

Spectroscopic and Thermodynamic Studies for Charge Transfer Complexes for some Schiff bases With Acceptors TCNQ and DDQ.

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Abstract

The complexes of some Schiff bases derived from p-N,N-dimethylaminobenzaldehyde and some p-anilines derivatives were used as charge donor with Tetracyano-p-quinodimethane (TCNQ) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as acceptors in 1,2-dichloroethane have been study by UV-visible spectrophotometer . The physical parameters such as ionization potentials of Schiff bases and dissociation energies of charge transfer complexes excited state have been calculated at λ_{max} . By using Benesi-Hildebrand's equation , the equilibrium constants and molar extinction coefficient for CT complexes also determined .Molecular compounds with acceptor are formed through $n \rightarrow \pi^*$ transition .The effect of temperature on the equilibrium constant and other thermodynamic parameters and the conductivity for the interaction of Schiff bases and TCNQ and DDQ (CT complexes) in $C_2H_4Cl_2$ solution have also been considered.

Key Words :Schiff bases;Charge transfer complexes; Conductivity ;Temperature effect .

دراسة طيفية وثرموديناميكية لمعقدات انتقال الشحنة لبعض قواعد شف مع المستقبلين TCNQ و DDQ

الملخص :

درست الاطياف الالكترونية لمعقدات انتقال الشحنة لخمس من قواعد شف الاروماتية المشتقة من بارا N,N ثنائي مثيل بنزليديهايد مع بعض معوضات الانلين كواهبات الكترونية مع المستقبلين TCNQ و DDQ . حسب المعاملات الفيزيائية مثل جهد التأين لقواعد شف وطاقة تفكك المعقد في حالة الإثارة عند الطول الموجي الاعلى، وب تطبيق معادلة بنسي- هيلدبراند تم حساب ثوابت التوازن للمعقدات ومعاملات امتصاصها المولارية، وتحديد نوع الانتقال الالكتروني $n \rightarrow \pi^*$ بالإضافة الى دراسة تأثير درجات الحرارة (298-325) كلفن على ثوابت اتزان المعقدات التي انخفضت كثيرا بارتفاع درجات الحرارة ومن ثم تأثيرها في قيم الدوال الثرموديناميكية، بالإضافة الى قياس التوصيلية الكهربائية لمحاليل معقدات انتقال الشحنة وبنفس درجات الحرارة المذكورة.

كلمات مفتاحية : قواعد شف ، معقدات انتقال الشحنة ، توصيلية ، تأثير درجة الحرارة

**Spectroscopic and Thermodynamic Studies for Charge Transfer Complexes
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Introduction

The solid complex of some benzylidene aniline containing p- N,N-Dimethyl substituent are prepared and investigated by IR,NMR ,and UV-visible spectroscopy⁽¹⁻²⁾. This investigation was undertaken in order to determine the effect of substituent's on the base strengths of p-substituted benzylidene aniline. Specifically, information was sought concerning the inductive and resonance effects of the substituent's on the availability of the non-bonded electrons on the central nitrogen atom for hydrogen bond formation^(3,4). substituent effects may depend, for example , on whether the substituent is in the 4- or 4'- position, since structures involving resonance interaction with the nitrogen atom can be draw with a negative charge on the nitrogen atom when the substituent is in the 4- but not the 4'- position⁽⁴⁾. Molecular compounds with the non-acidic or weak acidic acceptors are formed through $n-\pi^*$, $\pi-\pi^*$ transition, while those with strong acidic acceptors are formed through proton and electron transfer^(2,5,6). and charge transfer complexes(CTC) with some acceptors electrons⁽⁷⁾ exhibit wide applications. Accordingly, much interest have been paid to molecular CTC . Also ,it is possible that organic semiconductors of the CT type can find application as cheap sources for the construction of organic solar batteries in virtue semiconducting properties⁽⁸⁾. The CT complex of type these Schiff bases (donor) and some Schiff base a acceptors electrons in solution have been studies, but the thermodynamic and electrical conductance studies of CTC in solution are very little more⁽⁹⁾. In this paper , we report the physical parameters and the thermodynamic quantities and electrical conductance studies of CTC in solution for the formation of charge transfer complex (CTC) between p,N,N-Dimethylaminobenzylidene aniline and its some substitutents with acceptors tetracyano-p-quinodimethane (TCNQ), 2,3-dichloro-5,6-dicyano-1,4- benzoquinone (DDQ) and charge transfer complexes (CTC) in solution .

