

Spectroscopic and Thermodynamic Studies of Charge- Transfer Complexes Formation Between Cytosine, Uracil and Thymine With Electronic Acceptors

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Abstract

Charge-transfer complexes of 2, 3-dichloro-5, 6-dicyano-1, 4-benzo quinone (DDQ), 2, 3, 5, 6-tetrabromo-1, 4-benzoquinone (Bromanil) and iodine as electronic acceptors with cytosine, uracil and thymine as electronic donors were studied and their electronic spectra were recorded. In each case one charge-transfer (CT) band was observed and recorded. These spectroscopic investigation make in ethanol solvent at four different temperatures (20, 25, 30 and 35°C). The values of equilibrium constant (K_{CT}), molar extinction coefficient (ϵ_{CT}), absorption band energy of charge – transfer complexes ($h\nu_{CT}$) and the dissociation energy of the charge- transfer complexes excited state (W) were calculated and studied with discussed. The ionization potential of the donors (I_p) were calculated and discussed from the charge-transfer complex band lowest energy. Thermodynamic parameters i. e. change in standard free energy (ΔG°), change in standard entropy (ΔS°) and change in standard enthalpy (ΔH°) for all these CT complexes were also calculated and discussed.

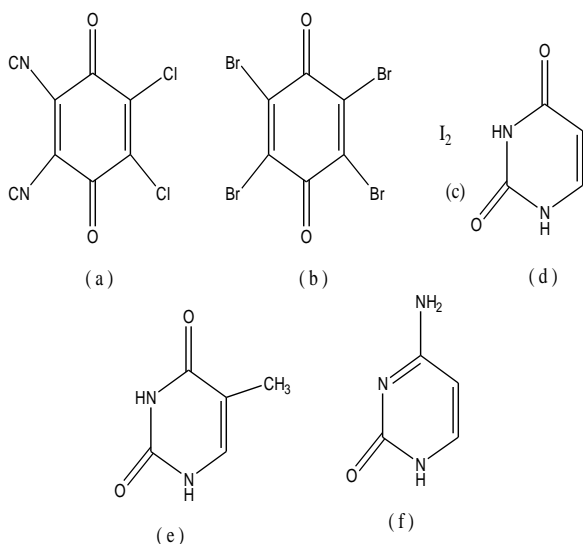
Introduction

Certain aromatic hydrocarbons, amines, phenols etc., when mixed with nitro compounds, quinones, carboxylic acids, sulfonic acids, halogens. 2, 5-dihydroxy-p-benzoquinone, 2-hydroxy-1, 4-naphthoquinone and tetracyanoquinodimethane formed intensely colored molecular complexes [1-4]. The formation of charge-transfer (CT) complexes may be proved by the study of associated characteristic abrupt changes from ideal behavior in certain physical properties [5]. These properties include melting point, vapor pressure, viscosity, surface tension, dielectric constants and refractive index. Mullikan has developed the theory of intermolecular interaction, which has been applied successfully to the interpretation of the UV absorbance band characteristics of molecular complexes in various system[6]. The pyrimidine from charge – transfer complexes with organic acceptors although in some cases, these may convert quite rapidly to chemical compounds. The weak complexes formed with aromatic hydrocarbons are stabilized in part by charge-transfer forces [7]. The calculation and spectroscopic studies showed that pyrimidine are electron donors that can enter into charge-transfer interactions with suitable electron acceptors [8-10].

In the present work, spectrophotometer studies have been carried out for charge-transfer complexes of each one DDQ, Bromanil and iodine with uracil, cytosine and thymine in ethanol solvent at four different temperatures (20, 25, 30, and 35°C). The equilibrium constant of charge-transfer complex (K_{CT}), molar extinction coefficient of CT complex (ϵ_{CT}), absorbance band energy of CT complex ($h\nu_{CT}$), dissociation energy of CT complex excited state (W) and ionization potential of the donors (I_p) were calculated. The thermodynamic parameters (ΔG°), (ΔS°) and (ΔH°) of CT complexes formation from donors and acceptors were also calculated.

