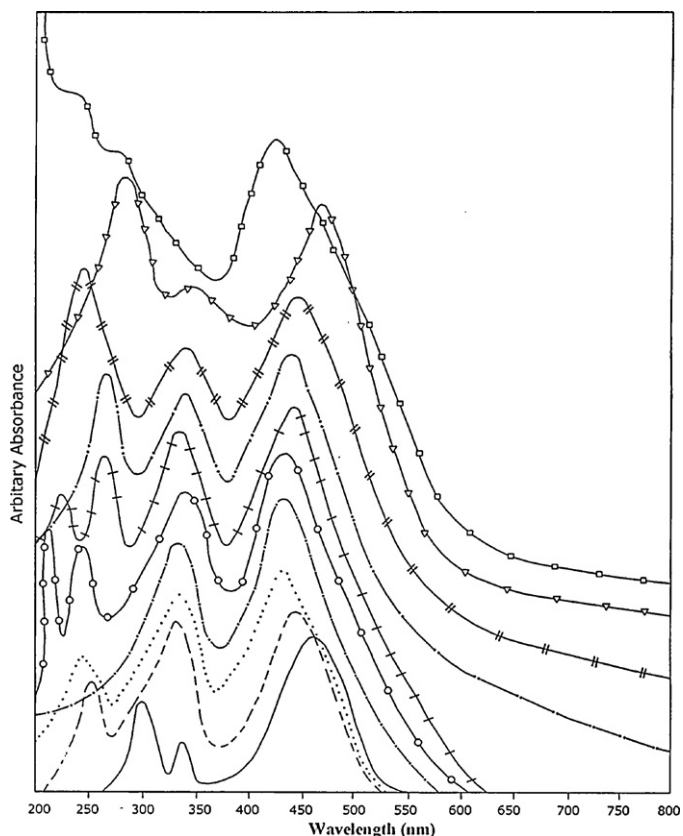


Fig. 4. Effect of solvents on the electronic absorption spectra of H_5L^3 , ——— CCl_4 , + + + + Methanol, — — — — Dioxane, - - - - - DMF, $CHCl_3$, || || || Acetonitrile, - - - - - Acetone, $\Delta \Delta \Delta$ DMSO, $\circ \circ \circ$ Ethanol, $\square \square \square$ H_2O .

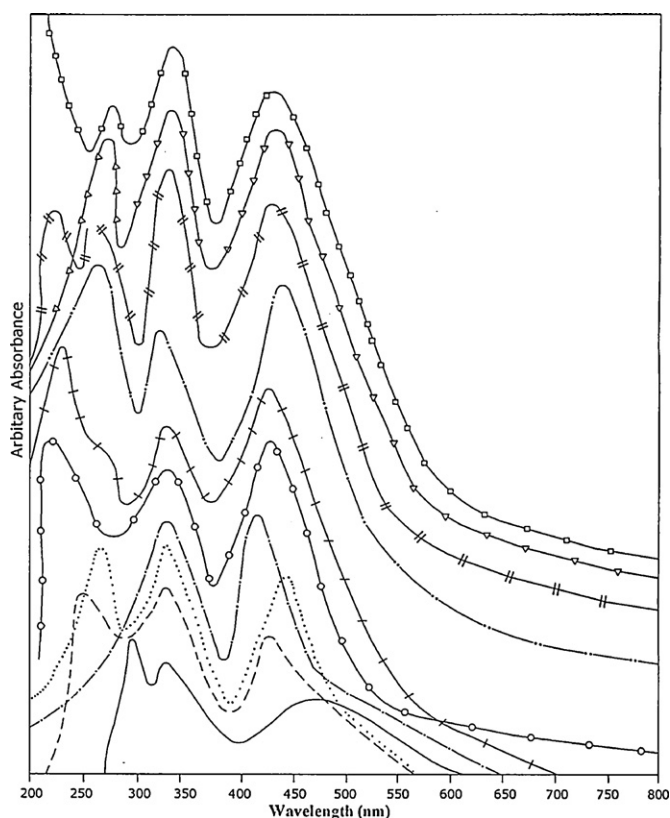


Fig. 5. Effect of solvents on the electronic absorption spectra of H_5L^4 , ——— CCl_4 , + + + + Methanol, — — — — Dioxane, - - - - - DMF, $CHCl_3$, || || || Acetonitrile, - - - - - Acetone, $\Delta \Delta \Delta$ DMSO, $\circ \circ \circ$ Ethanol, $\square \square \square$ H_2O .

which means that it should contain a non-localized bond [24,25]. Red shift occurs, when proceeding from non polar solvent (dioxan) to polar solvent (DMSO), spectral shift is mainly due to solute-solvent interactions, that cause stabilization of the π^* orbital more than the π -orbital in polar solvents. This suggested that, H_5L^3 compound is more polarized in the excited state than in the ground state and the red shift can also be explained by the hydrogen donor ability of H_5L^3 compound that occurs and the changes are represented in Fig. 8.

