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Spectroscopic and Thermodynamic Studies of Charge Transfer Complexes for 7,7,8,8-tetracyanoquinodimethane(TCNQ) and Some Organic Telluride compounds

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Abstract

The Charge Transfer complexes(CTC) between 7,7,8,8-tetracyanoquinodimethane (TCNQ) and some tellurium compounds have been investigated spectrophotometrically in the UV-Visible region. The values of energies of transition , ionization potential (IP), and the dissociation energies of charge transfer(CT). complexes excited state(w) of these complexes have been calculated and were in the range of 9.96 - 9.35 eV.

The charge transfer parameters of the tellurium compounds as a donor with TCNQ as acceptor which is represented by E_{CT} , K_{CT} , ΔG , ΔH , and ΔS , have been estimated. The data was analyzed using Benesi-Hildebrand equation, from which the formation of 1:1 charge transfer complex was concluded.

Keywords : charge transfer, tellurium compounds, 7,7,8,8-tetracyanoquinodimethane(TCNQ).

1.Introduction

In 1949 Benesi and Hildebrand[1] showed that benzene and iodine form complex in solution. Shortly thereafter Mulliken[2] supplied a theoretical interpretation in terms of charge transfer (CT), according to which the ground state of a donor and acceptor pair D-A is stabilized by a small ionic contribution of form $D^+ \cdot A^-$. In addition, such systems often exhibit new excited states which are not present in either component alone and which are interpreted as charge-transfer states, that is, states of

nearly pure $D^+ \cdot A^-$ character. Since then many donor-acceptor pairs have been studied and several reviews of the subject have been written. Calvin[3] has introduced the idea into a theory of photosynthesis and with Kearns and Calvin [4] have investigated solid-state photoconductivity of phthalocyanine and chloranil.

The formation of charge transfer complex(CTC) as the first step in the reaction between electron deficient and electron rich compound [5,6], therefore it seems interesting to investigate the possible

formation of CTC between dipolar (e.g. amino acid) as donor and electron deficient double bond compound (e.g. chloranil) as acceptor [7]. Many compounds like multi-rings aromatic hydrocarbons [8], thiophenes and phenylsulfides [9], furan and pyrrole, as well as their derivatives form charge transfer complex with many acceptors [10]. DDQ (2,3-dichloro-5,6-dicyano-p-benzoquinone) also form CT complexes with some aliphatic and aromatic amines [11,12] and with phenothiazines, chlorpromazines and thiaanthrene drugs [4,13].

The phenomenon of CT has been considered to have great biological importance. Many anilines which have physiological activities and have related structures to physiologically active molecules like anaesthetics are known to form CTC with biological molecules like FAD [14] and thiamine [15].

Samia J. Hasoon et al. [16] studied CTC between some substituted anilines and iodine to determine their equilibrium constants K_{CT} , and thermodynamic parameters.

A.A.H. Saeed [17,18] investigated some Schiff bases donors form stable $n \rightarrow \sigma^*$ CTC with iodine in chloroform, and $n \rightarrow \pi^*$ CTC with DDQ acceptor, and the study involved estimation of the ionization potentials I_p of Schiff bases, calculation of K_{CT} , extinction coefficients ϵ_{CT} , free energies ΔG° , transition energies $h\nu_{CT}$. CTC complexes of (DDQ), p-acetotoluidide, acetanilid, biphenyl and naphthalene were studied. [19]

There is no clear evidence of any role played by CTC in biology, they do possess certain properties which could be important

2.1 Materials and Methods

All tellurium compounds (1-3) throughout this work were prepared and purified according to the literature [25]. Chloroform (99.994%) from Riedel - deHaën. The 7,7,8,8-tetracyanoquinodimethane (TCNQ) 98.0% was

in biological systems, such electron transport system which are vitally important in biological processes like photosynthesis. [15] Spectrophotometric methods have been described for the assay of ibuprofen, lamotrigine (an anticonvulsant drug) in bulk drugs and pharmaceutical formulations. The developed methods are based on the formation of colored CTC of ibuprofen, lamotrigine with p-chloranil, 7,7,8,8-tetracyanoquinodimethane, bromothymol blue, methyl orange and picric acid in acetonitrile as solvent. Solid CTC were synthesized and characterized by IR and 1H NMR spectroscopy, Benesi-Hildebrand plots for each complex have been constructed. [20]