Experimental

Ethanol solvent was (AnalaR) of “BDH”, Acceptors and donors used were 2, 3-dichloro-5, 6-dicyano-1, 4-benzoquinone (DDQ) of “Fluka” of purity greater than 98%, and 2, 3, 5, 6-tetrabromo-1-4- benzoquinone (Bromanil) (G. R) of “BDH” and iodine (pure) of “BDH”, uracil and cytosine (puriss) of “Fluka” and thymine (G. R) of “BDH”. All donors and acceptors were used without further purification (shown in Scheme (I))

**Scheme (I)****Representative structures of compounds**

(a) *DDQ*, (b) *Bromanil*, (c) *Iodine* (d) *Uracil*,
(e) *Thymine* and (f) *Cytosine*.

Varian DMS 100 UV-Visible spectrophotometer was used to record the electronic spectra using 1 cm quartz absorption cell. The CT complexes of bases of uracil, thymine and cytosine were investigated with DDQ acceptor in ethanol solvent spectrophotometrically at wavelength maximum (λ_{\max}) of the complex. This limited work is done for the future since the CT complexes of bases with the electronic acceptor were investigated for first time in this study. The measurements of the optical density of CT complexes at their (λ_{\max}) were done directly from the preparation of the complexes at four different temperature (20,25,30 and 35°C). The concentration of acceptor being kept constant in all solutions.

Results and Discussion

The acceptors DDQ and Bromanil form a light yellow solutions, iodine forms a light violet solution in the ethanol solvent, whereas all the donors form colorless solutions. Wavelengths of absorbed maximum (λ_{\max}) and molar extinction coefficients values of donor or acceptor (ϵ) and (ϵ_{CT}) for CT complex in ethanol solvent were determined and summarized in Table (1). DDQ is strong acceptor having electron affinity (E_a) 1.95 eV [7,11]. On mixing solutions of acceptors with donors a distinct color change observed in ethanol solvent under study. Appearance of a new band on mixing solution of DDQ with one of the donors indicates the formation of CT

complex. Neither the donors or the acceptors alone was found to absorb in that region. Electronic spectra of CT complexes of DDQ with various donors (Figs.(1-3)) in ethanol solvent and with different temperatures were recorded and their λ_{\max} and equilibrium constant values (K_{CT}) for CT complexes are reported in Table (2). Rapson, Saunders and Stewart [12] have observed that the donor-acceptor ratio in aromatic complexes is usually one, unless two or more structurally independent coordination sites are available in donor molecule.

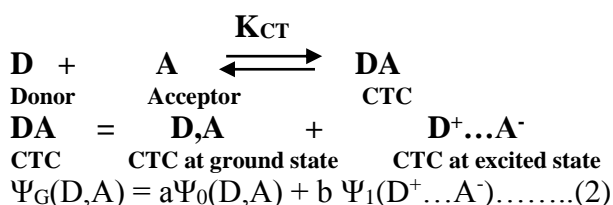
The equilibrium constants (K_{CT}) and the molar extinction coefficient of CT complexes (ϵ_{CT}) were determined using modified Benesi-Hildebrand [13] equation given as follows:

$$\frac{[DDQ] \cdot \ell}{OD_{CT}} = \frac{1}{K_{CT} \epsilon_{CT}} \cdot \frac{1}{[D^{\circ}]} + \frac{1}{\epsilon_{CT}} \dots \dots \dots (1)$$

Where $[DDQ]$ = initial concentration of DDQ as electron acceptor, ℓ = the path length of light for absorption cell ($L=1\text{cm}$), OD_{CT} = optical density of CT complex, $[D^{\circ}]$ = initial concentration of electron donor, K_{CT} = equilibrium constant of CT complex in solution and ϵ_{CT} = molar extinction coefficient of CT complex.

Values of K_{CT} and ϵ_{CT} are calculated from equation (1) by varying the concentration of donor concentration $[D^{\circ}]$ and keeping concentration of acceptor $[DDQ]$ such that $[D^{\circ}] \gg [DDQ]$. The plot of ($[DDQ]/OD_{CT}$) vs. ($1/[D^{\circ}]$) is given in Figures(4 – 6). Molar extinction coefficients and equilibrium constants were calculated from the intercept and slope of these plot.