H_5L^4 gives two bands in acetone, while in CCl_4 , $CHCl_3$, DMF, DMSO, dioxan and H_2O , three bands are appeared. However,

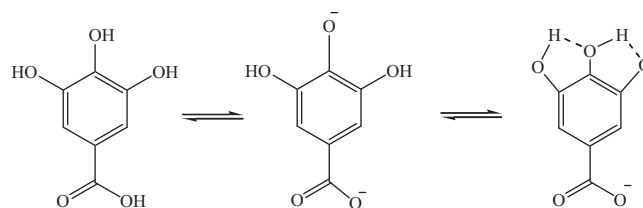


Fig. 6. Possible forms of H_4L^1 in a solution.

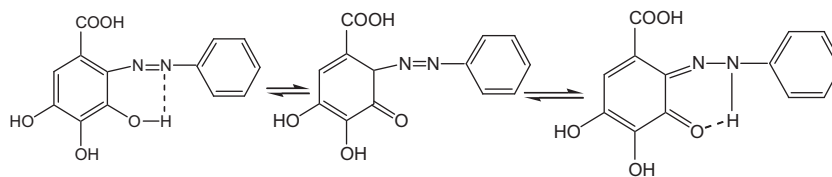


Fig. 7. Possible forms of H_4L^2 in a solution.

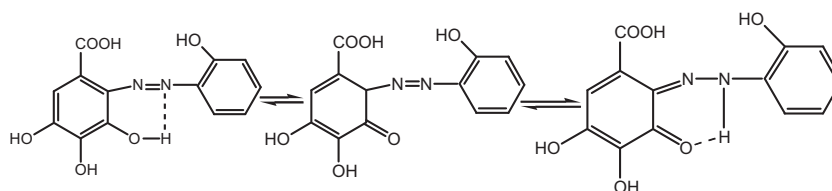


Fig. 8. Possible forms of H_5L^3 in a solution.

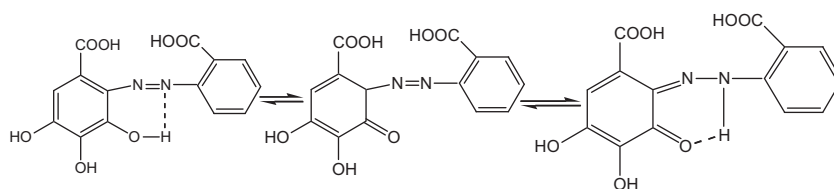


Fig. 9. Possible forms of H_5L^4 in a solution.

in ethanol, methanol and acetonitrile, four bands are appeared. An internal hydrogen-bond is depicted from the blue-shift that is observed during changing the solvent from ethanol to water [24,25]. The spectra was in the wavelength range 238–255 nm and 270–300 nm. This is due to different types of π – π^* transitions. The other two bands were in the wavelength range 322–339 and 270–300 nm are due to n – π^* transitions. The presence of electron attracting substituent increases the positive charge at the carbon atom which leads to greater stabilization, accompanied by a change of the more strongly polarizable C–O, C–NH linkage occurs. The changes are represented in Fig. 9.

3.2. Regression analysis calculations

Several one-, two-, three-, four-parameter equations are applied using suitable combinations between the solvent polarity parameters E , M , N and K [26]. The parameter E is sensitive to solute-solvent hydrogen bonding and dipolar interactions [26]. The dielectric function, K represents the dipolar interactions [27]. The functions M and N have been introduced to account for the solute permanent dipole-solvent permanent dipole interactions, respectively [28,29]. The values of the solvent parameters E , M , N , K , D and n in different solvents are collected in Table 1, D is the dielectric constant of the solvent and n is its refractive index. The electronic absorption spectra of the compounds under investigation in terms of λ_{\max} have been analyzed by multiple linear regression technique using the following equation [30]:

$$Y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + \dots + a_nx_n$$

where Y is the observed peak located on an absorption band in a given solvent, a_0 is the regression intercept. a_1 , a_2 , a_3 , ..., a_n are coefficients that could be determined by multiple regression technique and x_1 , x_2 , x_3 , x_n are the various empirical solvent polarity parameters. A program of statistical package of social sciences (SPSS) version 8 has been used on PC computer. The (MCC: multiple correlation coefficients) value is considered as a measure of the goodness of fit. The high value of MCC (near one) means that a certain solvent parameter has a good correlation to the spectral shifts. Alternatively, the small value (near zero) of the significance parameter (P) means the correlation is good. In a complementary study, the coefficients K_1 , K_2 and ν_{vapor} (cm^{-1}) were calculated using multiple regression technique based on the following equation [31,32]:

$$\nu_{\text{solution}} = \nu_{\text{vapor}} + K_1 \frac{2D - 2}{2D + 1} + K_2 \frac{2n^2 - 2}{2n^2 + 1}$$

ν_{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. The multiple correlation coefficient and the square of correlation were calculated for each $r^2(\nu, D)$ and $r^2(\nu, n)$ (Table 2).

