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 accepter which is represented by $E_{CT}, K_{CT}, \Delta G, \Delta H,$ and $\Delta S,$ 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$^+$. A $^\cdot$ character. 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$^+$. 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. aminoacid) as donor and electron deficient double bond compound (e.g. chlorani) as acceptor[7]. Many compounds like multirings 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 CTC complexes with some aliphatic and aromatic amines [11,12] and with phenothiazines, chloropromazines and thiaanthrene drugs [4,13].

The phenomenon of CTC 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 $\varepsilon_{CT}$, free energies $\Delta G^*$, transition energies $h\gamma_{CT}$, 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 in biological systems, such as 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 accepter 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 ($\Delta H^*$) and the entropy ($\Delta S^*$) were determined.[21]

A highly sensitive spectrofluorimetric method was developed for analysis of ten fluoroquinolones antibiotics 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]

### 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 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 pharmaceutics 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 2x10^{-5} mol .l^{-1} and that of donor compounds (1 –3) was variable in every set solutions 1x10^{-5} –8x10^{-5}mol .l^{-1} . The measurements were done after 30 min from their preparation at 291 – 318° K (18–45° C).

3. Results:
A new band in visible spectrum was observed when mixing solution of tellurium compounds (1,2,or 3) withπ- accepter 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 (acceptor) at 298 K.

<table>
<thead>
<tr>
<th>No. of compound</th>
<th>Structure</th>
<th>λmax. of compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(H-         - C- CH_{2})_{2}Te</td>
<td>304 nm</td>
</tr>
<tr>
<td>2</td>
<td>(Br-        - C- CH_{2})_{2}Te</td>
<td>346 nm</td>
</tr>
<tr>
<td>3</td>
<td>(H-         - C- CH_{3})_{2}Te</td>
<td>352 nm</td>
</tr>
<tr>
<td>TCNQ</td>
<td>7,7,8,8-Tetracyanoquinodimethane</td>
<td>404 nm</td>
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</table>
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

<table>
<thead>
<tr>
<th>No. of comp.</th>
<th>λmax. of C.T nm</th>
<th>Abs.(O.D)</th>
<th>E&lt;sub&gt;CT&lt;/sub&gt;(ev)</th>
<th>E&lt;sub&gt;CT&lt;/sub&gt; (KJ/mol)</th>
<th>E&lt;sub&gt;CT&lt;/sub&gt;(cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>IP(ev)</th>
<th>W(ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>317</td>
<td>0.1117</td>
<td>3.92324</td>
<td>378.5534</td>
<td>31644.854</td>
<td>9.95851</td>
<td>4.33527</td>
</tr>
<tr>
<td>2</td>
<td>378</td>
<td>0.2263</td>
<td>3.29012</td>
<td>317.4641</td>
<td>26538.108</td>
<td>9.31230</td>
<td>4.32218</td>
</tr>
<tr>
<td>3</td>
<td>374</td>
<td>0.2876</td>
<td>3.32531</td>
<td>320.8592</td>
<td>26821.950</td>
<td>9.34835</td>
<td>4.32304</td>
</tr>
</tbody>
</table>

Table 3. K<sub>CT</sub> and E<sub>CT</sub> values from Bensi- Hildebrand plot

<table>
<thead>
<tr>
<th>Complex</th>
<th>T(K)</th>
<th>intercept</th>
<th>Slope</th>
<th>E&lt;sub&gt;CT&lt;/sub&gt;</th>
<th>K&lt;sub&gt;CT&lt;/sub&gt; = intercept/slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>291</td>
<td>0.171 X 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>0.010</td>
<td>58479.53</td>
<td>1.70 X 10&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>1</td>
<td>313</td>
<td>0.165 X 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.0232</td>
<td>60606.06</td>
<td>7.11 X 10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>291</td>
<td>0.1684 X 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.111</td>
<td>59382.42</td>
<td>1.52 X 10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>313</td>
<td>0.1705 X 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.200</td>
<td>57142.86</td>
<td>8.75 X 10&lt;sup&gt;-5&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>291</td>
<td>0.1576 X 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.115</td>
<td>63816.20</td>
<td>1.36 X 10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>313</td>
<td>0.151 X 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.146</td>
<td>66312.99</td>
<td>1.03 X 10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Complex</th>
<th>T(K)</th>
<th>K&lt;sub&gt;CT&lt;/sub&gt;</th>
<th>- ΔG° KJ/mol</th>
<th>ΔH° KJ/mol</th>
<th>ΔS° J/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>313</td>
<td>7.11 X 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>18.863 X 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>69.1129</td>
<td>60.0444</td>
</tr>
<tr>
<td>2</td>
<td>313</td>
<td>8.75 X 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>24.319 X 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>1437.859</td>
<td>70.0899</td>
</tr>
<tr>
<td>3</td>
<td>313</td>
<td>1.03 X 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>23.891 X 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>22.616</td>
<td>76.2565</td>
</tr>
</tbody>
</table>
Bensi- Hildebrand plots of the charge transfer complexes (1, 2, and 3) at 35°C