According to Mulliken theory [6] Wave function of the ground state (1:1) complex is described as follows:



and that of first excited state as follows:

$$\Psi_E(\text{D}^+ \dots \text{A}^-) = a^* \Psi_1(\text{D}^+ \dots \text{A}^-) - b^* \Psi_0(\text{D},\text{A}) \dots \dots (3)$$

Where $\Psi_0(\text{D},\text{A})$ and $\Psi_1(\text{D}^+ \dots \text{A}^-)$ are non bond and dative bond wave functions respectively

and (a, b, a* and b*) are constant physical parameters.

For weakly interaction complexes $a \gg b$, the energy of transition from ground state to excited state of CT complex can be given as follow [14,15]:

$$h\nu_{CT} = I_P - E_a - W \dots\dots\dots (4)$$

Where ($h\nu_{CT}$) is absorption band energy of CT complex, (I_P) is the ionization energy of the donor, (E_a) is the electron affinity of the acceptor and (W) is the dissociation energy of the CT complex excited state .

Foster [7] has shown that the frequency of the CT spectra were proportional to the ionization energies of the donors:

$$h\nu_{CT} = aI_P + b \dots\dots\dots (5)$$

In the present work a and b from equation (3) are equal to (a = 0.5, b = -1.69 eV) of DDQ acceptor in ethanol solvent [7,11].

The comparison of the position of absorption bands with the ionization potential of the donor was found by McConnell, Han and platt [16,17] to facilitated by a equation (6) that was linear for ionization potential between (7-13) eV.

$$h\nu_{CT} = I_P - C_1 + \frac{C_2}{I_P - C_1} \dots\dots\dots (6)$$

Where ($h\nu_{CT}$) is transition energy for CT band, (C_1 and C_2) are physical constant parameters of electron acceptor in the solvent ($C_1=0.51\text{eV}$ and $C_2=1.27\text{eV}^2$ in ethanol solvent) [7,11].

According to the equation (4) of the formation CT complexes from two acceptors with one donor, electron affinity (E_a) calculates of acceptor 1 when other values are known by the following equation (7):

$$(E_a)_1 = (E_a)_2 + (h\nu_{CT})_2 - (h\nu_{CT})_1 \dots\dots\dots (7)$$

The above equation (7) used to calculate electron affinities of iodine and Bromanil acceptors. The electronic spectrum recorded of CT complex between Bromanil as acceptor with thymine as donor and the absorption band of CT complex was recorded at (476nm) for (thymine-Bromanil) complex in ethanol solvent. The results of physical constants parameters (a,b,C₁,C₂ and E_a) of Bromanil acceptor were obtained as follow:

$$\begin{aligned} a &= 0.515 & b &= -1.78 \text{ eV} \\ C_1 &= 6.401 \text{ eV} & C_2 &= 1.302 \text{ eV}^2 \\ \text{and } E_a &= (2.07 \pm 0.03) \text{ eV} \end{aligned}$$

while the absorption band of (iodine-thymine) complex was recorded at (405 nm) in ethanol solvent, the results of physical constants parameters of iodine acceptor were obtained as follow:

$$\begin{aligned} a &= 0.602 & b &= -1.959 \text{ eV} \\ C_1 &= 5.998 \text{ eV} & C_2 &= 1.685 \text{ eV}^2 \\ \text{and } E_a &= (2.51 \pm 0.03) \text{ eV} \end{aligned}$$

The calculated electronic affinities values of Bromanil and iodine in this work were very agreeable with their values in study of Chen and Wentworth which estimate the values (2.22 ± 0.2) eV for Bromanil acceptor and (2.56 ± 0.1) eV for iodine acceptor [18].