The analysis of spectral shift of high energy transitions in all investigated compounds is done using one-parameter equation, Tables 3–6, showed that the best MCC values in case of H_4L^1 at λ_1 are obtained for the parameter (M), which are sensitive to dipole-dipole interactions. However, in case of H_4L^2 at λ_2 , H_5L^3 and H_5L^4 at λ_1 , high correlation values obtained using the parameter K

indicate high influence of the dielectric constant on the position of the absorption peak. This inferred from high positive values of MCC (multiple correlation coefficients) for M and K . The correlation of the two-parameter equations with the solvent spectral shifts was also studied and gives, as expected, better fit to these spectral shifts than the corresponding one parameter fits. The solvent ability to form hydrogen bonds with the solute molecules, which is reflected by the parameter E , when combined with the previously mentioned parameters K , M or N , is the reason for improving the correlations. For instance, when the parameter E is combined with the parameters M , N and K , the MCC values jump to 0.923, 0.772 and 0.769, respectively for H_4L^1 at λ_1 . The correlation is improved as expected on analyzing the spectral shifts using three parameters equations and best MCC values are observed. For instance, when parameter E is added to (M , N), (M , K) and (N , K), MCC values are raised to higher values for all investigated compounds. Generally, it is concluded that the addition of a four solvent parameter to the three parameter equations always give rise to improvements in the correlation with the solvent induced spectral shifts.

The calculated K_1 , K_2 , ν_{vapor} , $r^2(\nu, D)$, $r^2(\nu, n)$ and MCC for all investigated compounds point that both the dielectric constant and the refractive index of solvents affect the electronic spectral properties of the compounds with different degrees. The negative values for K_2 for H_4L^1 , H_4L^2 and H_5L^3 indicate the occurrence of strong solute-solvent interaction and cause decrease in energy of electronic transition from LUMO to HOMO in comparison with the vapor phase.

3.3. Calculation of radius of solutes

Solvation energy can be defined quantitatively as energy of interaction between a solute and a solvent [33]. The two important and commonly used formulations for solvent-solute interactions are Born (point charge model) and Onsager (point dipole dielectric continuum model) formulations. In both models electric charges and lengths are combined to obtain the physical dimension of energy.

$$E_{\text{solv}}^{\text{ion}} = \frac{-q^2}{2a} F(D) \quad \text{Born equation} \quad (\text{i})$$

$$E_{\text{solv}}^{\text{dipol}} = \frac{-\mu^2}{2a^3} f(D) \quad \text{Onsanger equation} \quad (\text{ii})$$

The solvent polarity function [32–34] $F(D)$ and $f(D)$ are dimensionless numbers as they represent the relative strength of the electric field experienced by the ion or dipole. The reaction field model of solute-solvent interactions introduced by Onsanger equation is the most widely used. In this model; a neutral dipolar molecule is a sphere with central point dipole moment μ . The dipole produces an electric field and this field has two separate effects on the surrounding solvent molecules: the induction polarization and the orientation polarization. In case of induction polarization, the solute-solvent interaction is given by:

$$E_{\text{solv}} = \frac{-\mu_M}{2a^3} [f(D) - f(n^2)] \quad f(n^2) = \frac{2(n^2 - 1)}{(2n^2 + 1)}$$

Table 1
Solvent parameters and X_1 and X_2 for solvents.

Solvent	D	n	E	M	N	K	X_1	X_2
CCl ₄	2.2	1.460	32.5	0.22	0.01	0.20	0.4444	0.4300
Dioxan	2.2	1.422	36.0	0.20	0.03	0.22	0.4444	0.4300
CHCl ₃	4.7	1.446	39.1	0.21	0.29	0.36	0.7115	0.4191
Acetone	20.7	1.359	42.2	0.18	0.65	0.46	0.9300	0.3620
Ethanol	24.3	1.361	51.9	0.18	0.67	0.47	0.9395	0.3623
Methanol	32.6	1.329	55.5	0.17	0.71	0.48	0.9546	0.3381
DMF	36.7	1.427	43.8	0.2	0.67	0.48	0.9597	0.4086
Acetonitrile	37.5	1.346	46.0	0.18	0.71	0.48	0.9605	0.3496
DMSO	48.9	1.478	45.0	0.22	0.66	0.48	0.9696	0.4412
H ₂ O	78.5	1.333	63.1	0.17	0.76	0.49	0.9810	0.3442

Table 2
 K_1 , K_2 , ν_{vapor} and correlation analysis data for organic compounds.

