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Research Article

MOLECULAR COMPLEXES OF DDQ WITH SOME DRUGS

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ABSTRACT

*Molecular complexes of 2, 3- Dichloro5, 6-dicyano – para-benzoquinone (DDQ) with some antibiotic drugs have been studied spectrophotometrically in chloroform. All the Complexes exhibited charge transfer bands(s) in the visible region where neither donor accept or have any absorption. The stoichiometry of the each of the complexes is found to be1:1 and is unaffected by variation of temperature. The complexes are inferred to be π-π*type. The ionization potential of the donors has been evaluated from the energies of CT bands. The stabilities and thermodynamics parameters of the complexes have been determined from the absorption studies on the C T bands. The variation of position of CT bands and the stabilities of the complexes have been correlated with the structures of the drugs.*

KEYWORDS: *DDQ, CT complexes, Ofloxacin, Levofloxacin, Ciprofloxacin, Chloroform.*

INTRUDUCTION

2,3-dichloro 5,6-dicyano-p-benzoquinone (DDQ) has been shown to form complexes with a variety of organic donors, viz. aromatics, methoxy benzenes, heterocyclics, metal complexes, imidazoles, polymers etc [1]. The electron affinity of DDQ reported is 1.99 eV. In continuation of our work [3] it is thought worthwhile to study charge transfer complexes of DDQ with drugs like Ofloxacin, Ofloxacin, Levofloxacin, Ciprofloxacin which are currently a available in the market with a view to provide a tool for the quantitative estimation of the drugs. The results of the study are reported in this communication.

EXPERIMENTAL PROCEDURE

The commercial sample of DDQ obtained from Aldrich was recrystalized from benzene chloroform (2:3) mixture and its purity was checked by TLC (m.p 213-214^{0}C). The chloroform spectra grade sample was used without any further purification. Drugs procured from Pharmaceutical Laboratories and purified by crystallization. The UV-V is spectra of the complexes were recorded on Shimadzu-240 and ElicoSL 210UV-Visible double beam spectrophotometers using a matched pair of quartz cuvettes of 10mm path length. The concentration of DDQ was held constant. While those of drugs varied between in the range of 0.001 to 0.05M. The solution concentration was set such that it produced the complex with optical density between 0.2 to 1.8. The absorption bands due to acceptor or donor individually have fallen to the baseline much more before the wavelength of CT absorption. The complicated CT bands were analyzed by using the following relationship put forward by Briegle band Czekella [4]:

$$(V_h\text{-}V_l)/2(V_m\text{-}V_l) = 1.2$$

Where V_h and V_l refer to the frequency at half the maximum intensity on the high and low frequency side of the peak located at Vm. The stability constant of the CT complexes were determined by using the following Rose-Drago [5, 11] method:

$$K^{-1} = (d/\varepsilon) - ([Do] + [Ao]) + [Do][Ao]\,\varepsilon/d$$

Where d is the absorption; ε, the molar extinction coefficient of the complex; [Ao] and [Do] are the initial concentrations of acceptor and donor respectively.

RESULTSAND DISCUSSION

1. Molecular complexes of drugs with DDQ:

When pale yellow coloured solution of DDQ is mixed with drugs characteristic colors were observed. Each of the solution exhibited Charge Transfer (CT) band (s) in their electronic Spectra. Ofloxacin, Levofloxacin, Ciprofloxacin exhibited only one CT band. The appearance of color and exhibition of CT bands (Fig. 1-3) are attributed to the formation of charge transfer complexes between the drugs and DDQ since these absorption bands are uncharacteristic of the individual components. The wavelength (λmax) of CT band of all the complexes together With other spectral characteristics is presented in Table 1.

