



CHARGE-TRANSFER COMPLEX OF SOME THIOPHENE SCHIFF BASE COMPOUNDS WITH NITROBENZENE ACCEPTORS

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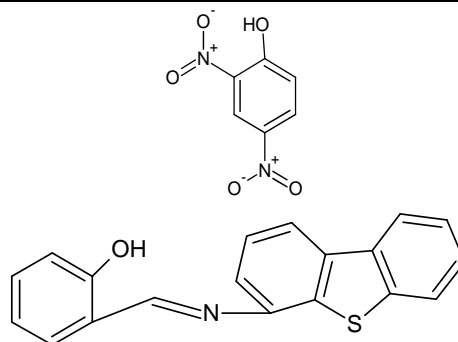
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Charge transfer complex (CTC) of some thiophene Schiff-base donor and Benzaldehyde, Salicylaldehyde and 2,4-dinitrophenol acceptors has been studied in ethanol, dichloromethane, carbon tetrachloride and acetonitrile solvents at four different temperatures (20, 30, 40, 50 °C) using absorption spectrophotometer. The results indicate that formation of CTC in non polar solvent is high. The stoichiometry of the complex was found to be 1: 1 ratio by straight-line method between donor and acceptor with maximum absorption bands. The data are discussed in terms of formation constant (K_{CT}), molar extinction coefficient (ϵ_{CT}), standard free energy (ΔG^0), oscillator strength (f), transition energy (E_{CT}), and ionization potential (ID). The formation constant (K_{CT}) for the complex was shown to be dependent upon the nature of electron acceptor, donor and polarity of solvents that were used. The CT complex was synthesized and characterized by elemental analysis, and electronic absorption spectra which indicate the CT interaction associated with proton migration from the acceptor to the donor followed by hydrogen bonding via N^+-HO^- .



INTRODUCTION

Charge transfer phenomenon was introduced first by Mulliken. The term charge transfer gives a certain type of complex resulting from interactions of donor and acceptor with the formation of weak bands¹⁻³ and discussed widely by Foster.⁴ Molecular interactions between donors and acceptors are generally associated with the formation of intensely colored charge transfer complexes, in which absorb radiation in the visible region.⁵ Molecular complexation and structural recognition are important processes in biological systems, for example drug action, enzyme catalysis and ion transfer through lipophilic membranes all

involve complexation.⁶ Charge transfer complexes are currently of great importance since these materials can be utilized as organic semiconductors,⁷ photo catalyst⁸ and dendrimers.⁹ They are also important in studying redox processes,¹⁰ second order nonlinear optical activity¹¹ and micro-emulsion.¹² These studies dealt mainly with the CT complex were formed between picric acid (acceptor) and thiophene derivatives (donor). Picric acid forms molecular complexes with aromatic hydrocarbons such as anthracene,¹³ some aniline derivatives¹⁴ and also with aromatic amines.¹⁵⁻¹⁷ Mulliken suggested that the formation of molecular complexes from two aromatic molecules can arise from the transfer of

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an electron from a π -molecular orbital of a Lewis base to a vacant π -molecular orbital of a Lewis acid, with resonance between this dative structure and the no-band structure stabilizing the complex.² He also noted the possibility of complex formation through the donation of an electron from a non-bonding molecular orbital in a Lewis base to a vacant π -orbital of an acceptor ($n-\pi$).¹⁸ With resonance stabilization of the combination. As part of such studies picric acid is able to form CT complex with thiophene in different polar solvents.

Accordingly the present article includes the characterization of CT-complexes of Thiophene Schiff-base as donors with Nitrobenzene derivatives as acceptors in solvents of different polarity at four temperatures by visible spectra data of CT complex ($\pi-\pi$), thiophene with π -acceptor, picric acid in said solvents, viz, ethanol, dichloromethane, carbon tetrachloride and acetonitrile and also studied the effect of solvents on the formation of CT complex.

EXPERIMENTAL

Materials used

To prepare Schiff bases we used compounds consisting of a primary amine: addition 2-aminodibenzothiophene to the

three aldehydes is: Benzaldehyde, Salicylaldehyde and 2,4-dihydroxybenzaldehyde, all from the Laboratory Rasayon (LR).

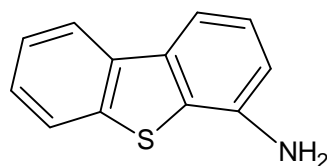
Analysis elements of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) and calculated practical and theoretical percentage and recorded in Table (1). And comparing these theoretically calculated ratios with those found in practice, was noted that it is close to a large extent. As shown by the elements analysis of the above-mentioned compounds that Schiff bases were obtained with molecular formulas shown in Table (2).

Results of elemental analysis, melting points in addition to the molecular formula in Table (1) clearly points to match the results of the analysis process with the ratios calculated, as can also be Charge Transfer Complexes by 1:1 and 1:2 donors: acceptor.

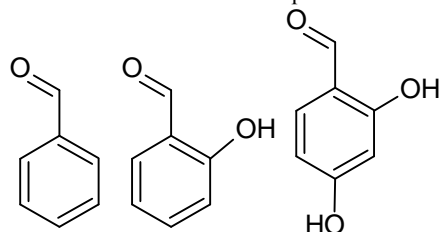
For the determination of the stability of formation constant (K_{CT}) with Bensi-Hilderbrand equation.¹⁵ The concentration of donors 1×10^{-2} M and of receptors concentration 1×10^{-3} M in the center of ethanol.

Taken from the donor compound 0.2 mL and is added to 0.5 ml of the solution to the acceptor compound and reduces to 10 ml using a solvent developed under study namely, ethanol, dichloromethane, carbon tetrachloride and acetonitrile spectrally sample was measured at a temperature of 20°C.

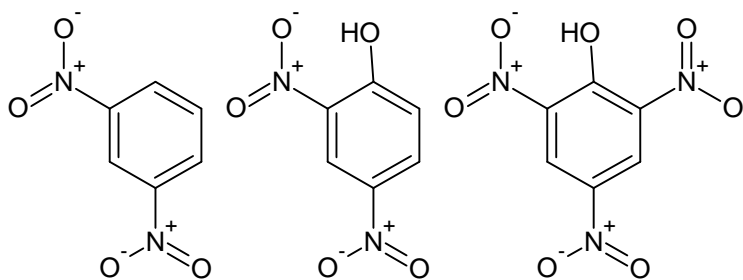
Repeat the previous steps using different sizes of the donor compound: 0.5, 1.2 mL at 30 °C, 40 °C, and 5 0°C. All absorption spectra measurements were made with Shimadzu UV-1650 P.C. spectrophotometer.