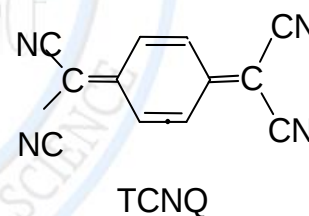
Experimental

The five aromatic Schiff's bases under investigation were prepared previously by heating together equimolar amounts of the properties of dimethyl N-benzaldehyde and aniline derivatives following a similar procedure as in literature⁽¹⁻³⁾, the compounds have the structural formulae (scheme.1). The acceptors in the present study are TCNQ, DDQ (Scheme.1) .The CT complexes Solution have been investigated with acceptor in $C_2H_4Cl_2$ solution spectrometrically at λ_{max} . The measurement of the optical densities of complexes at their λ_{max} were done after (30-60) minutes from the preparation of complexes⁽⁵⁻⁷⁾. The used concentration of all acceptors (2×10^{-4} M) was kept constant ,donor molecules (1-6) were varied in every set of solutions ,and was much greater than the initial concentration of the acceptors (at least 10 times) in every solution .This was done because Benesi – Hildebrand's equation must be held for 1:1 molecular complexes under this condition .The measurements of the electronic spectra of the Schiff bases and TCNQ and DDQ in CH_2Cl_2 solvent have been recorded by double-beam Cecil (UV – Visible) Spectrophotometer (UV - CE 3021)

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Xc1ccc(cc1)C(=N)c2ccc(cc2)YN#Cc1c(Cl)c(Cl)c(=O)c(=O)c1C#N

DDQ



Scheme.1

Scheme .1

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Table (1): The physical parameters of Schiff bases at $\lambda_{\max}$ of components and CT complexes with the two acceptors in $C_2H_4Cl_2$.

Compd. No	Compound	M.P /°C	λ /nm		
			Solvent	WithTCNQ	With DDQ
1	P,N,N-Dimethylaminobenzylidene aniline	97-98	360	405	420
2	P,N,N-Dimethylaminobenzylidene P'-Nitro aniline	172 -174	394	402	521
3	P,N,N-Dimethylaminobenzylidene P'-carboxy aniline	196- 197	405	418	450
4	P,N,N-Dimethylaminobenzylidene P'-methoxy aniline	232-234	339	431	453
5	P,N,N-Dimethylaminobenzylidene P'N,N-Dimethylamino aniline	141-140	364	428	426

Results and Discussion

Table (1) showed the absorption spectrum of compounds (1-5) and charge-transfer complex with TCNQ and DDQ in $C_2H_4Cl_2$ solvents. The solution of five CT complexes were obeyed Benesi-Hildbrands⁽⁷⁾ equation (Eq .1) ,which means that the ratio of Schiff base : acceptor in every is 1:1 ,

$$\frac{[A_o].L}{O.D_{CT}} = \frac{1}{K_{CT} \cdot \epsilon_{CT}} \cdot \frac{1}{[D_o]} + \frac{1}{\epsilon_{CT}} \dots\dots\dots(1)$$