The appearance of CT band is a attributed to the excitation of an electron from the highest occupied molecular orbital (HOMO) of the donor to the lowest un occupied molecular orbital (LUMO) of the acceptor. The appearance of double CT band is attributed to the excitation of electron from ultimate and penultimate molecular orbitals of donor to the LUMO of the acceptors. The appearance of double CT bands may occur due to (a) excitation of electrons from two different levels of donor to the same vacant level of acceptor or

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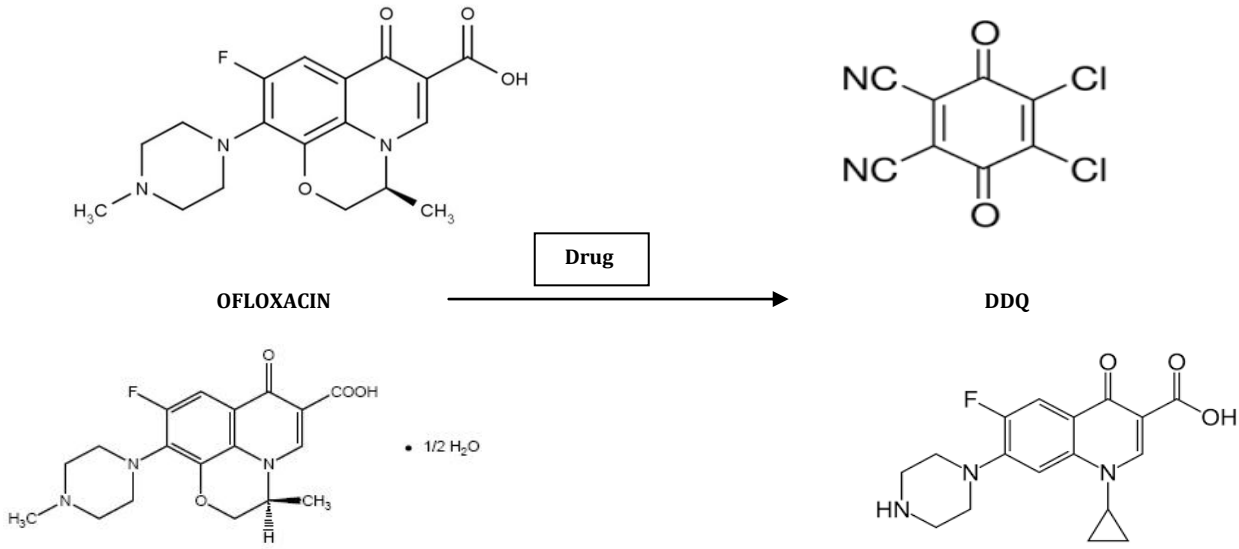
(b) excitation of electron from HOMO of donor to two different vacant levels of acceptor. In the former type of CT complexes the energy difference between two CT bands E= (E_{CT1}–E_{CT2}) depends upon the donor where as in the later type of complexes it is independent of nature of donor *i.e.* ΔE is constant. In our study it is observed that ΔE differs from donor to donor hence the complexes are in ferred to be of former type. The position of CT band ($_{max}$) of the drugs with DDQ is in the order: Ofloxacin > Levofloxacin > Ciprofloxacin. When two CT bands occurred the higher wavelength band is considered in the priority order. From the structures of the drugs it is clear that Ofloxacin, Levofloxacin and Ciprofloxacin containing N, N'-dimethyl amino aniline groups in the IR structure should have the highest donor abilities of the drugs studied.

Molecular complexes of drugs with 2, 3-dichloro-5, 6dicyanop-benzoquinone (DDQ):



2. Energies of charge– transfer bands: The energies of the intermolecular charge transfer bands are calculated from the frequencies of absorption, using the equation $E_{CT} = h_{CT}$ and the values are reported in Table 1.

3. Ionization potentials of the donors: The energies of CT bands of DDQ are linearly related to the ionization potentials of the donors in $CHCl_3$by the equation.

$$h_{CT}=0.70I_d- 3.86$$

Where $_{CT}$ is the frequency of the CT band, I_d is ionization potential of donor and h Planck's constant. The ionization potentials of the donors are calculated using this equation and are reported in Table4.The ionization potentials of donors in the present study are in the order: Ofloxacin < Levofloxacin < Ciprofloxacin.

4. Stoichiometry of the complexes: The stoichiometry of the complexes was determined by the Job's continuous variation method using equimolar solutions ($2.0x10^{-3}M$) of DDQ and drugs and stoichiometry is found to be1:1ineach case. The Job's plot of DDQ with Ofloxacin is shown in Fig. 4.