CTC formed by the interaction between, p-chloranilic acid as an acceptor and diethylcarbamazine as donor was adopted for the assay of the drug in pure powder and in tablets. The free energy change, enthalpy of formation (ΔH°) and the entropy (ΔS°) were determined. [21]

A highly sensitive spectrofluorimetric method was developed for analysis of ten fluoroquinolones antibacterials such as, amifloxacin, ciprofloxacin, enoxacin, ... etc, through CTC formation with bromanil. [22]

A spectrophotometric method is proposed for determining sulfonamides as donor by forming CTC with phenosafranine as an acceptor in acetate buffer. [23]

New CTC have been formed between antiseptic agent acriflavine with the acceptors quinol, picric acid, TCNQ and DDQ. The reactions have been studied spectrophotometrically in methanol. [24]

purchased from Aldrich chemical company and used without further purification.

Apparatus :- Specord 40 analytic jena AGUV-visible spectrophotometer, made in Germany, which is existing in pharmaceuticals and clinical pharmacy dept., college of pharmacy, university of Basrah.

2.2 Solutions

Solutions of compounds (1-3)and TCNQ in chloroform were prepared by standard procedure [17,18], and all measurements were achieved in college of pharmacy by using a quartz solution cell of 1 .0 cm path length .The reference solution used was chloroform containing the same concentration of TCNQ in every case , the absorbencies of CT.complexes were followed up by measuring their new

absorption bands in the region 220 –800 nm .

The concentration of acceptor (TCNQ) being kept constant $2 \times 10^{-5} \text{ mol .l}^{-1}$ and that of donor compounds (1 –3) was variable in every set solutions $1 \times 10^{-5} - 8 \times 10^{-5} \text{ mol .l}^{-1}$.The measurements were done after 30 min from their preparation at $291 - 318^\circ \text{ K}$ ($18-45^\circ \text{ C}$).

3. Results :

A new band in visible spectrum was observed when mixing solution of tellurium compounds (1,2,or 3) with π - acceptor TCNQ in chloroform at 291-318 K, this

absorption is ascribed to charge transfer complex ,since this band is not found in either tellurium compounds or TCNQ alone (Tables 1 and 2).

Table 1. Structures of tellurium compounds and absorption maxima of tellurium compounds (donor) ,and TCNQ (accepter) at 298 K.

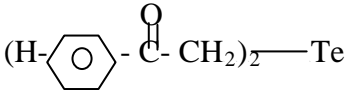
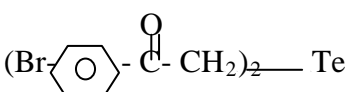
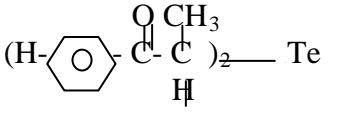
No. of compound	Structure	λ_{max} of compound
1		304 nm
2		346 nm
3		352 nm
TCNQ	7,7,8,8-Tetracyanoquinodimethane	404 nm

Table 2. Absorption maxima, energies of transition, the ionization potential values, and the dissociation energies of CT. complexes excited state(w) of complexes 1, 2 and 3 at 298K