Where $[A_o]$ and $[D_o]$ are the concentrations of the electron acceptor and the electron donor (Schiff bases :1-5), respectively , L is the path length , $O.D_{CT}$ the optical density of CT complex at $\lambda_{\max}$,the electronic absorption spectra of the CT complexes exhibit the CT complexes band with the visible region ,this band is assigned to the $n \rightarrow \pi^*$ CT interaction , the molar extinction coefficient ϵ_{CT} less than $10^3 \text{ m}^2.\text{mol}^{-1}$ (derived from donor denoting that only $n \rightarrow \pi^*$). This is CT supported by calculating the energy for this CT interaction using the relation given by Briegleb From⁽⁸⁾

$$E_{CT} = I_p - E_A - W \dots\dots\dots(2)$$

From the electronic spectra of CT complexes in CH_2Cl_2 solvent it be calculated , some important physical parameters such as ionization potentials (I_p) of prepared compound (donor) and dissociation energies of excited state of Charge transfer complex (W) were calculated using equation (2).Table (2).

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Table (2): The physical parameters of Schiff bases and of their CT complexes with the two acceptors in C₂H₄Cl₂.

CTC. No	λ_{CT}/nm		E_{CT}/Ev		Ip/ev		W/Ev		$K_{CT}/(mol^{-1}m^3)$		$\epsilon_{CT} /(m^2 mol^{-1})$	
	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ
1	405	420	3.06	2.91	9.25	9.67	4.485	4.83	6733	665	362	357
2	402	521	3.08	2.37	9.27	8.90	4.485	4.63	1673	566	372	303
3	408	450	3.04	2.72	9.23	9.49	4.485	4.84	3548	600	425	455
4	431	453	2.88	2.71	9.06	9.38	4.489	4.74	12589	710	330	325
5	428	426	2.90	2.88	9.08	9.62	4.484	4.82	7777	842	514	588

The plots of charge-transfer transition energies ($h\nu_{CT}$) of complexes at their λ_{max} of (1-6) compounds as a function of ionization potentials were linear relations with almost identical slopes but varied intercepts. The electron affinities (E_A) of the acceptors (= 1.70 , 1.93 eV for TCNQ and DDQ respectively which are derived in terms of simple valance-bond descriptors⁽⁷⁾). Similar linear relationships have been observed for complexes of many other acceptors, showing the correlation between these parameters. In general ⁽⁷⁾:

$$h\nu_{CT} = a Ip + b \quad \text{.....(3)}$$

This equation (3) is very important for the estimation of the values of ionization potentials (I_p) and the coefficient (a) and (b) are constant for a certain acceptor^(9,10).

From Benesi-Hildbrands equation ϵ_{CT} and K_{CT} of complexes were calculated. ϵ_{CT} is the molar extinction coefficient and K_{CT} is the equilibrium constant (association constant) at their λ_{max} .

The plot of $\frac{[A_o].L}{O.D_{CT}}$ vs $\frac{1}{[D_o]}$ gave a straight line with slope = $\frac{1}{K_{CT} \cdot \epsilon_{CT}}$ and intercept = $1/\epsilon_{CT}$.

From the value of intercept was calculated the ϵ_{CT} values. From slope and intercept values (Fig .1) the equilibrium constant was calculated as follow :

$$\frac{\text{Intercept}}{\text{Slope}} = \frac{1/\epsilon_{CT}}{1/ K_{CT} \cdot \epsilon_{CT}}$$

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Table (2), summarizes the results , there are three important points concerning the data of Table (2): (i) the K_{CT} values of DDQ are generally lower than the values of the TCNQ , (ii) electron donating groups increase the K_{CT} value and electron – withdrawing groups decrease the K_{CT} values , (iii) the values of I_p and W are almost the same for all Schiff bases and their CTC and agree well with each other's.