2-aminodibenzothiophene



Benzaldehyde Salicylaldehyde 2,4-dihydroxybenzaldehyde



1,3-dinitrobenzene (A_1) 2,4-dinitrophenol (A_2) Picric acid (A_3)

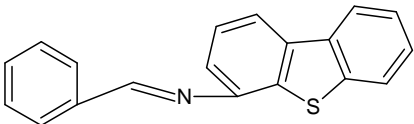
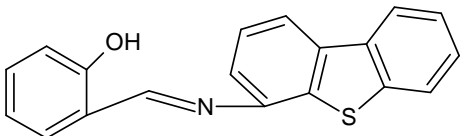
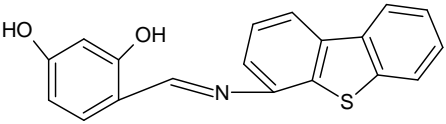
Table 1

Elemental analysis and melting point for Schiff base and some charge transfer complexes

Comp.	C%		H%		N%		S%		Melting Points (°C)
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
D₁	79.41	79.74	4.56	4.55	4.87	4.34	11.16	11.00	87-90
D₁A₃ 1:1	58.14	57.98	3.12	3.02	10.85	10.39	6.21	6.01	88-91
D₁A₃ 1:2	49.94	49.74	2.57	2.46	13.15	12.85	4.30	4.03	75-77
D₂	75.22	75.63	4.32	4.47	4.62	4.51	10.57	10.02	102-103
D₂A₃ 1:1	56.39	58.41	3.03	3.93	10.52	10.25	6.02	5.81	96-98
D₂A₃ 1:2	48.89	48.69	2.51	2.54	12.87	12.76	4.21	4.20	102-104
D₃	71.45	70.98	4.10	4.18	4.39	3.66	10.04	10.02	59-60
D₃A₃ 1:1	54.75	54.93	2.94	2.88	10.21	10.76	5.85	5.65	138-140
D₃A₃ 1:2	47.88	47.92	2.46	2.37	12.61	12.91	4.12	4.06	54-57

Table 2

Molecular compounds formula for donor Schiff bases

Proposed Molecular Structure Formula	Molecular Structure Molecular weight	Material code
	C ₁₉ H ₁₃ NS 287.38	D₁
	C ₁₉ H ₁₃ NOS 303.38	D₂
	C ₁₉ H ₁₃ NO ₂ S 319.38	D₃

RESULTS AND DISCUSSION

Observation of CT bands

The electronic absorption spectra of the donor Salicylaldehyde (D₂), acceptor 2,4-dinitrophenol (A₂) and the resulting complex in ethanol, dichloromethane, carbon tetrachloride and acetonitrile were recorded in the visible range 300-600 nm using Shimadzu UV-1650 P.C.

spectrophotometer with a 1 cm quartz cell path length.

The electronic absorption spectra of different solvents are shown in figs 1-4. For the reaction mixture of donor (10 ml) and acceptor (10 ml) in different solvents viz., carbon tetrachloride, dichloromethane, acetonitrile and ethanol. A dark color charge transfer complex was formed (the complex for each of the reaction mixture standing overnight at room temperature to form stable

couple before analysis at the maximum absorbance) 457.5 nm for carbon tetrachloride, 458 nm for dichloromethane, 457.5 nm for Ethanol and 452.5 nm for acetonitrile. The concentration of the donor in the reaction mixture was kept greater than acceptor $[D] > [A]$ ¹⁶⁻¹⁷ and changed over a wide range of concentration from 0.01 M to 0.5 M while concentration of acceptor 2,4-dinitrophenol (A_2) was kept fixed¹⁶ at 0.01 M in each solvents.

To obtain the CT bands, the spectrum of solution of 0.01 M 2,4-dinitrophenol (A_2), and 0.01 M salicylaldehyd in different solvents was recorded with solvents used as a reference, it is observed that new absorption peak appear in the visible region. In some cases multiple peaks were obtained, the longest wavelength peak was considered as CT peak.¹⁸

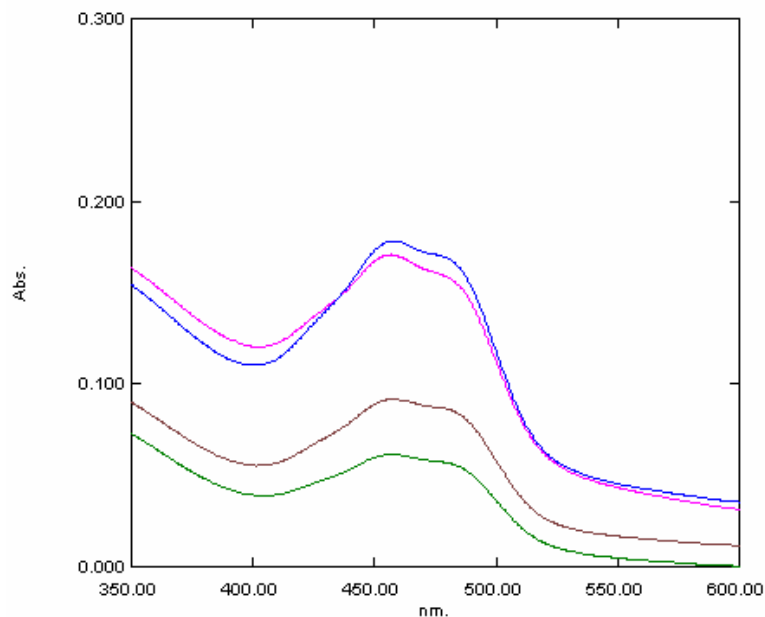


Fig. 1 – absorption spectra donor compound D_1 [$C = 0.2 \times 10^{-3}, 0.5 \times 10^{-3}, 0.8 \times 10^{-3}, 1.2 \times 10^{-3}M$] with compound acceptor A_1 [$0.5 \times 10^{-4}M$] in ethanol at temperature [30°C].

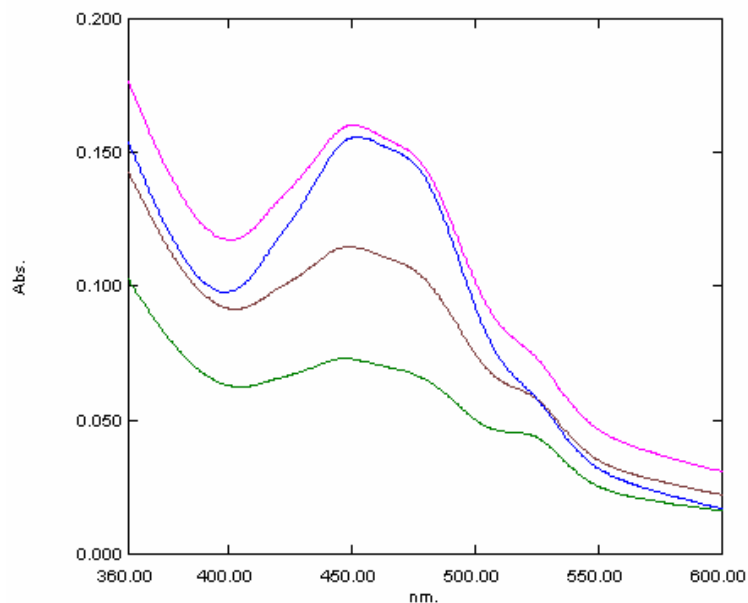


Fig. 2 – absorption spectra donor com pound D_1 [$C = 0.2 \times 10^{-3}, 0.5 \times 10^{-3}, 0.8 \times 10^{-3}, 1.2 \times 10^{-3}M$] with compound acceptor A_1 [$0.5 \times 10^{-4}M$] in acetonitrile at temperature [30 ° C].