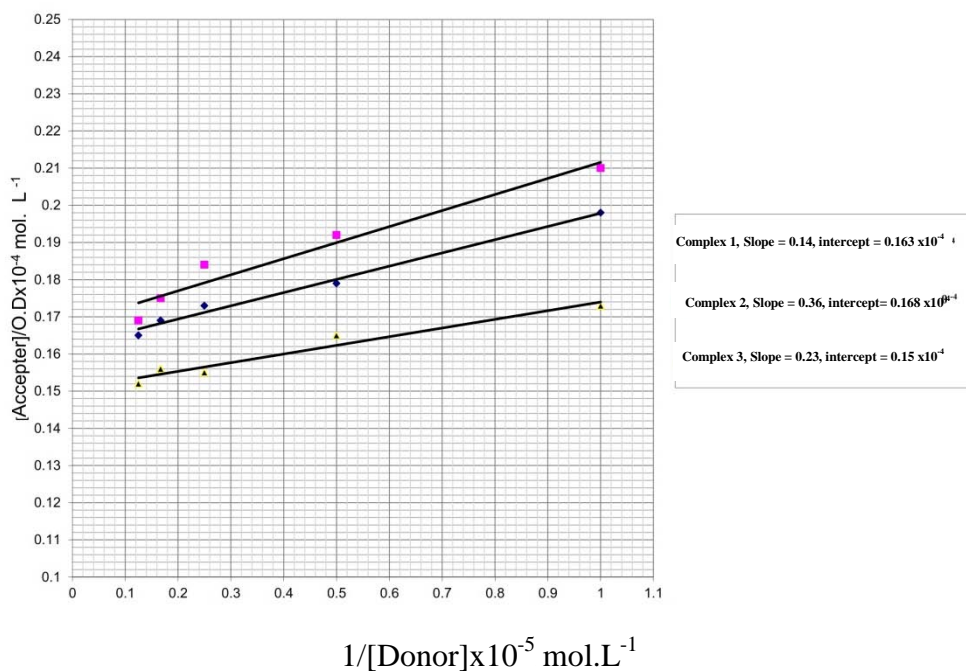
No. of comp.	λ_{max} of C.T nm	Abs.(O.D)	$E_{\text{CT}}(\text{ev})$	$E_{\text{CT}}(\text{K.J.mol}^{-1})$	$E_{\text{CT}}(\text{cm}^{-1})$	IP(ev)	W(ev)
1	317	0.1117	3.92324	378.5534	31644.854	9.95851	4.33527
2	378	0.2263	3.29012	317.4641	26538.108	9.31230	4.32218
3	374	0.2876	3.32531	320.8592	26821.950	9.34835	4.32304

Table 3. K_{CT} and E_{CT} values from Bensi-Hildebrand plot

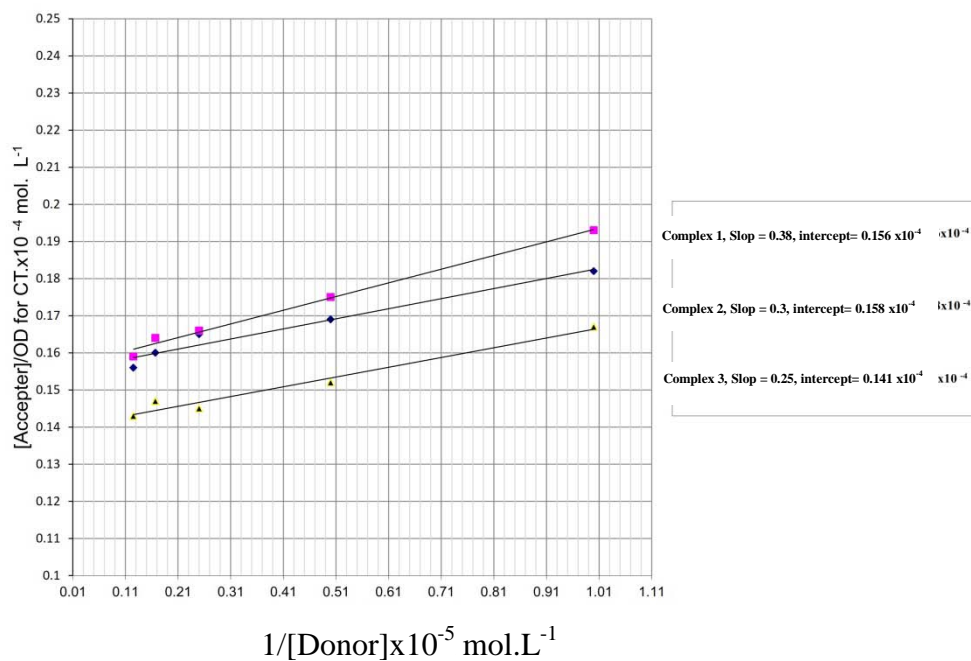
Complex	T(°K)	intercept	Slope	$\epsilon_{\text{CT}} = \frac{1}{\text{intercept}}$	$K_{\text{CT}} = \text{intercept/slope}$
1	291	0.171×10^{-4}	0.010	58479.53	1.70×10^{-3}
1	313	0.165×10^{-4}	0.0232	60606.06	7.11×10^{-4}
2	291	0.1684×10^{-4}	0.111	59382.42	1.52×10^{-4}
2	313	0.1705×10^{-4}	0.200	57142.86	8.75×10^{-5}
3	291	0.1576×10^{-4}	0.115	63816.20	1.36×10^{-4}
3	313	0.151×10^{-4}	0.146	66312.99	1.03×10^{-4}