The mechanism of CTC could be determined through other thermodynamic parameters such as change in free energy (ΔG°) , change in enthalpy of complexes (ΔH) , and change in entropy (ΔS°). The thermodynamic equilibrium constant K_C for CTC were determined by Benesi-Hildbrand equation. The decrease in K_{CT} with increase in temperature indicate the exothermic nature of the process⁽¹⁰⁾ . The ΔG° , ΔH° , and ΔS° were calculated using the equations⁽¹¹⁾

$$\Delta G^\circ = -RT \ln K_{CT} \dots\dots\dots (4)$$

$$\ln K_{CT} = \Delta S^\circ / R - \Delta H^\circ / RT \dots\dots\dots (5)$$

A plot of $\ln K_{CT}$ vs $1/T$ was found to be linear (Fig.2) ΔH° and ΔS° determined from the slope and intercept (or : $\Delta S^\circ = (\Delta H - \Delta G^\circ) / T \dots\dots\dots (6)$

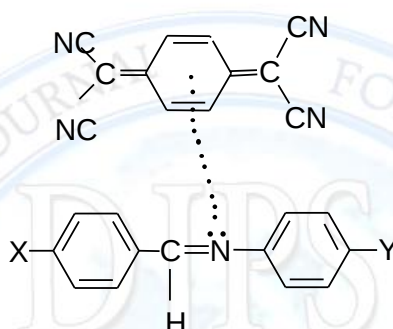
The values of all the physical parameters (I_p , K_{CT} , and ϵ_{CT} (Table.2) and thermodynamic functions (Tables 3-7) are affected by the nature of both donor and acceptor molecules and, the nature of substituent's on the donor molecules. The effect of temperature on the equilibrium constant (K_{CT}) of the interaction were found to decrease monotonically on raising the temperature .The temperature dependence of the equilibrium constant has been used to calculate the thermodynamic function ($\Delta G^\circ, \Delta H, \Delta S^\circ$) of the formed CTC , also that the stability of CTC depends on the nature of substitute. However, the electron donating substitute ($-OCH_3$, $N(CH_3)_2$ in compounds (4 and 5) increase the electron density around the nitrogen of the azomethine group and consequently increases the formation of interaction (stability of the formed K_{CT} of CTC (Table.2) ,but, the electron withdrawing substitute such as compounds (2,3) which show a marked decrease on the formation of CTC , and consequently reduce the value of equilibrium constant (K_{CT}) of these complexes .very agreements with others as the strength of the CTC by the donating substituent group. This means CTC existant increases the stability of this interaction and consequently increases the value of equilibrium constant (K_{CT}) of these complexes . In the presence of NO_2 , $COOH$ group in the para position of the aniline ring , the polarization increases toward the ring by conjugative interaction of the electronic density with it .whereas in the case of methoxy group , polarization increases in the opposite direction which stabilizes the carbonium ion character by conjugation with the dimethyl aminobenzylidene ring which causes a higher stability for the latter Schiff bases. In the presence of $N(CH_3)_2$ substitution in the para position of the benzal ring is low stability compared with that of the anilium of benzylidene

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p-,N,N-Dimethylamino aniline ring .

The thermodynamic parameters for the interaction between Schiff bases and the two acceptors molecules were estimated in the temperature range of 298-325 °k in C₂H₄Cl₂ solvent .Tables.(3-7) .The negative values of ΔG° indicate the process to be feasible and CTC to be spontaneous. The negative values of ΔH and the values ΔS° (depend on the value of ΔH , ΔG° and the interaction with the solvents) indicate that the interaction is exothermic and there is increased or decrease the randomness at the solution interface⁽¹²⁾. Based on the above results the CT interaction may be formulated as (Scheme 2) :



Scheme 2

Table (3) :Thermodynamic parameters of CTC (1) at various temperature in C₂H₄Cl₂ .

T (°K)	K /M ⁻¹		-ΔG° /KJ mol ⁻¹		ΔS° / J mol ⁻¹ k ⁻¹		-ΔH /KJ mol ⁻¹	
	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ
298	6733	665	21.839	16.103	15.34	83	26.413	40.979
303	5709	386	21.790	15,003	15.25	85		
308	4749	281	21.678	14.438	15.37	86		
313	4083	189	21.636	13.640	15.26	87		
318	3265	125	20.391	12.765	18.93	88		
323	3033	81	20.529	11.800	18.21	90		

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Table (4) :Thermodynamic parameters of CTC (2) at various temperature in C₂H₄Cl₂ .