The ratios of these complexes are (1:1), and since: (i) the lowest unoccupied molecular orbital LUMO available in DDQ and Bromanil are π^* molecular orbital and (ii) molecules of donors are very rich in n-electronic pairs, therefore the expected type of electronic transition for CT complexes from highest occupied molecular orbital HOMO in donor to LUMO in DDQ or Bromanil acceptors are the transition type ($n \rightarrow \pi^*$), while the LUMO in iodine is the (σ^*) molecular orbital, hence the expected type of electronic transition for CT complexes from HOMO in donor to LUMO in iodine is the transition type ($n \rightarrow \sigma^*$) [7,17]. The kinetic of the association of electron donors with electron acceptors have been reported in literature [7,15]. Ionization potentials were calculated by using of equations (5) and (6) as evident in Table (4), which also include determined ionization potentials values in the literatures [20–21]. All these results arrived to agreeable degree greater than 99%. The calculated ionization potentials values in this work of the donors were with average (8.155 ± 0.188) eV by using of equation (5) and (8.099 ± 0.33) eV by using of equation (6), and explain that resume the like molecules structure of donors by contained all molecules on the pyrimidine ring as basic in the molecule. The ionization potential value of the uracil greater than those of the thymine because presence of methyl group as electron with donating group in

thymine and this lead to increase electronic density on pyrimidine ring, hence the electron in electronic pair on nitrogen atom is more active to transition from HOMO.

The variation in equilibrium constants values (Table (2)) of formation CT complexes depend on the electronic density factor of nitrogen atom (*) of amino group in cytosine and nitrogen atom of pyrimidine ring which was steric hindrance lower in uracil and thymine. The electronic density increase with certainly facilitate the formation of CT complexes. The K_{CT} value of (DDQ-thymine) complex is about twofold nearly than those of (DDQ-uracil) complex. This can be explained by the presence of methyl group as electron donating group may enhance the formation of CT complexes by increasing the charge density of the nitrogen atoms in the pyrimidine ring of thymine, whereas the K_{CT} value of (DDQ-cytosine) complex is large nearly because the lone pair of electrons of NH_2 group is available in the molecular structure same of pyrimidine ring. The equilibrium constants values of CT complexes of donors with DDQ increased as follows:

K_{CT} of Cyt. > K_{CT} of Thy. > K_{CT} of Ura.

Effect of the nature of donors and temperature on spectroscopically calculated equilibrium constant, molar extinction coefficient and ionization potential is discussed below:

Effect of Donor

All the donors used in this study are substituted pyrimidine rings. The donors are a different in the spectral behavior as observed from Table (3). This different due to presence of methyl group at 5-position in pyrimidine ring of thymine and amino group at 4- position of cytosine and without presence of methyl or amino group on the ring of uracil. CT complexes of cytosine and thymine are much more than those of uracil as evident from their respective K_{CT} values (Table (2)). Large value of K_{CT} indicates greater stability of a given CT complex. Increase in the values of K_{CT} of thymine complex in comparison with uracil complex may be due to substituted methyl group in.

(*) According to program [19] of molecular orbital theory which shows HOMO in the molecules (charge density distribution in the molecules).

thymine. Methyl group increase the electron donating effect by hyper conjugating inductive effect. It is expected that presence of methyl group at 5-position of pyrimidine ring in thymine may enhance the electron donating effect. Same effect is reported for iodine mono-chloride complexes [23]. Very strong absorption band is absorbed for cytosine complex which may be to due to the presence of strong electron donating resonance effect of amino group.

Ionization potential of uracil is greater than cytosine and thymine as shown in Table (4). On the basis of ionization potential of donors lower K_{CT} values are expected for uracil, which is in agreement with our experimental results (Table(2)). Cytosine have larger λ_{max} (highest) value as compared to all the other donors, this may be due to strong electron donating resonance effect of amino group.

Effect of Temperature

Temperature effects with the value of K_{CT} and width of the absorption band as well as the absorbance of CT complexes. Therefore studies of these CT complexes of DDQ are carried out at different temperatures (20°, 25°, 30° and 35°C). In a reversible chemical interaction the equilibrium constant may increase with temperature. In the CT complexes under study generally K_{CT} values of donors increased with increase in temperature. This may be due to an increase in the stability of these complexes upon increasing temperature. This trend is similar to one reported in may systems [23-26].

Generally as evident from Table (3) the values of molar extinction coefficients increase with the increase in temperature for cytosine and thymine complex in a similar fashion as reported for (N,N-dimethyl formamide-iodine) system in dichloromethane solvent [24]. But in case of uracil complex of DDQ the value of ϵ_{CT} found to decrease with the increase of temperatures further investigation are required for the understanding of this trend.