Table 4. values of free energy, entropy, enthalpy (thermodynamic parameters)

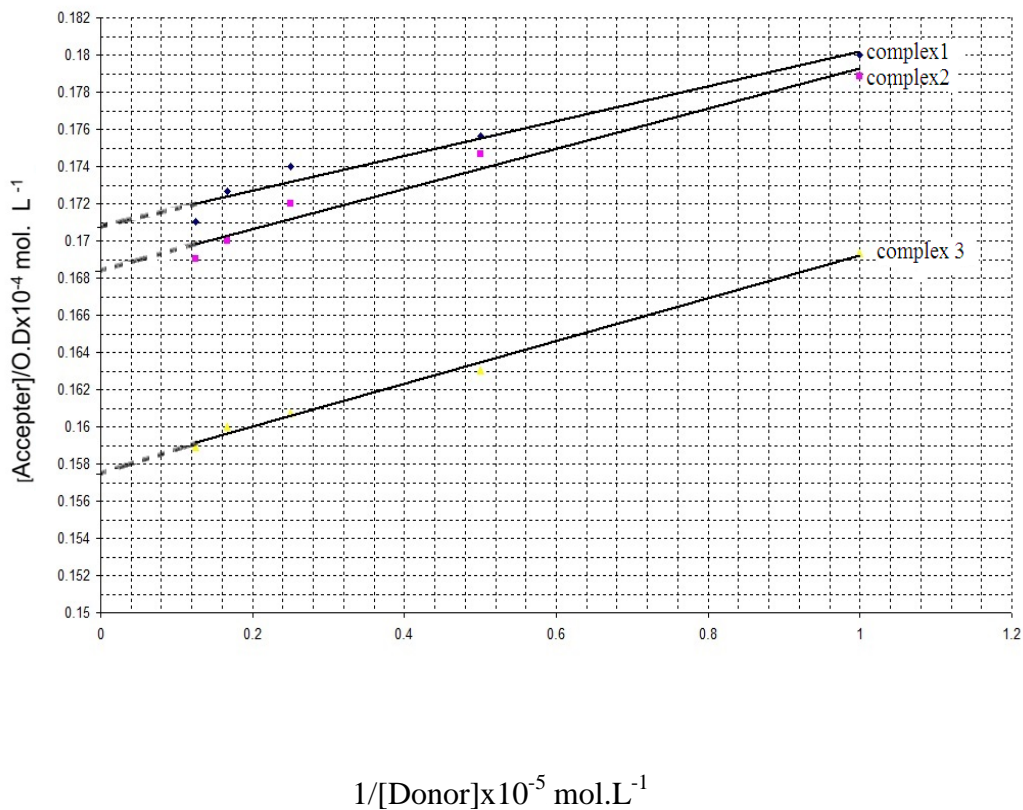
Complex	T(°K)	K_{CT}	$-\Delta G^\circ \text{ KJ/mol}$	$\Delta H^\circ \text{ KJ/mol}$	$\Delta S^\circ \text{ J/mol}$
1	313	7.11×10^{-4}	18.863×10^3	69.1129	60.0444
2	313	8.75×10^{-5}	24.319×10^3	1437.859	70.0899
3	313	1.03×10^{-4}	23.891×10^3	22.616	76.2565