1/[Donor] x 10^{-5} mol. L^{-1}

Complex 1, Slope = 0.14, intercept = 0.163 x10^{-4}

Complex 2, Slope = 0.36, intercept= 0.168 x10^{-4}

Complex 3, Slope = 0.23, intercept = 0.15 x10^{-4}

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

1/[Donor] x 10^{-5} mol. L^{-1}

Complex 1, Slope = 0.38, intercept= 0.156 x10^{-4}

Complex 2, Slope = 0.3, intercept= 0.158 x10^{-4}

Complex 3, Slope = 0.25, intercept= 0.141 x10^{-4}
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 2,3dichloro-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 $λ_{AD}(accepter-donor)$ 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(2x10⁻⁵ mol.L⁻¹) while the concentration of tellurium compounds were much greater than TCNQ(1x10⁻⁵ -8x10⁻⁵ 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 (table1 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:

\[ \psi_n = a \psi_{DA} + b \psi_{DP+PA-P} \] ..........................(1)

and that of the first excited state as

\[ \psi_E = a^* \psi_{DP+PA-P} + b^* \psi_{C.A} \] ..........................(2)

where \( \psi_{DA} \) and \( \psi_{DP+PA-P} \) are the nonbond and the dative bond wave functions respectively.

For weakly interacting complexes \( a >> b \), the energy of transition, \( \tau_N \) can be given as follows:

\[ \hbar \nu = I_P - E - W \] ........................................(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).

\[ \hbar \nu_{CT} = a I_P + b \] .......................................(4)

For TCNQ, \( a \) and \( b \) are equal to 0.83 and -4.42 respectively.

The ionization potential calculated from the following equation:

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

\[ \frac{[A]}{[D]} L = \frac{1}{K_{CT} \varepsilon_{CT}} \times \frac{1}{\varepsilon_{CT}} \]

\[ OD_{CT} = K_{CT} \varepsilon_{CT} \]

[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 \( \lambda_{max} \) only, this equation predicts a very good straight line of the intercept equal to \( (1/\varepsilon_{CT}) \) and slope equals to \( (1/\varepsilon_{CT}.K_{CT}) \).

\[ \Delta G^0 = -RT \ln K_{CT} \] or \( \Delta G^0 = -2.303RT \log K_C \)

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

The standard entropy change \( \Delta S^0 \) was calculated from:

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]
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 types 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 ΔG°=18.86 KJ/mol, and complex 2 showed higher values =24.3 KJ/mol. While complex 3 showed the highest value of ΔS°=76.3 J/mol.

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I would like to acknowledge the Dean of pharmacy college Dr. Shaker Abdul Sallam for his assistance and supply me with equipments, compounds and references, and I thank Dr. Ebtihal Handhal and Dr. Suha Shayal, Pharmacy college for solving the mathematical equations, in due to thank Mr. Ali Sh. Al Shara, agriculture college for his assistance and kind help to me, and my thanks for those who help me to achieve this work.

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دراسة طيفية وترمودینامیکیه لمعوقات انتقال الشحن بین رباعی سیانو-کوینوثنایی میتان (TCNQ) و بعض
الترموثناییات العضویه

لیلى جاسم عباس
فرع الكیمیاء الصیادلیه/كلیة الصیانه / جامعه البصرة

الخلاصه
درس تکوین ومعقات نقل الشحن بین رباعی سیانو-کوینوثنایی میتان (TCNQ) و بعض
الترموثناییات العضویه طیفیا 
در المنطقات الفوق بنفسجیه- المنزور وحسبت قیم طاقه الانتقال وجهد التأیین و ثابت النفق وطاقه الایثر لهذه المعقات.
وکانت تتراوح بین (9.35 - 9.96).

کلمات مفتاحیة: نقل شحن، مركبات تلریوم، 8,8,7,7 - تیتراتیاسیاکوتلریومدی میتان

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