Compound	ν_{vapor} (cm ⁻¹)	K_1	K_2	MCC	$r^2(\nu, D)$	$r^2(\nu, n)$
H ₄ L ¹	59,689.33	-1202.75	-35,441.98	0.957	0.623	0.947
H ₄ L ²	35,752.453	4423.618	-10,122.809	0.600	0.288	0.415
H ₅ L ³	40,297.765	2895.434	-5545.600	0.589	0.031	0.244
H ₅ L ⁴	32,168.909	6303.799	10,490.775	0.993	0.153	0.380

Table 3
Regression analysis for H₄L¹ in different solvents at λ_1 .

Parameters	a_0	a_1	a_2	a_3	a_4	MCC	P
E	41,117.46	88.78	-	-	-	0.768	0.047
M	55,926.05	-56,121.82	-	-	-	0.904	0.013
N	43,774.46	2847.89	-	-	-	0.666	0.149
K	42,573.94	6636.99	-	-	-	0.623	0.187
E, M	63,998.42	-56.97	-84,471.79	-	-	0.923	0.057
E, N	41,376.51	76.96	540.10	-	-	0.772	0.257
E, K	41,099.37	82.469	752.60	-	-	0.769	0.261
M, N	62,310.29	-83,496.20	-2166.04	-	-	0.938	0.042
M, K	62,436.249	-79,754.268	-4843.39	-	-	0.937	0.042
N, K	59,255.164	34,155.693	-78,231.03	-	-	0.863	0.129
E, M, N	70,143.392	-55.799	-110,949.49	-2141.41	-	0.955	0.129
E, M, K	70,737.74	-58.08	-108,917.35	-4896.69	-	0.956	0.125
E, N, K	61,950.21	-18.93	38,980.88	-88,869.63	-	0.865	0.352
M, N, K	62,309.69	-83,509.52	-2174.05	18.00	-	0.938	0.176
E, M, N, K	72,310.561	-66.031	-99,925.34	7514.88	-21,708.019	0.958	0.417

The last equation is a measure of the permanent dipole-induced dipole interactions, the correlation of ν_{max} and $f(n^2)$, gives a straight line with a negative slope, which equals to $-\mu_M/a_M^3$, where, n is refractive index and a_M is the radius of the spherical cavity, which contains the solvent molecule. For orientation polarization of the solvent dipoles, the total solvation energy is given as follows:

$$E_{\text{solv}} = \frac{-\mu_M}{a_M^3} [f(D) - f(n^2)] \quad f(D) = \frac{2(D-1)}{2D+1}$$

Table 4
Regression analysis for H₄L² in different solvents at λ_2 .

Parameters	a_0	a_1	a_2	a_3	a_4	MCC	P
E	314.101	-0.612	-	-	-	0.627	0.096
M	277.843	45.098	-	-	-	0.091	0.829
N	297.013	-21.605	-	-	-	0.724	0.042
K	308.900	-55.723	-	-	-	0.729	0.040
E, M	455.810	-1.442	-529.781	-	-	0.909	0.013
E, N	300.251	-0.099	-19.130	-	-	0.726	0.154
E, K	311.938	-0.148	-46.742	-	-	0.736	0.143
M, N	350.157	-247.982	-30.380	-	-	0.831	0.053
M, K	353.467	-194.180	-71.363	-	-	0.803	0.075
N, K	307.698	-2.257	-50.003	-	-	0.729	0.150
E, M, N	436.169	-1.026	-492.452	-13.338	-	0.943	0.022
E, M, K	441.932	-1.081	-482.917	-29.004	-	0.938	0.026
E, N, K	320.838	-0.208	14.390	-79.542	-	0.738	0.324
M, N, K	341.951	-300.514	-67.481	91.078	-	0.843	0.141
E, M, N, K	429.448	-0.999	-515.035	-34.164	50.050	0.946	0.079

where, D is the dielectric constant, $[f(D) - f(n^2)]$ is a measure of the interactions between the permanent dipoles. Solvent-solute interaction is dependent on the properties of both the solvent, polarity of the solute and the type of the electronic transition. The solvatochromic shifts are often used to assign the transition as $\pi-\pi^*$, $n-\pi^*$ or charge transfer. Fig. 10 shows the relation between the wavenumber (cm⁻¹) against $[f(D) - f(n^2)]$ for polar and non polar solvents. The slopes for all compounds are positive and equal to $-\mu_M/2a^3$ which indicate that, E_{solv} is negative. Hence, it can be

Table 5
Regression analysis for H_5L^3 in different solvents at λ_1 .