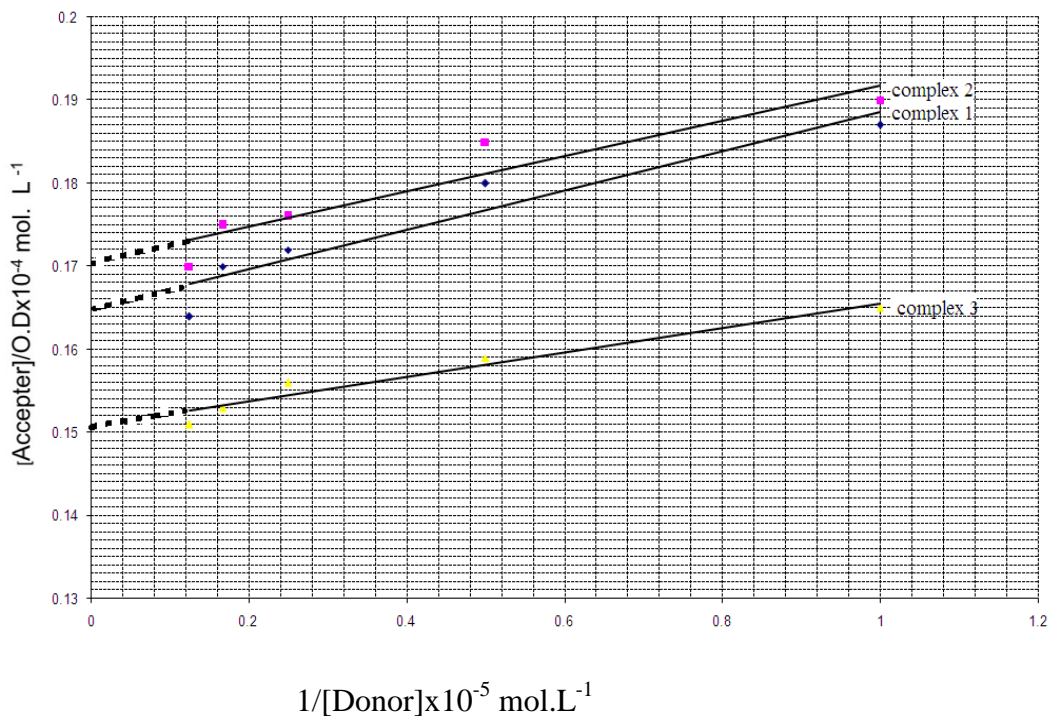
Bensi- Hildebrand plots of the charge transfer complexes(1,2and 3) at 35° C



Bensi- Hildebrand plots of the charge transfer complexes(1,2,3) at 25° C



Bensi- Hildebrand plots of the charge transfer complexes(1,2,3) at 18° C



Bensi- Hildebrand plots of the charge transfer complexes(1,2,3) at 40° C

4.1 .Discussion

The aim of this work is to study CTC between some tellurium compounds as donor and TCNQ which is well known as a powerful electron acceptor and is expected to favor electron transfer from tellurium compounds into TCNQ molecules and determine their ionization potentials (IP), and thermodynamic parameters in order to understand the role of the substituent upon the stability of these complexes, and it represents introductory study in pharmacy science because the charge transfer complexes have been utilized in pharmaceutical analysis.