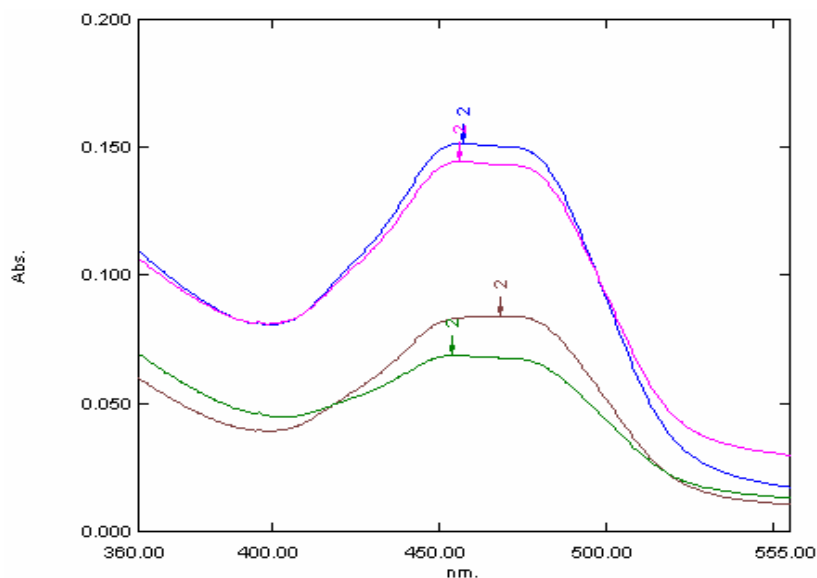


Fig. 3 – absorption spectrum donor compound D_1 [$C = 0.2 \times 10^{-3}, 0.5 \times 10^{-3}, 0.8 \times 10^{-3}, 1.2 \times 10^{-3} M$] with acceptor compound A_1 [$0.5 \times 10^{-4} M$] in dichloromethane at temperature [30 °C].

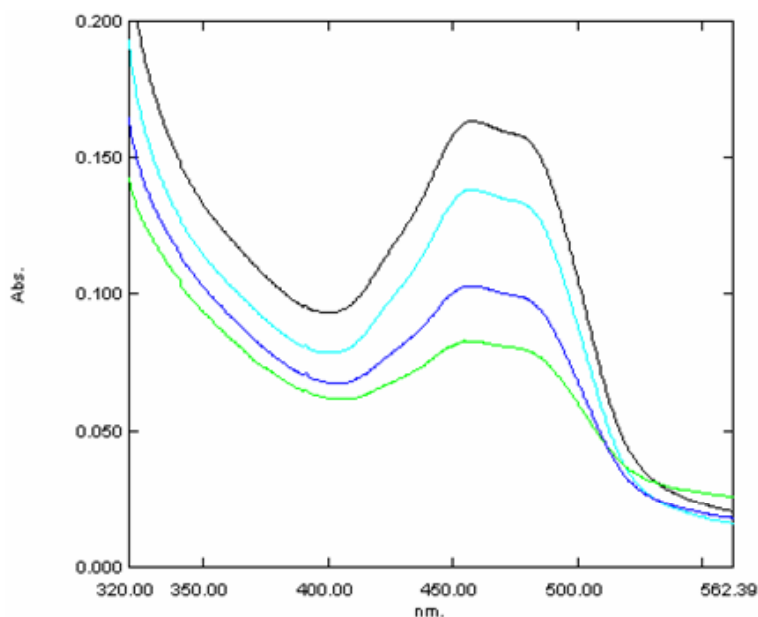


Fig. 4 – absorption spectrum donor compound D_1 [$C = 0.2 \times 10^{-3}, 0.5 \times 10^{-3}, 0.8 \times 10^{-3}, 1.2 \times 10^{-3} M$] with acceptor compound A_1 [$0.5 \times 10^{-4} M$] in carbon tetrachloride at four different temperatures [20, 30, 40, 50 °C].

Acetonitrile > ethanol > dichloromethane > tetrachloride

The electronic absorption spectrum of donor compound D_2 [$C = 0.2 \times 10^{-3}, 0.5 \times 10^{-3}, 0.8 \times 10^{-3}, 1.2 \times 10^{-3} M$] acceptor compound A_3 [$0.5 \times 10^{-4} M$] in different solvents of various polarities viz. ethanol, dichloromethane, carbon tetrachloride and acetonitrile. The results obtained show that the spectrophotometric data are markedly affected by changing the solvent in which the measurements are carried out. The most striking feature of the data is that the stability of the formed CT complex increases as the dielectric constant of the solvent is increased.

This behavior can be supported by the observed large shift in the band along the same sequence. This can be explained on the basis of the high stabilization of the ground state of the complex upon increasing the solvent polarity. This is due to the increase in the interaction between the dipole of the solvent and that of the complex. This in turn, consistent with the strong nature of the investigated CT complexes (*i.e.* n-o kind). Similar behavior has been observed for other donor-CT complexes¹⁹. In this respect, it is worth mentioning that specific interactions of the solvents with the donors or the formed complexes are of major importance.²⁰

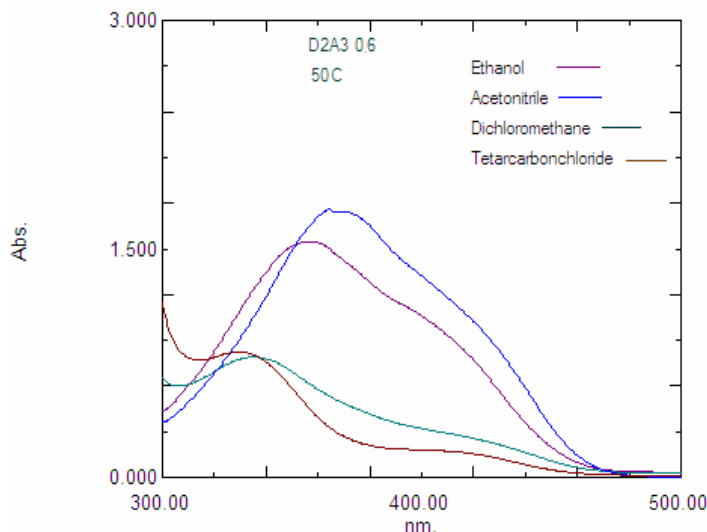


Fig. 5 – absorption spectrum donor compound D₂ [$C = 0.2 \times 10^{-3}$, 0.5×10^{-3} , 0.8×10^{-3} , 1.2×10^{-3} M] compound with the acceptor A₃ [0.5×10^{-4} M] in acetonitrile at temperature [50°C].