T (°K)	K _{CT} /M ⁻¹		-ΔG° /KJ mol ⁻¹		ΔS° /J.mol ⁻¹ k ⁻¹		-ΔH/ KJ mol ⁻¹	
	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ
298	1673	566	18.381	15.763	9.12	51	15.671	31.119
303	1403	333	18.254	14.631	8.52	54		
308	1230	225	18.218	13.869	8.27	56		
313	1177	164	18.400	13.271	8.72	57		
318	1066	114	18.432	12.521	8.68	59		
323	1000	73	18.550	11.520	8.91	60		

Table (5) :Thermodynamic parameters of CTC (5) at various temperature in C₂H₄Cl₂ .

T (°K)	K / M ⁻¹		-ΔG° / KJ mol ⁻¹		ΔS° / J mol ⁻¹ k ⁻¹		ΔH / KJ mol ⁻¹	
	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ
298	3548	600	20.252	15.848	1.00	93	20.552	43.665
303	3195	333	20.327	14.613	0.74	95		
308	2818	266	20.341	14.297	0.68	95		
313	2488	150	20.347	13.039	0.65	97		
318	2136	100	20.269	12.175	0.88	99		
323	1871	71	20.232	11.447	1.00	99		

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Table (6) :Thermodynamic parameters of CTC (4) at various temperature in C₂H₄Cl₂ .

T (°K)	K / M ⁻¹		-ΔG° / KJ mol ⁻¹		-ΔS° / J mol ⁻¹ k ⁻¹		-ΔH / KJ mol ⁻¹	
	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ
298	12589	710	23.389	16.265	42.16	77	10.824	39.175
303	10944	486	23.381	15.583	41.43	79		
308	10233	163	23.644	14.738	41.62	79		
313	9772	162	23.550	14.047	40.65	80		
318	9289	160	24.289	13.418	42.34	81		
323	8709	99	24.362	12.339	41.91	83		

Table (7) :Thermodynamic parameters of CTC (5) at various temperature in C₂H₄Cl₂ .

T (°K)	K / M ⁻¹		-ΔG° / KJ mol ⁻¹		ΔS° / J mol ⁻¹ k ⁻¹		-ΔH / KJ mol ⁻¹	
	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ
298	7777	842	22.196	16.688	16.39	89	17.30	43.324
303	6666	550	22.180	15.895	16.07	90		
308	6015	330	22.283	14.849	16.15	92		
313	5391	245	22.360	14.315	16.14	92		
318	5222	148	22.633	13.211	16.74	94		
323	4292	99	22.426	12.339	15.84	95		

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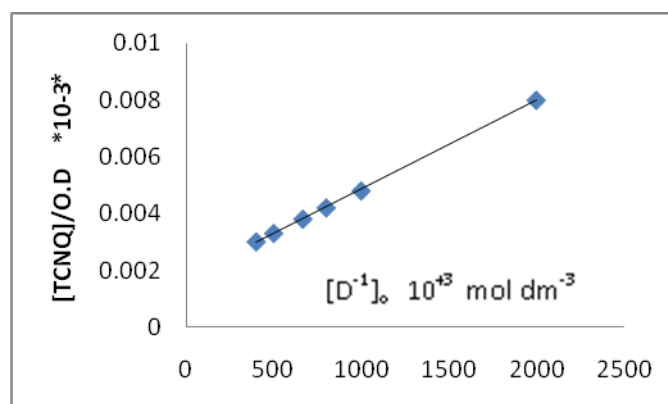


Fig (1) : A typical example of application of Benesi-Hildebrand equation for the CTC (1)