The TCNQ- π -acceptor yield a stable highly colored radical anion yields CT. complexes with retinol which is known to be a powerful electron donor[26]

The procedures were successfully utilized in the determination of nizatidine and ranitidine hydrochloride drugs with either p-chloranilic acid or 2,3-dichloro-5,6-dicyanoquinone (DDQ) in pharmaceutical preparations.[27]

Charge transfer complexes of some drugs of amino acid derivatives, such as carbocysteine, aminobutyric acid, and levodopa, as electron donors with 7,7,8,8-tetracyanoquinodimethane (TCNQ) as electron acceptor have been studied. The thermodynamic standard reaction quantities of the complexes between donors and acceptor were estimated. Different variables affecting the reaction were carefully studied and optimized. The developed methods could be applied successfully for the

determination of the studied compounds in their pharmaceutical dosage forms with a good precision and accuracy when compared to official and reported methods as revealed by *t*- and *F*-tests.[28]

The interaction between 7,7',8,8'-tetracyanoquinodimethane (TCNQ) and oxamniquine, azithromycin, omeprazole, pantoprazole, and benzydamine hydrochloride was investigated. The reaction conditions were optimized to obtain typical charge transfer complexes (CTC). The nature of the formed complexes was proved by thorough study of the thermodynamic parameters namely ΔG (free energy), ΔH (enthalpy), and ΔS (entropy). The association constant K_{CT} and the molar absorptivity λAD (acceptor-donor) of the formed complexes were determined using the Benesi-Hildebrand equation. The effect of temperature on these constants gave evidence of CTC formation. The reaction of TCNQ with I-V was found to be in 1:1; as being determined by the Foster method. Spectrophotometric measurements of the formed CTC were used for the quantitative determination of the studied drugs in both pure or pharmaceutical formulation.[29]

Also Hesham Salem[30] investigates CTC between gabapentin as n -electron donor with σ -acceptors: iodine, and π -acceptor: TCNQ.

4.2. Absorption Spectra

The concentration of TCNQ being kept constant ($2 \times 10^{-5} \text{ mol.L}^{-1}$) while the concentration of tellurium compounds were much greater than TCNQ (1×10^{-5} - $8 \times 10^{-5} \text{ mol.L}^{-1}$) to fulfill the condition of Benesi - Hildebrand equation for 1:1 complexes. [1,17]

A new absorption band due to neither electron donor nor electron acceptor was observed in the near-UV or visible region for the electron donor - electron acceptor

system, when the absorption spectra of tellurium compounds - TCNQ complex (table 1 and 2) is compared with the absorption maxima of tellurium compounds [comp.1 = 304 nm, comp.2 = 346 nm, comp.3 = 352 nm] and TCNQ (404 nm), it is evident that the absorption bands in the 317, 378, 374 nm in complexes 1, 2 and 3 respectively can neither be attributed to tellurium compounds nor to TCNQ, this is characteristic of the CT complex.

According to the Mulliken theory eq. (1), the wave function of the ground state of the 1:1 complex is described as follows:[2]

$$\tau n = a\phi(DA) + b\phi(D^+A^-) \dots\dots\dots(1)$$

and that of the first excited state as

$$\tau E = a^*\phi(D^+A^-) + b^*\phi(CA) \dots\dots\dots(2)$$

where $\phi(DA)$ and $\phi(D^+A^-)$ are the nonbond and the dative bond wave functions respectively. For weak interacting complexes $a \gg b$, the energy of transition, $\tau N\tau E$ can be given as follows[13] :

$$h\nu = I_p - E - W \dots\dots\dots(3)$$

where I_p is the ionization energy of the donor, E the electron affinity of the acceptor (for TCNQ = 1.7 eV), and W the dissociation energy of the CT excited state. Foster⁽¹³⁾ has shown that the frequencies of the CT spectra were proportional to the ionization energies of the donor (eq. 2). [22]

$$h\nu_{CT} = aI^D + b \dots\dots\dots(4)$$

For TCNQ, a & b are equal to 0.83 and -4.42 respectively .