Determination of ionization potentials of the donor

The ionization potentials of the donor (ID) in the charge transfer complexes are calculated using empirical equation derived by Aloisi and Pignataro:²¹

$$IP (eV) = a + b \nu_{CT}$$

where a and b is constants take the values of 4.39 and 0.85,²² 5.156, and 0.778²³ and 5.11 and 0.701²⁴ and compensation for the values of a and b in the case of Picric Acid (A₃) becomes the equation as follows:

$$IP (eV) = 5.76 + 1.53 \times 10^{-4} \nu_{CT}$$

In the case of A₁ and A₂ is the equation as follows:

$$IP (eV) = 4.89 + 0.78 \times 10^{-4} \nu_{CT}$$

where ν_{CT} is the wave number in cm^{-1} of the complex,²¹ which was determined in different solvents, viz, carbon tetrachloride, dichloromethane, and ethanol. The values of ionization potentials (IP), of the studied complexes increase with temperature in all the systems studied, where values ranged between 9.923-9.963 eV for the compound with D₁ A₃ in ethanol. It is also affected by the solvent polarity.

Determination of oscillator strength (f) and transition dipole moment (μ)

From the CT absorption spectra, one can extract oscillator strength. The oscillator strength f is estimated using the formula:

$$f = 4.32 \times 10^{-9} \int \epsilon_{CT} d\nu$$

where $\int \epsilon_{CT} d\nu$ is the maximum extinction coefficient of the band and $\Delta\nu_{1/2}$ is the half-width, *i.e.*, the width of the band at half the maximum extinction. To a first estimate gives the following formula:²¹

$$f = 4.32 \times 10^{-9} \epsilon_{CT} \Delta\nu_{1/2}$$

The observed oscillator strengths of the CT bands and the values of the power of the oscillation (f) to the absorption of Charge Transfer Complexes are summarized in Table 3. These values were found to be affected by temperature and often values in polar solvents is higher than in non-polar solvents in D₁ with A₂, we find that the value of (f) in ethanol 40.88, in carbon tetrachloride 3.520, and with the acceptor compounds was A₃ value (f) 24.834 and 17.295 in ethanol in carbon tetrachloride, where the value of the power oscillation (f) is increasing with the increase in the dielectric constant.

The relatively high values (f) refer to the strong interaction between the parts of the donor and the acceptor. This also supports the small energy CT values and high values of dissociation energy (W).²⁵

Molar absorption coefficient associated with the determination of the transition dipole. Where $\Delta\nu \approx \nu$ at ϵ_{CT} and values transition dipole (μ) was determined for, absorption Charge Transfer Complexes in CT Tables (4-7).

Table 3

The spectral functions of the compound with the donor D₁ acceptor A₁, A₂ in the presence of some different polar solvent at different temperatures

Acc.	Solvent	Temp. (C)	$\nu^{1/2} \times 10^4$ (cm-1)	f	μ	IP	
A ₁	Ethanol	20	15.385	3.069	17.177	6.595	
		30	16.393	2.954	16.842	6.597	
		40	16.949	2.794	16.361	6.599	
		50	17.391	2.093	14.152	6.601	
	Acetonitrile	20	16.807	3.683	18.919	6.614	
		30	16.260	3.523	18.494	6.616	
		40	16.000	3.400	18.158	6.619	
		50	16.000	3.322	17.939	6.621	
	dichloromethane	20	15.748	2.872	16.709	6.593	
		30	16.000	2.781	16.424	6.597	
		40	15.625	2.710	16.202	6.604	
		50	16.129	2.862	16.641	6.606	
	Carbon tetrachloride	20	14.925	2.506	15.617	6.595	
		30	16.129	2.659	16.067	6.599	
		40	15.873	2.567	15.753	6.601	
		50	16.393	2.591	15.816	6.602	
	A ₂	Ethanol	20	74.074	40.880	59.563	6.612
			30	64.516	35.129	55.146	6.614
			40	60.606	32.324	52.867	6.619
			50	57.143	29.828	50.660	6.633
Acetonitrile		20	55.556	10.745	32.157	6.799	
		30	57.143	10.475	31.732	6.804	
		40	62.500	11.343	32.966	6.806	
		50	80.000	13.861	36.302	6.816	
dichloromethane		20	15.504	2.305	14.953	6.614	
		30	16.000	2.334	15.037	6.618	
		40	16.129	2.314	14.964	6.619	
		50	17.094	2.447	15.364	6.621	
Carbon tetrachloride		20	18.349	3.520	18.394	6.599	
		30	17.094	3.189	17.490	6.601	
		40	17.241	3.216	17.554	6.602	
		50	17.857	3.264	17.675	6.608	

Table 4

The spectral functions of the compound with the donor D₁ A₃ in the acceptor and there are some different polar solvent at different temperatures

Solvent	Temp. (C)	$\nu_{1/2} \times 10^4$ (cm ⁻¹)	<i>f</i>	μ	I _P
Ethanol	20	14.184	24.834	44.032	9.923
	30	14.599	24.720	43.902	9.929
	40	14.184	23.784	42.915	9.958
	50	13.986	23.218	42.373	9.963
Acetonitrile	20	14.706	23.284	42.112	10.028
	30	15.625	24.261	42.925	10.040
	40	13.889	21.123	40.026	10.046
	50	14.815	22.108	40.919	10.052
dichloromethane	20	90.909	13.053	35.520	9.123
	30	86.957	15.836	39.104	9.126
	40	39.216	6.271	24.594	9.130
	50	32.258	6.223	24.472	9.137
Carbon tetrachloride	20	23.529	17.295	35.887	10.125
	30	25.974	17.418	35.860	10.163
	40	27.027	16.836	35.001	10.227
	50	31.746	18.865	36.996	10.240

Table 5

The spectral functions of the compound with the donor D₂ acceptor A₁, A₂ in the presence of some different polar solvent at different temperatures

Acc.	Solvent	Temp. (C)	$\nu_{1/2} \times 10^4$ (cm ⁻¹)	<i>f</i>	μ	I _P
A ₁	Ethanol	20	74.074	26.076	42.333	7.272
		30	76.923	22.168	39.002	7.275
		40	76.923	19.190	36.260	7.286
		50	80.000	18.030	35.119	7.29
	Acetonitrile	20	50.000	15.618	32.964	7.301
		30	48.780	14.574	31.819	7.305
		40	46.512	14.878	32.076	7.309
		50	47.619	15.010	32.192	7.312
	dichloromethane	20	111.111	35.130	49.288	7.271
		30	90.909	28.496	44.357	7.275
		40	105.263	32.263	47.161	7.279
		50	133.333	37.691	50.934	7.283

Acc.	Solvent	Temp. (C)	$\nu_{1/2} \times 10^4$ (cm ⁻¹)	<i>f</i>	μ	<i>I_p</i>
A₂	Carbon tetrachloride	20	55.556	16.636	34.022	7.286
		30	54.054	14.753	32.014	7.29
		40	54.054	16.589	33.922	7.294
		50	51.282	15.117	32.357	7.297
	Ethanol	20	90.909	43.153	61.046	6.587
		30	83.333	38.740	57.698	6.593
		40	80.000	36.862	56.247	6.597
		50	76.923	35.843	55.361	6.601
	Acetonitrile	20	16.807	3.628	18.819	6.809
		30	16.260	3.514	18.490	6.818
		40	16.000	3.469	18.353	6.821
		50	16.000	3.481	18.363	6.828
	dichloromethane	20	15.748	2.771	16.411	6.548
		30	16.000	2.806	16.505	6.560
		40	15.625	2.742	16.307	6.567
		50	16.129	2.870	16.664	6.569
	Carbon tetrachloride	20	14.925	2.382	15.429	6.595
		30	16.129	2.530	15.845	6.597
		40	15.873	2.482	15.660	6.599
		50	16.393	2.545	15.846	6.602