Thermodynamic Parameters

Thermodynamic parameters ΔG° , ΔH° and ΔS° are the measure of the stability of the CT complexes as evident in Table (5). It is generally accepted that for CT complex DA, if the excited state is like $D^+ \dots A^-$ then increase in solvating power (ethanol solvent in this work) of medium shift CT band to low energy [27,28]. This expected trend from the Mulliken theory that there should be a slight admixture of CT states so that D and A acquires slight positive and negative charge respectively [29]. The polar solvent molecules will tend to become oriented so as to stabilize these partial charges and despite the restriction of the Frank-Condon principle leading in a greater stabilization of excited states and hence resulting a lower energy shift.

Table (1)

λ_{max} and ϵ values of donors and acceptor in ethanol solvent at 20°C.

Comp.	λ_{max} / nm ($\epsilon / m^2.mol^{-1}$)		
Cytosine	199 (670±50)	sh. 230 (300±10)	261 (280±10)
	198 (340±5)	sh. 225 *	251 (250±5)
Thymine	202 (670±10)	-----	256 (640±5)
	215 (2320±100)	247 (1610±50)	sh.285 (1230±40) 340 (550±20)
Bromanil	220 (1730±30)	232 (820±40)	sh.283 (1410±50) 292 (1750±60) 360 (80±5)
	220 (2100±90)	sh.246 (1720±70)	279 (1090±80) 351 (640±30) 433 (810±50)

λ_{max} Wavelength of absorption maximum.

ϵ Molar extinction coefficient.

sh. Shoulder.

* Not clear-cut shoulder nearly.

Table (2)*

λ_{max} and K_{CT} values for CT complexes of different of donors with DDQ as acceptor in different temperatures, and λ_{max} only for CT complexes of Bromanil and iodine in ethanol solvent.

CT complex	λ_{max} / nm	$K_{CT} / dm^3.mol^{-1}$			
		20°C	25°C	30°C	35°C
DDQ-Cytosine	456 ^a	204.69	241.06	286.69	330.07
	510	---	---	---	---
	541 ^b	---	---	---	---
DDQ-Uracil	394 ^a	48.12	59.71	73.58	90.08
	454 ^b	---	---	---	---
DDQ-Thymine	411 ^a	96.90	117.54	141.99	170.86
	499 ^b	---	---	---	---
Bromanil	476	---	---	---	---
Iodine-Thymine	405	---	---	---	--

* Reference solution contain same concentration of acceptor in the sample cell.

a This λ_{max} equal to highest transition energy for CT complex and in this value was applied Benesi-Hildebrand equation to calculate equilibrium constant and molar extinction coefficient of CT complex formation .

b This λ_{max} equal to lowest transition energy for CT complex and this value was used to calculate ionization potential of electron donor by the appliance equations (5) and (6).

Table (3)

The λ_{max} values equal to highest transition energies and molar extinction coefficients values for CT complexes (ϵ_{CT}) of DDQ in different temperatures.

CT Complex	λ_{max} / nm	$\epsilon_{CT} / m^2.mol^{-1}$			
		20°C	25°C	30°C	35°C
DDQ-Cytosine	456	570	595	610	634
DDQ-Uracil	394	520	460	568	552
DDQ-Thymine	411	390	427	479	525

Table (4)

Lowest transition energy values of CT band of donors with DDQ ($h\nu_{CT}/\text{ev}$), and dissociation energy of formed CT complex excited states of donors with DDQ (W/ev), and ionization potential of donors (IP/ev) in 20°C .

Donors	$\lambda_{\text{max}}/\text{nm}$	ν/cm^{-1}	$h\nu_{CT}$	W	IP_a	IP_b	IP_c
Cytosine	541	18480	2.2934	3.724	7.967	7.768	7.98
Uracil	454	22030	2.7330	3.963	8.846	8.430	8.78
Thymine	499	20040	2.4866	3.916	8.343	8.305	8.25

a Ionization potential were calculated by equation (5).

b Ionization potential were calculated by equation (6) which can be its rewrite the equation from second order as follows:

$$IP_2 - (2C_1 + h\nu_{CT}) IP + (C_1 h\nu_{CT} + C_2 + C_1^2) = 0$$

The solution of the above equation to calculate IP by appliance the law method as follows:

$$IP = \frac{[(2C_1 + h\nu_{CT}) \pm \sqrt{(2C_1 + h\nu_{CT})^2 - 4(C_1 h\nu_{CT} + C_2 + C_1^2)}]}{2}$$

c Measurements results of ionization potentials from references [20 – 22].