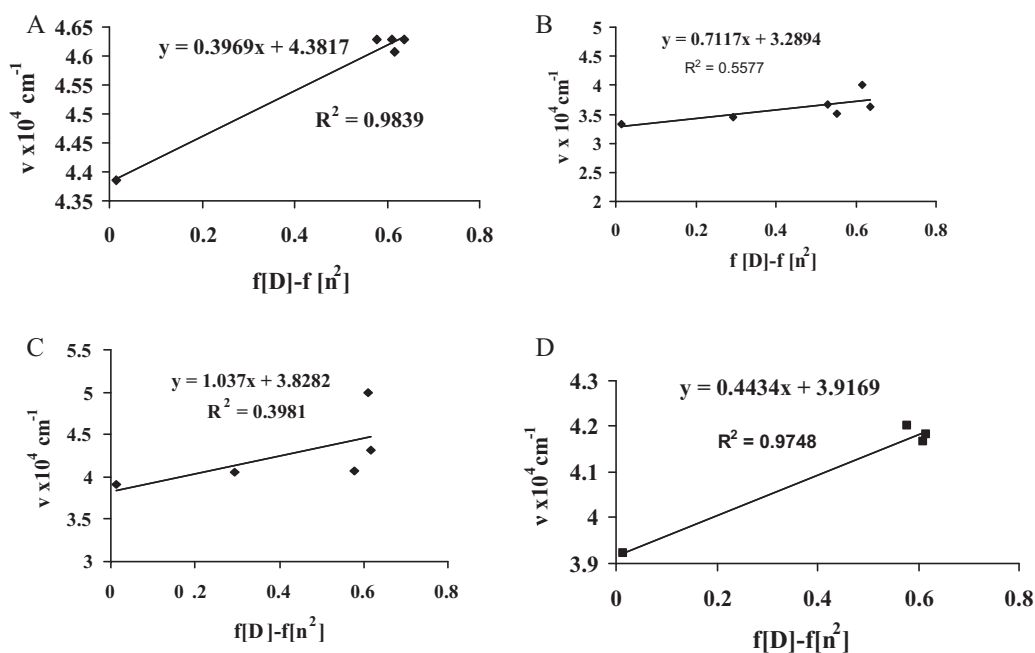
Parameters	a_0	a_1	a_2	a_3	a_4	MCC	P
E	262.298	−.332	−	−	−	0.430	0.395
M	201.630	240.741	−	−	−	0.500	0.312
N	254.288	−15.371	−	−	−	0.580	0.228
K	264.921	−45.011	−	−	−	0.614	0.195
E, M	192.125	0.063	275.639	−	−	0.501	0.648
E, N	247.475	0.207	−21.477	−	−	0.595	0.519
E, K	262.130	0.173	−58.479	−	−	0.627	0.473
M, N	255.314	−4.882	−15.604	−	−	0.580	0.541
M, K	260.321	19.561	−42.656	−	−	0.614	0.492
N, K	285.326	33.353	−136.274	−	−	0.641	0.452
E, M, N	222.015	0.303	106.048	−19.248	−	0.602	0.782
E, M, K	217.711	0.382	174.528	−53.743	−	0.647	0.729
E, N, K	282.833	0.039	30.299	−130.928	−	0.641	0.736
M, N, K	126.052	1559.631	372.549	−876.594	−	0.899	0.273
E, M, N, K	5.092	0.836	2216.246	449.307	−1072.690	0.994	0.164

Table 6
Regression analysis for H_5L^4 in different solvents at λ_1 .

Parameters	a_0	a_1	a_2	a_3	a_4	MCC	P
E	283.768	−0.861	−	−	−	0.912	0.088
M	135.421	589.474	−	−	−	0.922	0.078
N	255.616	−23.804	−	−	−	0.988	0.012
K	268.596	−62.052	−	−	−	0.991	0.009
E, M	189.236	−0.324	378.769	−	−	0.927	0.374
E, N	261.609	−0.169	−19.989	−	−	0.992	0.127
E, K	272.133	−0.153	−53.070	−	−	0.994	0.111
M, N	258.655	−15.102	−24.337	−	−	0.988	0.152
M, K	271.417	−12.810	−63.223	−	−	0.991	0.134
N, K	350.681	151.389	−455.556	−	−	0.999	0.051
E, M, N	352.120	−0.515	−389.047	−25.931	−	1.000	−
E, M, K	351.159	−0.450	−327.632	−65.582	−	1.000	−
E, N, K	346.036	−0.105	138.333	−415.439	−	1.000	−
M, N, K	344.472	100.000	180.556	−522.222	−	1.000	−

concluded that the main solvent-solute interaction is of dipole-dipole behavior. Fig. 11, gives a relation between the wavenumber (cm^{-1}) with refractive index as given by the function $f(n^2)$. The linearity of the plot is satisfactory with a negative sign

and it is of a small value, which reflects a weak solvent-solute interaction and that is due to the variation of the solvent refractive index. Table 7 shows calculated values of the radius of the spherical cavity. The radius obtained by orientation polarization