Table 6

The spectral functions of the compound with the donor D₂ A₃ in the acceptor and there are some different polar solvent at different temperatures

Solvent	Temp. (C)	$\nu_{1/2} \times 10^4$ (cm ⁻¹)	<i>f</i>	μ	<i>I_p</i>
Ethanol	20	12.270	21.420	40.922	9.918
	30	12.658	19.961	39.477	9.923
	40	12.500	20.411	39.757	9.958
	50	12.270	20.164	39.488	9.963
Acetonitrile	20	12.739	20.279	39.135	10.064
	30	12.346	19.470	38.320	10.070
	40	12.346	19.547	38.368	10.076
	50	12.346	18.119	36.914	10.082
dichloromethane	20	71.429	53.981	61.47	10.403
	30	74.074	54.129	61.509	10.410
	40	80.000	57.771	63.496	10.418
	50	64.516	47.010	57.234	10.425
Carbon tetrachloride	20	22.727	19.419	37.535	10.240
	30	25.316	19.980	38.045	10.247
	40	28.986	21.216	38.974	10.300
	50	32.258	22.705	40.168	10.334

Table 7

The spectral functions of the compound with the donor D₃ acceptor A₂, A₃ in the presence of some different polar solvent at different temperatures

Acc.	Solvent	Temp. (C)	$\nu_{1/2} \times 10^4$ (cm ⁻¹)	<i>f</i>	μ	I _p	
A ₂	Ethanol	20	100.000	53.563	67.929	6.587	
		30	95.238	50.452	65.845	6.616	
		40	76.923	40.027	58.576	6.619	
		50	76.923	41.484	59.485	6.635	
	Acetonitrile	20	55.556	9.898	31.085	6.814	
		30	57.143	9.961	30.927	6.818	
		40	62.500	10.836	32.222	6.823	
		50	80.000	13.792	36.190	6.833	
	dichloromethane	20	15.504	2.284	14.851	6.606	
		30	16.000	2.374	15.131	6.614	
		40	16.129	2.409	15.236	6.619	
		50	17.094	2.578	15.752	6.627	
	Carbon tetrachloride	20	18.349	3.270	17.770	6.606	
		30	17.094	3.080	17.208	6.608	
		40	17.241	3.141	17.348	6.610	
		50	17.857	3.340	17.849	6.612	
	A ₃	Ethanol	20	17.544	30.247	48.727	9.901
			30	17.391	29.468	47.998	9.918
			40	17.094	28.339	47.038	9.923
			50	16.260	28.803	47.389	9.929
Acetonitrile		20	27.397	42.154	56.582	10.040	
		30	27.027	42.527	56.792	10.046	
		40	25.974	39.753	54.870	10.052	
		50	26.316	39.377	54.572	10.058	
dichloromethane		20	64.516	24.554	45.907	9.547	
		30	80.000	24.948	46.216	9.557	
		40	58.824	16.503	37.542	9.566	
		50	51.282	12.124	32.058	9.595	
Carbon tetrachloride		20	48.780	44.513	57.531	10.131	
		30	100.000	83.861	78.400	10.195	
		40	95.238	78.876	74.812	10.341	
		50	133.333	112.448	89.258	10.348	

These values are affected by temperature and values are often high in polar solvents compared to non-polar solvents, in the compound with the acceptor donor D₁ A₁ values were 17.177 in ethanol and in carbon tetrachloride with 15.617

and A₂ amounted to 42.333 and 34.022 in ethanol in carbon tetrachloride.

Determination of standard free energy changes (ΔG^*), and transition energy, (ECT) of the π - π^* interaction between donor and acceptor.

Table 8

Energy complex values ($h\nu_{CT}$) CT corresponding to a frequency band higher wavelength (ν_{max}), wave number (ν'), transition Energy E_T , Molar transition energy (Z-Val.), Refractive Index $f(n)$, and Dielectric constant electrical $f(D)$ of the donor compound D_1 with acceptors A_1, A_2 in the presence of some of the various polar solvents

Acc	Solvent	Tem (C)	λ (nm)	$h\nu_{CT}$ (eV)	$\nu_{max} \times 10^{14}$ (s ⁻¹)	$\nu' \times 10^3$ (cm ⁻¹)	E_T (cal.K.mol ⁻¹)	Z-Val. $\times 10^{-4}$ (cal.K.mol ⁻¹)	f(n)	f(D)
A ₁	Ethanol	20	457.5	2.708	6.553	21.858	61.836	61.768	1.36	24.55
		30	457	2.711	6.560	21.882	61.904	61.836		
		40	456.5	2.714	6.567	21.906	61.971	61.904		
		50	456	2.716	6.575	21.930	62.039	61.971		
	Acetonitrile	20	452.5	2.738	6.625	22.099	62.519	62.451	1.34	37.5
		30	452	2.741	6.633	22.124	62.588	62.520		
		40	451	2.747	6.647	22.173	62.727	62.659		
		50	450.5	2.750	6.655	22.198	62.797	62.728		
	Carbon dichloromet thane	20	458	2.705	6.546	21.834	61.769	61.701	1.42	8.93
		30	457	2.711	6.560	21.882	61.904	61.836		
		40	455	2.722	6.589	21.978	62.176	62.108		
		50	454.5	2.725	6.596	22.002	62.244	62.176		
	Carbon tetrachloride	20	457.5	2.708	6.553	21.858	61.836	61.768	1.46	2.24
		30	456.5	2.714	6.567	21.906	61.972	61.904		
		40	456	2.716	6.575	21.930	62.039	61.971		
		50	455.5	2.719	6.582	21.954	62.108	62.040		
A ₂	Ethanol	20	453	2.734	6.618	22.075	62.450	62.382	1.36	24.55
		30	452.5	2.738	6.625	22.099	62.519	62.451		
		40	451	2.747	6.648	22.172	62.727	62.659		
		50	447.5	2.768	6.699	22.346	63.218	63.149		
	Acetonitrile	20	408.5	3.032	7.339	24.480	69.253	69.177	1.34	37.5
		30	407.5	3.040	7.357	24.540	69.423	69.347		
		40	407	3.044	7.366	24.570	69.509	69.432		
		50	405	3.059	7.402	24.691	69.852	69.775		
	Dichloromethane	20	452.5	2.738	6.625	22.099	62.519	62.451	1.42	8.93
		30	451.5	2.744	6.640	22.148	62.658	62.589		
		40	451	2.747	6.647	22.172	62.727	62.659		
		50	450.5	2.750	6.655	22.197	62.797	62.728		
	Carbon tetrachloride	20	456.5	2.714	6.567	21.906	61.972	61.904	1.46	2.24
		30	456	2.716	6.574	21.930	62.039	61.971		
		40	455.5	2.719	6.582	21.954	62.108	62.040		
		50	454	2.728	6.604	22.026	62.313	62.244		

The standard free energy changes of complexation (ΔG^*) were calculated from the association constants by the following equation derived by Martin *et al.*²⁶

$$\Delta G^* = -RT \ln K_{CT}$$

where ΔG^* is the free energy change of the complexes (kJ mol^{-1}), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature in Kelvin degrees ($273 + ^\circ\text{C}$) and K_{CT} is the association constant of the complexes (l mol^{-1}) in different solvents at room temperature.