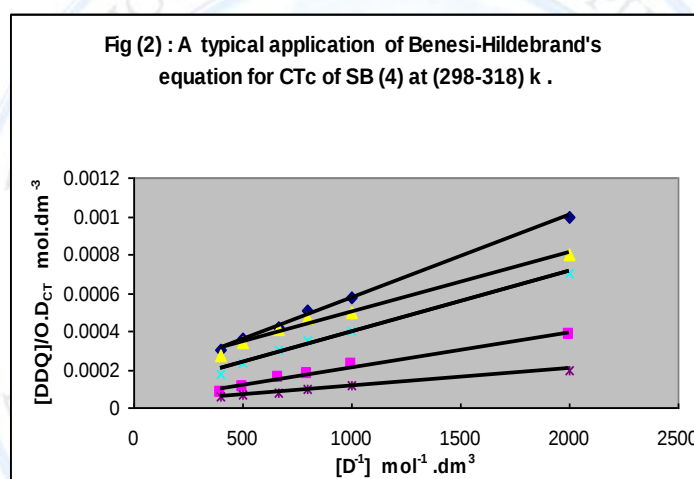


Fig (2) : A typical application of Benesi-Hildebrand's equation for CTC of SB (4) at (298-318) °K .

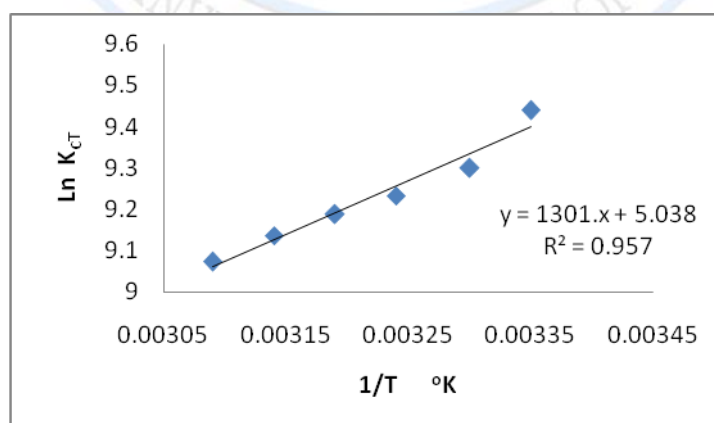


Fig (3) : A typical relation between $\ln K_{CT}$ versus T^{-1} (°K) for CTC (2) , with TCNQ

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Finally ,The study includes the following parts : the measurement of the electrical conductivity for each of the following CTC compounds, (1×10^{-4} mole. dm^{-3}) . It is found that the electrical conductivity for each solution of the CTC increases with increasing temperature. By comparing the values of the five Schiff's bases under investigation .Table (8) show the electrical conductivity of the (1-5) CTC with two acceptors are following sequences : CTC-1 > CTC-4 > CTC-5 $\geq$ CTC-2 > CTC-3 which agreement with ionization potential of Schiff bases and observing effects with the increase of the polarization of azomethane group which affected with the substitution group at various temperature in $\text{C}_2\text{H}_4\text{Cl}_2$. Fig.(4) , show the plot of log conductivity (log κ) as a function of the reciprocal of temperature

($\text{T}^{-1} \text{K}^0$) which is merely obey to Arrhenius equation (8).

$$\kappa = \kappa_0 e^{-\Delta E/RT} \dots\dots\dots(8)$$

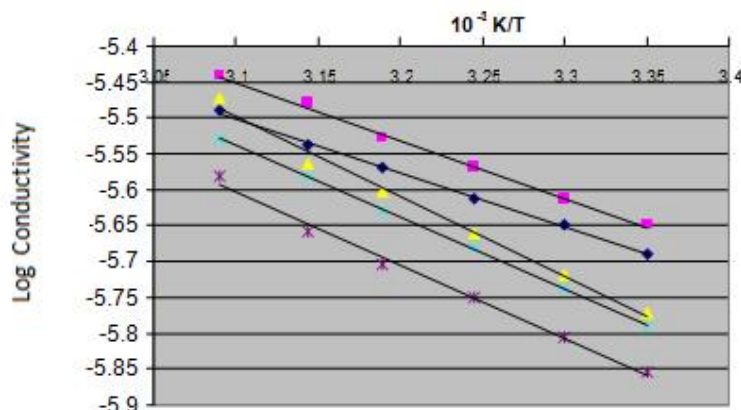
Where κ is the electrical conductivity at a given T , κ_0 is the initial conductivity, ΔE is the activation energy of conduction has been done as shown in Figure (4) , and R is the gas constant .As expected the raise in temperature led to the enhancement of the conductivity. The data were used to calculate the activation energies of the process which are decrease in order 1.768, 1.441, 1.077, 0.890, and 0.786 Kcal.mol $^{-1}$ for CTC , respectively.