**Fig. 10.** Variation of band maximum with $f[D]-f[n^2]$. (A) H_4L^1 , (B) H_4L^2 , (C) H_5L^3 and (D) H_5L^4 .

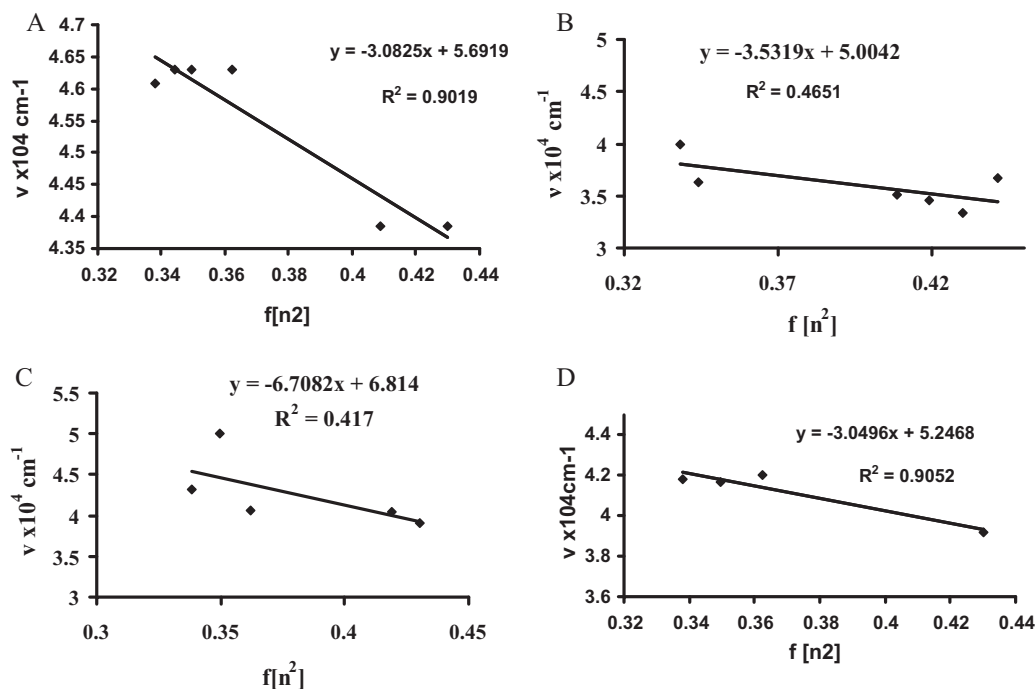


Fig. 11. Variation of band maximum with the refractive index of the solvent: (A) H_4L^1 , (B) H_4L^2 , (C) H_5L^3 and (D) H_5L^4 .

Table 7
Calculations of the radius of the solutes, a .

Solvent	Dipole moment	a^*			
		H_4L^1	H_4L^2	H_5L^3	H_5L^4
Dioxan	0.45	0.82 (0.52)	0.68(0.50)	0.82(0.55)	0.79 (0.52)
$CHCl_3$	1.04	–	0.90(0.66)	1.08(0.72)	1.05(0.69)
Ethanol	1.69	1.28(0.81)	1.38(1.02)	1.67(1.12)	1.62(1.07)
Methanol	1.70	1.28(0.82)	1.40(1.03)	1.68(1.13)	1.64(1.08)
H_2O	1.85	1.32(0.84)	1.09(0.8)	1.31(0.88)	1.27(0.84)
Acetone	2.88	–	1.25(0.93)	1.52(1.02)	1.47(0.98)
DMF	3.82	1.68(1.07)	1.40(1.03)	1.69(1.13)	1.64(1.08)
Acetonitrile	3.92	1.70(1.08)	1.05(0.78)	1.27(0.85)	1.23(0.82)
DMSO	3.96	1.70(1.08)	1.05(1.78)	1.27(0.85)	1.24(0.82)

* a is the radius of the spherical cavity by orientation polarization and the values between brackets refer to the radius of the spherical cavity by induction polarization.

is greater than the radius calculated by induction polarization and that happen in most of the cases. Whenever the dipole moment increases, the radius of the solute increases.

3.4. Kamlet–Taft equation

It was used in order to describe the overall solvent effects. It has been successfully applied to separate the influence of non specific chemical interactions, including electrostatic effects (dipolarity/polarizability) from specific interactions as hydrogen bonding, which are related to the molecular structure of a compound [35–38].

$$\nu_{\max} = \nu_0 + s\pi^* + b\beta + \alpha\alpha$$

where ν_{\max} is the wavenumber (cm^{-1}) in the maximum absorption band of the investigated compounds in pure solvents, ν_0 is the regression intercept corresponds to the gaseous of the spectrally active compounds, π^* is a measure of the solvent dipolarity/polarizability, β is the scale of the solvent hydrogen-bond acceptor (HBA) basicity, α is the scale of the solvent hydrogen-bond donor (HBD) acidities and ν_0 , a , b , s are solvent independent constants, their magnitudes and sign provide measure of the influence of the corresponding solute-solvent interactions on the

wavenumber in the maximum of electronic absorption band, which have been determined by multiple regression analysis, using SPSS statistics program. The solvent parameters [39–41] and ν_{\max} values for the H_4L^1 , H_4L^2 , H_5L^3 and H_5L^4 compounds are given in Tables 8 and 9. The results of the multiple regressions are presented in Table 10. The contribution of each parameter to solvatochromism, on a percentage basis was calculated from the values of regression coefficients, it can be observed that, in case of the H_4L^1

Table 8
 ν_{\max} of electronic absorption spectra (cm^{-1}) in different solvents.