The (K_{CT}) and ΔG^* values obtained are given in Table (8) values obtained for each ϵ and K_{CT} , with increasing temperature and that of the compound per donor. Where the results of experiments for the interaction of donor compound with acceptor compound using different solvents showed that the values of constant formation K_{CT} increases with temperature, for example, the values of the K_{CT} donor compound D_1 with acceptor compound A_1 in ethanol at 293K $1.825 \times 10^3 \text{ L mol}^{-1}$, with high temperature 303K $1.876 \times 10^3 \text{ L mol}^{-1}$ and raised to $1.915 \times 10^3 \text{ L mol}^{-1}$ at 313K and its value was $2 \times 10^3 \text{ L mol}^{-1}$ which explains that the high temperature leads to activate portability ions on to polarization in the solution ($D\delta^+ \cdots A\delta^-$) (polar ability of ions in solution) leading to increased ions combine with each other, and that their large size, which requires ϵ K_{CT} values increase with rising temperature and indicates the stability of charge Transfer Complexes. As the high values of constants K_{CT} assembly refers to the bonding strength between the donor and acceptor greater stability for the output complex.²⁷

Determination energy (E_{CT}), of the π - π^* interaction between donor and acceptor:

Transition energy (E_{CT}) was calculated for transfer's π - π^* between the donor thiophene and the acceptor 2,4-dinitrophenol (A_2) using the following equation:

$$E_T (\text{K Cal mol}^{-1}) = 2.829 \times 10^{-3} \nu (\text{cm}^{-1})$$

As well as the calculated molar transition energy (Z) from the relationship:

$$Z = \frac{2.8259}{\lambda_{(nm)}} (\text{K Cal mol}^{-1})$$

The results recorded in Table (8), and noted that the values of the energy transition (E_{CT}) and Energy Jump molar (Z) increase with the temperature as they are affected by the nature of the solvent used depending on the spectral properties of the precise solvent.

Effect of solvents on the formation of CT complexes

Spectroscopic properties were markedly affected by the variation in solvent polarity in which measurements were carried out. In the present investigation the K_{CT} values increase significantly from methanol to carbon tetrachloride with decreasing solvents polarity. Moreover, the increase in K_{CT} values with decreasing solvents polarity, may also be due to the fact that, CTC should be stabilized in non-polar solvent.²⁸⁻²⁹ Dissociation of the complexes into $D^+ \cdots A^-$ radicals have been found to occur in the ground state.³⁰ It means the CTC should be strong in non-polar solvent than polar solvent. The red shift occurred in CTC complex caused by polarity change on going from carbon tetrachloride to ethanol. The spectral properties that have been measured are significantly affected as a result of differing polarity of the solvent. It was observed that the values of K_{CT} of complex formed between D_1 and A_1 increased clearly from ethanol to carbon tetrachloride with low polarity solvent, where the value of is K_{CT} equal to $1.825 \times 10^3 \text{ L mol}^{-1}$, $2.5 \times 10^3 \text{ L mol}^{-1}$, $2.833 \times 10^3 \text{ L mol}^{-1}$ where the decomposition complexes occurs to incisions $D^+ \cdots A^-$ in stable state (3). This means that the Charge transfer Complexes are stronger in a non polar solvent than in polar solvent. Polar solvents are highly effective in the separation (blocking ions for some of them) forces of attraction and repulsion between ions shall be weak and dependent on polarity of the solvent and the value of the dielectric constant electrical complexes which has fixed isolate electrical equal to 15 or higher be solvent polarity and that have a fixed dielectric constant less 15 are non-polar solvents, while the results of experiments for the interaction of compound donor D_1 with the acceptor A_2 using different solvents showed that the values of a formation stability, $2.793 \times 10^3 \text{ K}_{CT} \text{ L mol}^{-1}$ in ethanol, $20 \times 10^3 \text{ L mol}^{-1}$ in acetonitrile, $2.457 \times 10^3 \text{ L mol}^{-1}$ in the dichloromethane and $4.854 \times 10^3 \text{ L mol}^{-1}$ in carbon tetrachloride. Notes that there has been a change to the values of formation constant solvent change but there is no clear relationship with the solvent properties of solvent (33). But the results for the interaction of compound donor D_1 with the acceptor A_3 using different solvents showed that the values of a formation constant, 142 K_{CT} , $857 \times 10^3 \text{ L mol}^{-1}$ in ethanol, $16.667 \times 10^3 \text{ L mol}^{-1}$ in acetonitrile, $14.706 \times 10^3 \text{ L mol}^{-1}$ in dichloro methane and $2.488 \times 10^3 \text{ L mol}^{-1}$ in carbon

tetrachloride, and here shows that the values of K_{CT} increases with polar solvent as the increased polarity of the medium increases the amount of transmitted complex from the donor compound to the acceptor compound as a result of the increasing overlap between the association of dipolar solvent each of donor compound and acceptor compound and accordingly increase values K_{CT} . And impartiality on this phenomenon is sometimes due to the large molecules of both the donor and the acceptor, which in turn increases the distance between the molecular charge on both of them ($D\delta^{+} \cdots A\delta^{-}$) leading to incompatibility K_{CT} values with polar solvents sometimes. In the donor compound D_2 and with all the receptors, there was no clear relationship with the properties of the solvent. In the donor compound D_3 and with A_2 there was no clear relationship with the properties of the solvent and with acceptor A_3 the values of K_{CT} increase as the solvent polarity increases where the values are as follow: $19.231 \times 10^3 \text{ L mol}^{-1}$ acetonitrile, $15.385 \times 10^3 \text{ L mol}^{-1}$ ethanol, $20.833 \times 10^3 \text{ L mol}^{-1}$ dichloro methane, $2.506 \times 10^3 \text{ L mol}^{-1}$ carbon tetrachloride. Formation of constant values is different for all compounds per solvent due to the molecular structure nature of compounds, which play the key role in determining the values of formation constant. In the current research, the values of K_{CT} increase significantly from ethanol to acetonitrile solvent with low polarity. Overall, the increase in the values of with K_{CT} low polarity of the solvent may also lead to the fact that the Charge Transfer Complexes are stable in low-polar solvents. This means that the Charge Transfer Complexes are stronger in low polar solvents compared to the polar solvent. Complex dissociation to radicals A- and D + is happening in the Ground State (3) this means that the Charge Transfer Complexes are stronger in low polar solvents compared to the polar solvent. Red shift in Charge Transfer Complexes is due to the changing polarity by using acetonitrile to ethanol. Overall, picric acid is powerful and strong receptors form complexes in all the different solvents. The molar absorption coefficient E shows that of complexes in all systems generally decrease at high temperature and slight differences can be observed for both molar absorption and temperature. It was also observed that the values of absorption coefficient molar of a compound D_1 with receptors three A_1 , A_2 and A_3 increases with dielectric constant for the medium, reaching the value of absorption molar $46.18 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$, $127.75 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $405.27 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$ in

acetonitrile with acceptor compounds A_1 , A_2 and A_3 , respectively reaching the value of absorption molar $81.49 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$, $109.88 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $404.11 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$ in acetonitrile with acceptor compounds A_1 , A_2 and A_3 respectively. Also in the donor compound D_3 increases with dielectric constant to compromise with acceptors A_2 and A_3 , where the value of the absorption molar $123.99 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $399.09 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$ in acetonitrile with acceptor compounds A_2 and A_3 on, respectively Also in the donor compound D_3 increases with dielectric constant to compromise with acceptors A_2 and A_3 , where the value of the absorption molar coefficient $123.99 \times 10^2 \text{ mol}^{-1}$.