Table (5)

Thermodynamic parameters of CT complexes of DDQ in ethanol solvent at 20°C .

CT Complex	$\Delta G^\circ / \text{kJ.mol}^{-1} a$	$\Delta H^\circ / \text{kJ.mol}^{-1} b$	$\Delta S^\circ / \text{JK}^{-1} \text{mol}^{-1} b$
DDQ-Cytosine	-12.96	-13.19	-0.79
DDQ-Uracil	-9.44	-15.82	-21.76
DDQ-Thymine	-11.14	-14.27	-10.68

a ΔG° calculates by the equation as follows:

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

b ΔH° and ΔS° calculate by Van't Hoff equation as follows:

$$\ln K_{CT} = -\Delta H^\circ/RT + (\Delta S^\circ/R)$$

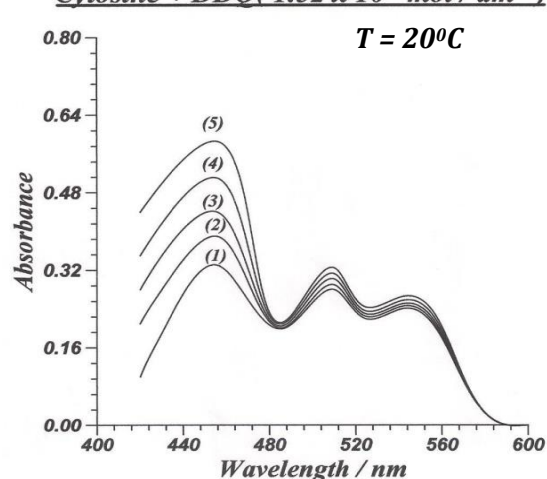
Cytosine + DDQ ($1.52 \times 10^{-4} \text{ mol / dm}^3$)

Fig.(1) Electronic spectrum of change-transfer complex between acceptor DDQ (constant conc.) and cytosine donor (variable conc.) at ethanol solvent. Reference cell contain concentration same of DDQ in the sample cell.

[cytosine]

- (1) $3.00 \times 10^{-3} \text{ mol/dm}^3$
- (2) $4.00 \times 10^{-3} \text{ mol/dm}^3$
- (3) $5.00 \times 10^{-3} \text{ mol/dm}^3$
- (4) $6.99 \times 10^{-3} \text{ mol/dm}^3$
- (5) $9.99 \times 10^{-3} \text{ mol/dm}^3$

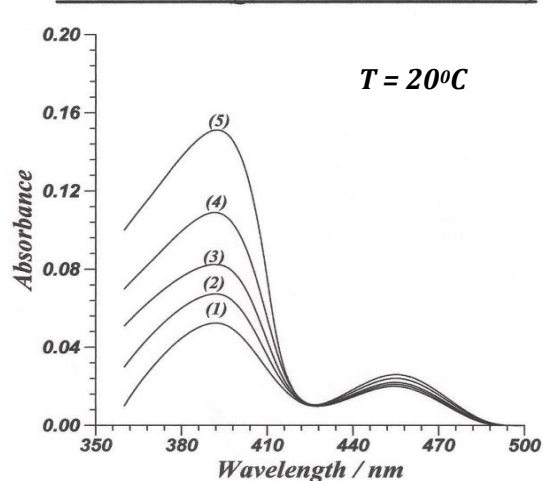
Uracil + DDQ ($1.45 \times 10^{-4} \text{ mol / dm}^3$)

Fig.(2) Electronic spectrum of change-transfer complex between acceptor DDQ (constant conc.) and uracil donor (variable conc.) at ethanol solvent. Reference cell contain concentration same of DDQ in the sample cell.