Table (8) : Electrical conductivity of the (1-5) CTC at various temperature in $\text{C}_2\text{H}_4\text{Cl}_2$.

T (°K)	$\kappa / \mu\text{s cm}^{-1}$ CTC-1		$\kappa / \mu\text{s cm}^{-1}$ CTC-2		$\kappa / \mu\text{s cm}^{-1}$ CTC-3		$\kappa / \mu\text{s cm}^{-1}$ CTC-4		$\kappa / \mu\text{s cm}^{-1}$ CTC-5	
	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ	TCNQ	DDQ
298	30.04	31.15	26.24	26.67	21.42	21.65	28.64	29.21	26.85	26.98
303	32.93	31.22	27.97	27.21	24.04	23.44	30.00	28.41	28.15	28.02
308	35.64	35.84	29.78	31.22	26.36	26.94	31.35	31.68	29.73	31.04
313	39.09	41.00	31.79	32.17	29.37	30.43	32.88	33.09	31.33	31.51
318	42.46	42.77	33.82	34.55	32.73	33.14	34.55	34.73	32.88	32.96
323	46.56	47.03	36.42	36.86	37.23	37.87	36.37	36.82	35.21	35.74

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Fig(4) : Log Conductivity verse T^{-1} for CTC (1-5) with DDQ in $C_2H_4Cl_2$

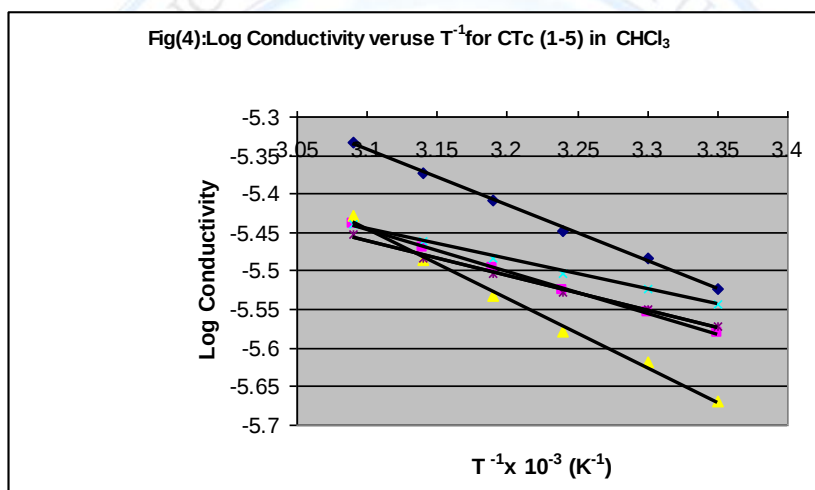


Fig (5): Log Conductivity verse T^{-1} for CTC (1-5) with TCNQ in $C_2H_4Cl_2$

Conclusion :

The CT complexes of five Schiff bases with the acceptors DDQ and TCNQ have been investigated in methylene chloride . The solution of all complexes were obeyed Benesi-Hildbrands equation which means that the ratio of Schiff bases : acceptor in every is 1:1 , all complexes are $n \rightarrow \pi^*$ type . The negative values of ΔG° for CTC indicate the process to be feasible and CTC to be spontaneous. The negative values of ΔH and the values ΔS° indicate that the interaction is exothermic and there is increased or decrease of the randomness at the solution interface. It is found that the electrical conductivity for each solution of the CTC increases with increasing temperature.

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