Solvent/Compound	ν_{\max} (cm^{-1})			
	H_4L^1	H_4L^2	H_5L^3	H_5L^4
CCl_4	43,859.6	–	29,761.9	–
Dioxan	–	–	29,498.5	39,215.6
$CHCl_3$	–	40,650.4	29,239.7	–
Acetone	–	–	29,498.5	–
Ethanol	46,296.3	42,372.8	29,069.7	42,016.8
Methanol	46,082.9	40,000	29,498.5	4184
DMF	43,859.6	37,735.8	29,069.7	–
Acetonitrile	46,296.3	42,372.8	29,325.5	41,666.6
DMSO	–	–	27,472.5	–
H_2O	46,296.3	42,918.4	–	–

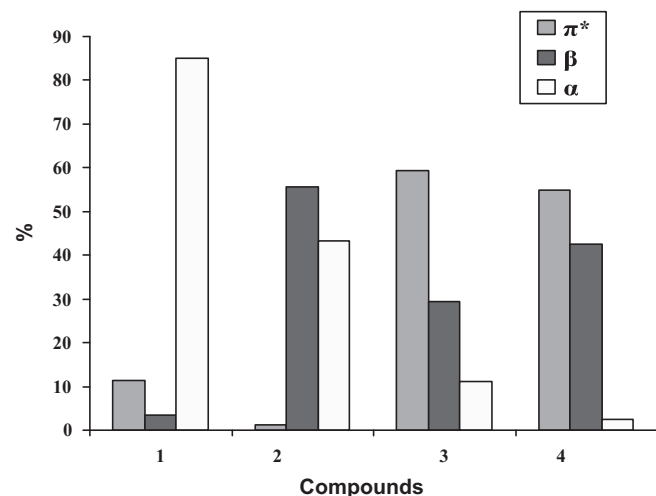
Table 9
Kamlet–Taft solvatochromic parameters [37,38].

Solvent	α	β	π^*
CCl ₄	0.00	0.10	0.59
Dioxane	0.37	0.00	0.55
CHCl ₃	0.20	0.10	0.58
Acetone	0.08	0.43	0.71
Ethanol	0.86	0.75	0.84
Methanol	0.98	0.66	0.60
DMF	0.00	0.69	0.88
Acetonitrile	0.19	0.40	0.75
DMSO	0.00	0.76	1
H ₂ O	1.17	0.47	1.09

Table 10
Solvent independent correlation coefficient a , b , s of the Kamlet–Taft parameters.

Compound	ν_0	a	b	s	MCC
H ₄ L ¹	44,329.03	1733.11	71.66	229.69	0.77
H ₄ L ²	41,317.48	2713.28	−3497.88	−76.83	0.67
H ₅ L ³	30,528.21	303.52	−807.33	−1626.65	0.76
H ₅ L ⁴	29,650.32	−528.02	8867.05	11,426.46	1.00