Spectrophotometric study of formation constants of the charge transfer complexes $D_1 / A_1, A_2, A_3$ in different solvents

Stoichiometries and the formation constants of the charge transfer complex D_1 with A_1 , A_2 , and A_3 have been determined in different solvents, viz., carbon tetrachloride, dichloromethane, acetonitrile, and ethanol at four temperatures using Benesi-Hildebrand equation.²⁷⁻²⁸ The spectrophotometric data were employed to calculate the values of formation constants, K_{CT} of the complex. The changes in the absorbance upon addition of D_1 to a solution of A_1 , A_2 , A_3 of different concentration follow the Benesi-Hildebrand²⁷⁻²⁸ equation in the form:

$$[A] + [D] = \frac{\epsilon L [A][D]}{d} - \frac{1}{K_{CT}} \quad (5)$$

where $[A]$ and $[D]$ are initial molar concentration of the acceptor and donor, respectively, L the length of light path in cm, and d the optical density. The values of (K_{CT}) and ϵ are determined from the gradient and the negative intercept of the linear plot of $[A] + [D]$ against $[A][D]/d$ Fig. 6 in which both ϵ and (K_{CT})^{22, 30} were evaluated. The Benesi-Hildebrand²⁷⁻²⁸ method is an approximation that has been used many times and gives decent results. But the extinction free species that absorbs at the same wavelength. The intensity in the visible region of the absorption bands, measured against the solvent as reference, increases with increase in the polarity and addition of PTD. The typical absorbance data for charge transfer complexes of D_1 with A_1 , A_2 , and A_3 in different solvents at four temperatures are reported in Fig6. In all systems

very good linear plots according to Eq. (5)²⁷⁻²⁸ are obtained, the linear plot of $[A] + [D]$ in carbon tetrachloride is shown in Fig. 7. Formation

constants for the complex in different polar solvents at four different temperatures (20, 30, 40, 50 °C).

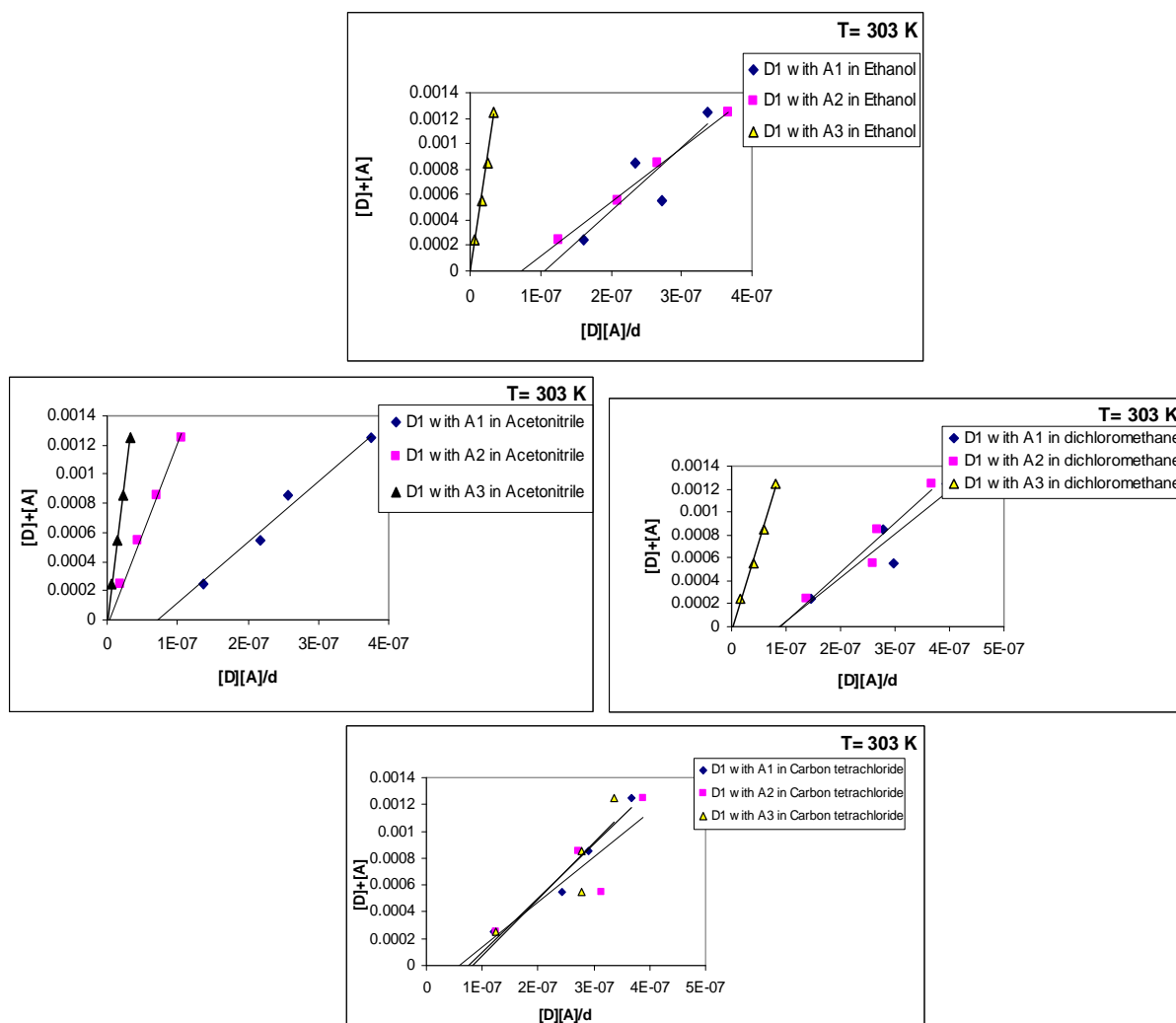


Fig. 6 – The relationship between the graphs $[A] + [D]$ versus $[A][D] / d$ as an application of the equation Bensi-Hildebrand revised donor compound D_1 receptors with three A_1, A_2, A_3 in different solvents at four different temperatures.