[Uracil]

- (1) $1.53 \times 10^{-3} \text{ mol/dm}^3$
- (2) $2.03 \times 10^{-3} \text{ mol/dm}^3$
- (3) $2.54 \times 10^{-3} \text{ mol/dm}^3$
- (4) $3.56 \times 10^{-3} \text{ mol/dm}^3$
- (5) $5.09 \times 10^{-3} \text{ mol/dm}^3$

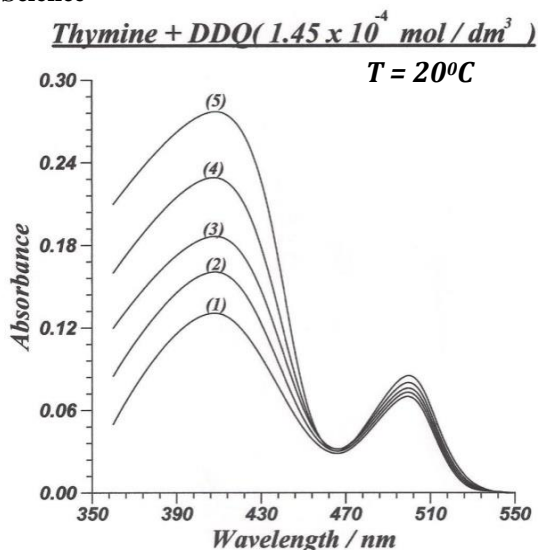


Fig.(3) Electronic spectrum of charge-transfer complex between acceptor DDQ (constant conc.) and thymine donor (variable conc.) at ethanol solvent. Reference cell contain concentration same of DDQ in the sample cell.

[Thymine]

- (1) $3.01 \times 10^{-3} \text{ mol/dm}^3$
- (2) $4.01 \times 10^{-3} \text{ mol/dm}^3$
- (3) $5.02 \times 10^{-3} \text{ mol/dm}^3$
- (4) $7.02 \times 10^{-3} \text{ mol/dm}^3$
- (5) $10.03 \times 10^{-3} \text{ mol/dm}^3$

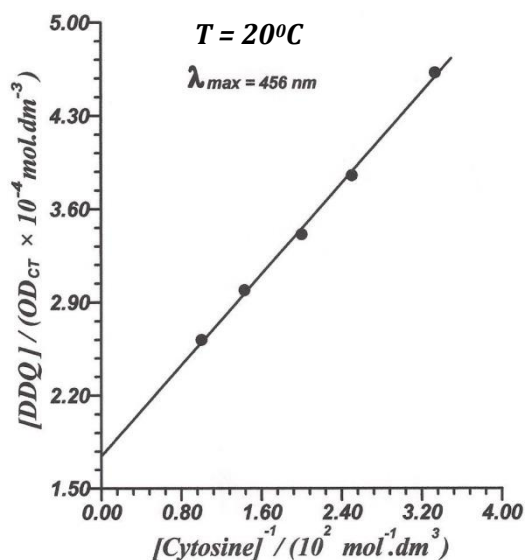


Fig.(4) Application of Bensi-Hildebrand equation for charge-transfer complex between the DDQ acceptor and the cytosine donor.

Coefficient of Correlation = 0.9991
 Linear equation:
 $Y = 8.52366 \times 10^{-7} X + 1.74473 \times 10^{-4}$
 $\epsilon_{CT} = 1/\text{Intercept} = 570 \text{ m}^2.\text{mol}^{-1}$
 $K_{CT} = \text{Intercept}/\text{Slope} = 204.69 \text{ mol}^{-1}.\text{dm}^3$

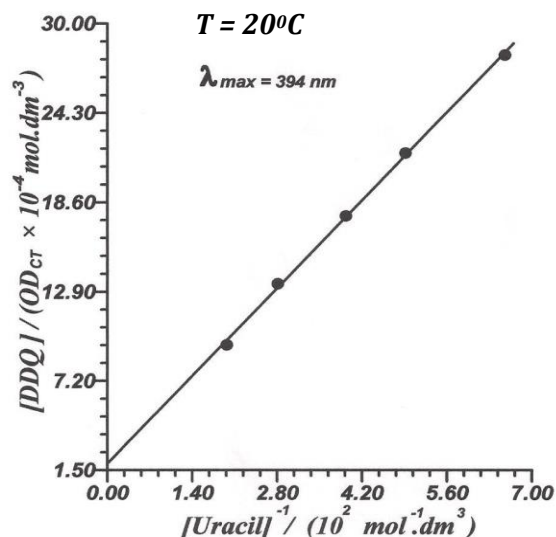


Fig.(5) Application of Bensi-Hildebrand equation for charge-transfer complex between the DDQ acceptor and the uracil donor.