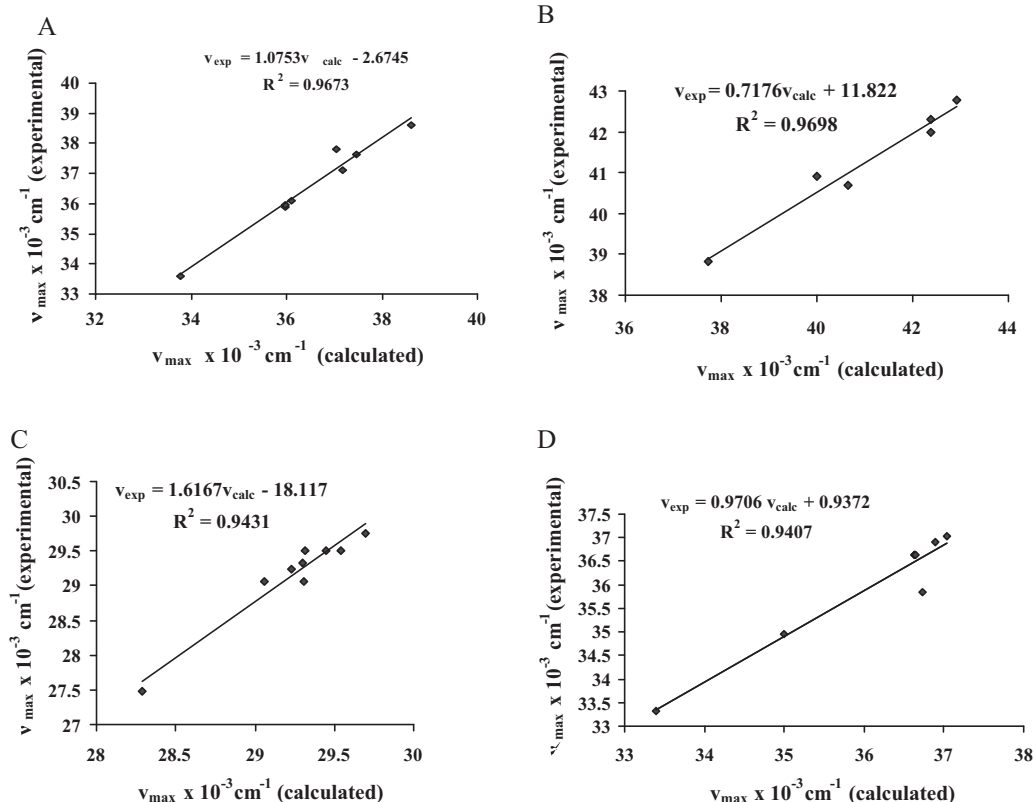
the contribution of HBD, α acidity is the highest and so the solvatochromic behavior of H₄L¹ will be governed by hydrogen bonding interactions. High positive value of the coefficient (a) indicates a hypsochromic shift which occurs with increasing solvent-hydrogen

**Fig. 12.** Percentage contributions to the solvatochromic effects: (1) H₄L¹, (2) H₄L², (3) H₅L³ and (4) H₅L⁴.

bond acidity. This conclusion implies stabilization of the ground state relative to the excited state [42]. Negative signs of (s) and (b) coefficients of H₄L² and H₅L³ indicate that there is a bathochromic shift with increasing solvent dipolarity/polarizability and solvent

Table 11
Solvatochromism and percentage contribution of the solvatochromic parameter for H₄L¹ and its azo derivatives.

Compound	ν_{\max} most non polar solvent (10 ³ cm ^{−1})	ν_{\max} most polar solvent (10 ³ cm ^{−1})	$\Delta\nu$ (10 ³ cm ^{−1})	Solvato-chromism	P_{α} (%)	P_{β} (%)	P_{π^*} (%)
H ₄ L ¹	43.8	46.2	+2.4	+	85.10	3.50	11.28
H ₄ L ²	40.6	42.9	+2.3	+	43.15	55.62	1.20
H ₅ L ³	29.7	27.2	−2.5	−	11.08	29.49	59.42
H ₅ L ⁴	33.3	36.6	+3.3	+	2.50	42.58	54.87

**Fig. 13.** Plot of ν_{\max} experimental versus ν_{\max} calculated for: (A) H₄L¹, (B) H₄L², (C) H₅L³ and (D) H₅L⁴.

hydrogen bond basicity. This information suggests that stabilization of the electronic excited state is relative to the ground state. Fig. 12 and Table 11, point that the contribution of the solute-solvent dipole-dipole interactions (π^*) to bathochromic shift are much more pronounced than the specific ones (α , β) in case of H_5L^3 . In H_5L^4 and H_4L^2 compounds, the dominate solvent effect is due to hydrogen bond acceptor basicities. The negative sign of (α) coefficient for H_5L^4 , shows a positive solvatochromism with increasing solvent dipolarity/polarizability (π^*). In order to obtain the sign (negative or positive), the wavenumber maximum absorption in the band was subtracted from that determined in most non polar solvent and it was considered as spectral shift $\Delta\nu$. Positive and negative signs of $\Delta\nu$ are indicators of red or blue spectral shifts, respectively. All investigated compounds, Table 11, exhibits a bathochromic shift (positive solvatochromism) as resulted of an increase in the solvent polarity except in case of H_5L^3 . To demonstrate the quality of the multilinear regressions analysis, the correlation between the predicted absorption maxima (ν_{calc} calculated) versus the experimental values (ν_{exp} experimental) is given in Fig. 13. This gives good results due to the fact that, it accounts both universal interactions and specific interaction. Universal interactions are expressed by $F(n)$ and $F(D, n)$.

4. Conclusion

The electronic spectra of gallic acid and its azo compound are affected by the nature of the solvents that differ in their properties. We can express this effect quantitatively by applying different models: mainly multiple regression and Kamlet-Taft equations. Solvation energy was defined quantitatively as energy of interaction between the solute and the solvent. The two important and commonly used formulations for solvent-solute interactions are Born (point charge model) and Onsager (point dipole dielectric continuum model) formulations. In both models electric charges and lengths are combined to obtain the physical dimension of energy.

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