Table 9

Molar extension coefficient (ϵ) formation constant (K_{CT}), and thermodynamic parameters (ΔG , ΔH , ΔS) for donor compound D_2 with the different recipients in ethanol, acetonitrile, dichloro methane and carbon tetrachloride at four different temperatures

solvent	Acc.	T (K)	$\epsilon \times 10^2$ ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	$K_{CT} \times 10^3$ ($l \text{ mol}^{-1}$)	$\Delta G \times 10^2$ - (kJ. mol^{-1})	$\Delta H \times 10^2$ (kJ. mol^{-1})	ΔS ($\text{kJ. mol}^{-1} \text{ K}^{-1}$)
Ethanol	A_1	293	72.31	2.833	193.64	101.36	101.14
		303	69.16	3.663	206.72		
		313	74.05	4.065	216.25		
		323	72.96	4.184	223.94		
	A_2	293	49.97	1.667	180.72	38.00	74.92
		303	50.02	1.898	190.15		
		313	50.19	1.919	196.73		
		323	50.36	1.946	203.38		
	A_3	293	368.50	19.231	240.29	158.89	135.71

solvent	Acc.	T (K)	$\epsilon \times 10^2$ ($\text{l mol}^{-1}\text{cm}^{-1}$)	$K_{CT} \times 10^3$ (l mol^{-1})	$\Delta G \times 10^2$ - (kJ. mol^{-1})	$\Delta H \times 10^2$ (kJ. mol^{-1})	ΔS ($\text{kJ. mol}^{-1} \text{K}^{-1}$)	
Acetonitrile		303	365.07	20.408	249.99			
		313	366.50	27.027	265.55			
		323	339.73	34.483	280.58			
		323	380.41	25.000	271.94			
	A ₁	293	81.49	2.500	190.59	356.85	185.98	
		303	66.71	3.333	204.35			
		313	57.75	5.000	221.64			
	A ₂	323	52.17	10.000	247.34			
		293	109.88	16.667	236.81	281.79	177.01	
		303	107.61	25.000	255.10			
		313	106.66	33.333	271.01			
	A ₃	323	107.86	50.000	290.56			
		293	404.11	14.286	233.05	145.99	129.19	
		303	365.02	16.667	244.89			
		313	377.99	20.000	257.72			
Dichloromethane	A ₁	293	69.32	2.967	194.77	80.63	93.99	
		303	63.18	3.650	206.63			
		313	71.04	2.985	208.22			
		323	68.24	4.484	225.80			
	A ₂	293	36.94	3.030	195.28	47.38	82.93	
		303	36.32	3.356	204.51			
		313	36.20	3.460	212.06			
		323	35.93	3.663	220.37			
	A ₃	293	197.79	12.048	228.90	295.79	178.34	
		303	182.69	15.385	242.87			
		313	169.43	20.833	258.78			
		323	162.93	38.462	283.51			
	Carbon tetrachloride	A ₁	293	73.19	3.546	199.11	78.24	94.31
			303	72.56	3.610	206.36		
			313	70.95	4.016	215.94		
323			65.44	4.785	227.54			
A ₂		293	40.73	3.135	196.11	32.41	78.10	
		303	40.60	3.333	204.35			
		313	40.62	3.571	212.89			
		323	41.18	3.509	219.21			
A ₃		293	174.94	20.000	241.25	125.51	124.98	
		303	169.15	23.256	253.28			
		313	167.16	25.000	263.52			
		323	168.67	33.333	279.67			

Effect of different solvents polarity on charge transfer complexes

Microscopic solvents polarity parameters

The first empirical parameters is the so called Z_{value} introduced by Kosower^{31,32} who was the first to set up comprehensive scale for solvent polarity. He termed the molar transition energy calculated from the position of the absorption maximum, Z -value:

$$Z - \text{Val.} = \frac{2.8259}{\lambda_{(nm)}} \text{ (K Cal.mol}^{-1}\text{)}$$

Reichardt and Dimroth^{33, 34} applied Kosower's technique to a series of pyridinium-N-phenol betamine which are perhaps the most solvent dependent spectra known. The molar transition energies of the betamines termed E_T value can be calculated using the following relation:

$$E_T = 2.829 \times 10^{-3} \bar{\nu}$$

Table 10
Effect of different solvents polarity on charge transfer complexes

Solvent	Temp (C)	λ (nm)	E_{CT} (eV)	E_T (cal.K.mol-1)	Z-Val. $\times 10^{-4}$ (cal.K.mol-1)	f(n)	f(D)
Ethanol	20	358.5	3.455	78.912	78.826	0.18	0.94
	30	357.5	3.465	79.133	79.046		
	40	357	3.470	79.244	79.157		
	50	356.5	3.475	79.355	79.268		
Acetonitrile	20	367.5	3.371	76.980	76.895	0.17	0.96
	30	367	3.375	77.084	77.000		
	40	364.5	3.398	77.613	77.528		
	50	364	3.403	77.720	77.635		
Dichloromethane	20	350.5	3.534	80.713	80.625	0.2	0.84
	30	347.5	3.565	81.410	81.321		
	40	342.5	3.617	82.599	82.508		
	50	341.5	3.627	82.840	82.750		
Carbon Tetrachloride	20	455	2.722	62.176	62.108	0.22	0.45
	30	454.5	2.725	62.244	62.176		
	40	454	2.728	62.313	62.244		
	50	453	2.734	62.450	62.382		

Macroscopic solvents polarity parameters

Solvent properties which show reasonable degree of correlation with the transition energy are the dielectric constant (D) and the refractive index (n). The more precise relations are the functions of dielectric constant given by Suppan³⁵ in the following form:

$$F(n) = (n^2 - 1) / (2n^2 + 1)$$

So, it is clear that the macroscopic solvent polarity parameters are not the main factors affecting the position of the CT band, it is more possible to suggest that some sort of specific solute-solvent interaction (solvating or more effectively hydrogen bonding between solute and solvent molecules) may also contribute to the solvent shift. Hence, the shift in CT band position is actually the resultant effect of, the excited state since this would be a more polar structure. (i) the changed solvent polarity, (ii) the shift due to intermolecular hydrogen bond formed between solvent molecules and OH or most probably the -CH=N- group and (iii) the shift due to intermolecular hydrogen bonding. It must be also noted that red shift of the CT band with increased

solvent polarity denotes the increased solvent stabilization of the excited state since this would be a more polar structure.

CONCLUSIONS

The effect of some different polar organic solvents such as ethanol, acetonitrile, dichloromethane and carbon tetrachloride has been studied on the absorption electronic spectrum of the Schiff base compounds at four different temperatures (20,30,40,50 °C) by changing the concentration of donor compounds (0.2-1.2 $\times 10^{-3}$ M) and stabilizing the concentration of acceptor compound (0.5 $\times 10^{-4}$ M). It was found that the absorption is directly proportional to the concentration and temperature. We also calculated K_{CT} , ϵ and some thermodynamic parameters (ΔG° , ΔH° and ΔS°), for Schiff base compounds and we found out that the values of K_{CT} are directly proportional with the increase in temperature. The stability of CT compounds increased relatively with increasing polar solvents also ϵ values decreased with increasing temperatures. It was noted that the negative signal of ΔG° values calculated for the formed CT compounds in all

solvents showed that the combine of CT between the donor and acceptor are spontaneous calculated for these compounds. Conversely accompanied positive values ΔH° and ΔS° for these compounds. In contrast it was accompanied by positive enthalpy values which showed that the reactions were endothermic. It was also noted that the entropy values indicated that the system moves at irregularly.

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