Coefficient of Correlation = 0.9995
 Linear equation:
 $Y = 4.00113 \times 10^{-8} X + 1.92546 \times 10^{-4}$
 $\epsilon_{CT} = 1/\text{Intercept} = 570 \text{ m}^2.\text{mol}^{-1}$
 $K_{CT} = \text{Intercept}/\text{Slope} = 48.12 \text{ mol}^{-1}.\text{dm}^3$

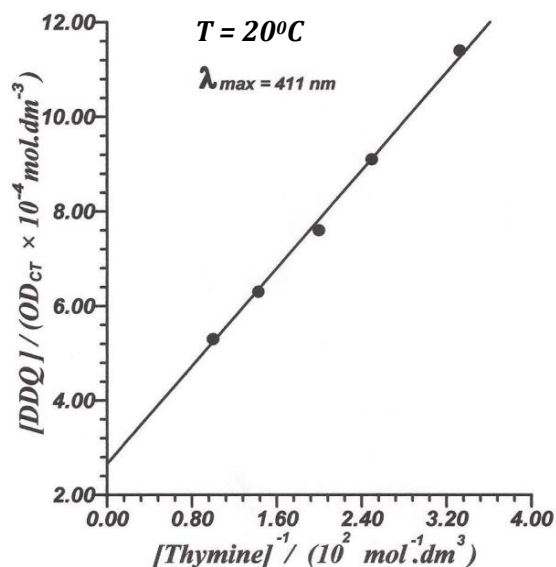


Fig.(6) Application of Bensi-Hildebrand equation for charge-transfer complex between the DDQ acceptor and the thymine donor.

Coefficient of Correlation = 0.9985
 Linear equation:
 $Y = 2.63334 \times 10^{-8} X + 2.55167 \times 10^{-4}$
 $\epsilon_{CT} = 1/\text{Intercept} = 390 \text{ m}^2.\text{mol}^{-1}$
 $K_{CT} = \text{Intercept}/\text{Slope} = 96.90 \text{ mol}^{-1}.\text{dm}^3$

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الخلاصة

درست معقدات انتقال - الشحنة للمستقبلات الالكترونية 3,2- ثنائي كلورو-6,5- ثنائي سيانو- 4,1- بنزوكوينون (DDQ) و 6,5,3,2 - رباعي برومو- 4,1- بنزوكوينون (Bromanil) واليود مع مانحات الكترونية السايبتوسين واليوراسيل والثايمين كما سجلت اطيافها الالكترونية. تم تعيين وتسجيل حزمة انتقال - الشحنة لكل من معقدات انتقال- الشحنة المتكونه. لقد تمت هذه الفحوصات الطيفية في مذيب الكحول الايثيلي وبأربع درجات حرارية مختلفة (20، 25، 30، 35°C). حسبت ونوقشت قيم ثابت التوازن (K_{CT})، معامل الامتصاص المولاري (ε_{CT}) وطاقة حزمة الامتصاص (hν_{CT}) لمعقدات انتقال - الشحنة وطاقة تفكك حالة اثاره معقد انتقال- الشحنة (W). كما حسبت ونوقشت جهود تأين المانحات (I_p) من الطاقة الاقل لحزمة معقد انتقال- الشحنة. وايضاً حسبت ونوقشت المعاملات الترموديناميكية وهي التغير في الطاقة الحرة القياسية (ΔG°) والتغير في الانتروبي القياسية (ΔS°) والتغير في الانتالبي القياسية (ΔH°) لتكوين كل معقد من معقدات انتقال-الشحنة.