The ionization potential calculated from the following equation :

$$h\nu(\text{ev}) = I_p - C_2 + \{ C_2 / (I_p - C_1) \} \dots\dots\dots(5), \text{ since } C_1 = 6.1, C_2 = 0.25 \text{ for TCNQ. The association constant for the complexes were calculated by the Benesi-Hildbrand equation [1,17,18]}$$

$\frac{[A] \cdot L}{OD_{CT}} = \frac{1}{K_{CT} \cdot \epsilon_{CT}} \times \frac{1}{[D]} + \frac{1}{\epsilon_{CT}}$

[A], [D] the initial concentration of acceptor and donor respectively, L is the path length of solution cell (1.0 cm), OD_{CT} is the optical density of the complex at λ_{max} only, this equation a very good straight line of the intercept equal to $(1/\epsilon_{CT})$ and slope equals to $(1/\epsilon_{CT} \cdot K_{CT})$.

It has been accounted the values of electronic transitions energies ($h\nu_{CT}$) for complexes (table 2) according to the following equations :

$$h\nu_{CT}(\text{ev.}) = 1243.667 / \lambda_{CT}$$

$$h\nu_{CT}(\text{K.J.mol}^{-1}) = h\nu_{CT}(\text{ev.}) + 96.49$$

$$h\nu_{CT}(\text{cm}^{-1}) = h\nu_{CT}(\text{ev}) + 8066$$

4.3. Thermodynamic Parameters:

Thermodynamic parameters including ΔG , ΔH , and ΔS , for complexes of TCNQ with tellurium compounds were calculated and showed in table 4 .

The standard enthalpy change, ΔH° , of an interaction can be obtained from :

$$\ln K (K_2 / K_1) = (-\Delta H / 2.303R) \times (1/T_2 - 1/T_1)$$

The standard free energy ΔG° , was calculated from:

$$\Delta G^\circ = -RT \ln K_{CT} \text{ or } \Delta G^\circ = -2.303RT \log K_{CT}$$

R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature in Kelvin, and K_{CT} is the association constant of donor-acceptor complex (L mol^{-1}) at room temperature.

The standard entropy change ΔS° , was calculated from: $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$

4.4. The effect of time and temperature on the complexes :

There was no effect of time on the charge transfer complex until after a week from preparing them which indicate their stabilities. According to the effect of

temperature it is noticed that increasing in the intensity of the absorption of all complexes as increasing in the temperature.

5. Conclusion

The results obtained from the present study indicate that π - π CT complex formation between three of tellurium compounds and TCNQ was applied in the spectrophotometric assay and the values of ΔG° , ΔH° , and ΔS° have been estimated

at 40°C, complex 1 showed the lowest value in $\Delta G^\circ=18.86$ KJ/mol, and complex 2 showed higher values $=24.3$ KJ/mol. and $\Delta H^\circ=1437$ KJ/mol. While complex 3 showed the highest value of $\Delta S^\circ=76.3$ J/mol.

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دراسة طيفيه وثرموديناميكيه لمعقدات انتقال الشحنة بين رباعي سيانو-كوبالتيثان (TCNQ) وبعض التلوريدات العضويه

ليلي جاسم عباس

فرع الكيمياء الصيدلانيه /كلية الصيدله / جامعة البصره

الخلاصه

درس تكوين معقدات نقل الشحنة بين رباعي سيانو-كوبالتيثان (TCNQ) وبعض التلوريدات العضويه طيفيا في المنطقة فوق بنفسجيه- المرئيه وحسبت قيم طاقه الانتقال وجهد التأين وثابت التفكك وطاقه الاثاره لتلك المعقدات وكانت تتراوح بين (9.35 - 9.96) .
كذلك قدرت قيم معاملات نقل الشحنة والمتمثله ب ΔS , ΔH , ΔG , K_{CT} , E_{CT} للمركبات التلريوم كواهب مع TCNQ كمستقبل بنسبه 1:1 , وحللت البيانات باستخدام معادله بنسي –هلديراند .
كلمات مفتاحية : نقل شحنة , مركبات تلريوم , 8,8,7,7 - تيتراسيانوكوبالتيثان