5. Extinction co-efficient (), Oscillatory Strength (f) and Transition Dipole moments (D) of complexes: The extinction coefficients of the complexes are determined at different temperatures from the intersection points of Rose-Drago plots and are reported inTable1. The extinction coefficients of a CT complex are found to be almost constant over the temperature range studied. The oscillatory strength defined by Mullikan [6].

$$f=4.319\ x10^{-9}\cdot max\cdot 1/2$$

have also been calculated. Transition Dipole moment of the complex a s defined by Tsubomura *et al* [7]

$$D=0.09582\ (\Delta\ V_{max}.1/2/V_{max})^{1/2}$$

Have also been computed from the extinction coefficients and half–band widths and are reported inTable4 together with the oscillatory strengths. The randomness of ε, f and D may be due to variation of $V_{.1/2}$ from drug to drug and also due to Contact Charge Transfer (CCT) which alters the ε to a greater extent [8].

For a given complex the extinction coefficients, the oscillatory strengths and the dipole moments are also found to be almost independent of temperature. The randomness in the values of ε,*f* and D may be due to CCT. The observed value is related to ε_{max} of CT and ε'max of CCT by α ε'

$$\varepsilon_{obs}=\varepsilon_{CT}+ \quad \text{-----} \quad \text{…….} \quad (7)$$

K

Where α is number of possible contact sites for the species in excess, around and molecule of the second species, ε' is the extinction coefficients for the CCT process base don't the potential contact concentration and K is stability constant. Thus the ε_{obs} observed depends on the α, ε' and K which cannot be evaluated a properly the values of' are found to be order 10^6, thus the second term of the equation determines the observed ε.

6. Stability constants and Thermodynamic parameters [9]: The optical density (d) at$_{max}$ C Tismonitored by varying the concentration of donor while concentration of acceptor is held constant. The'd' increased with increasing concentration of donor at a given temperature. The'd' also is found to decrease with increasing temperature for a set of constant donor and acceptor concentration. The stability constants have been evaluated from the intersection point of Rose-Drago plots. The stability constants of the complexes increased with electron releasing ability of the drug and are in the order: Ofloxacin > Levofloxacin > Ciprofloxacin.

The *K* values are also found to decrease with the increasing ionization potentials and a straight line was obtained when logarithmic functions of *K* are plotted against ionization potentials of donors with some exceptions because all the donors are not structurally related (there are mono nuclear, binuclear aromatics and heterocyclics) [10, 13].

The thermodynamic parameters *viz.,* Hands was evaluated from variation of stability constants with temperature using vant Hoff's method. A plot of log KVs1/T gave straight line, from the slope and intercept of which the H and Shave been evaluated. The G values at 25^{0}C were calculated using the equation [11, 12].

$$\Delta G = H - TS$$

And are presented in Table 2. A linear relationship is obtained between Hands for all CT complexes. It is interesting to note that the satirically unhindered complex formation indicates that the interaction is of π-π* type.

Table No. 1: Spectral characteristics of Charge Transfer complexes of DDQ with drugs

S.No	Name of the Drug	λ max	E_{CT} (eV)	VCT×10^{-3}	I.P	ΔV1/2	ε max	D	F
1	Dolutegravir	295	12.34	7.32	7.56	4225	5876	2.65	0.13
2	Asunaprevir	305	12.43	7.80	7.72	5520	4356	3.12	0.21
3	Beclabuvir	275	13.52	7.73	8.13	6770	3215	3.56	0.19
4	Daclatsavir	255	13.61	7.52	9.86	7800	5733	4.02	1.17

Table No. 2: Stability Constants & Thermodynamic parameters of CT complexes of DDQ with Drugs

S.No	Name of the Drug	Stability Constants at (K) Various Temperatures					-ΔH	-ΔS	-ΔG
		K_{10}^{0}C	K_{20}^{0}C	K_{30}^{0}C	K_{40}^{0}C	K_{50}^{0}C			
1	Dolutegravir	19.13	17.30	16.75	15.63	9.23	19.20	57.45	3.25
2	Asunaprevir	18.85	14.99	12.94	11.27	8.72	18.67	55.56	3.01
3	Beclabuvir	17.81	13.87	10.55	9.85	7.61	16.15	44.89	2.45
4	Daclatsavir	16.53	12.87	10.55	8.85	6.49	1.64	41.2	1.23

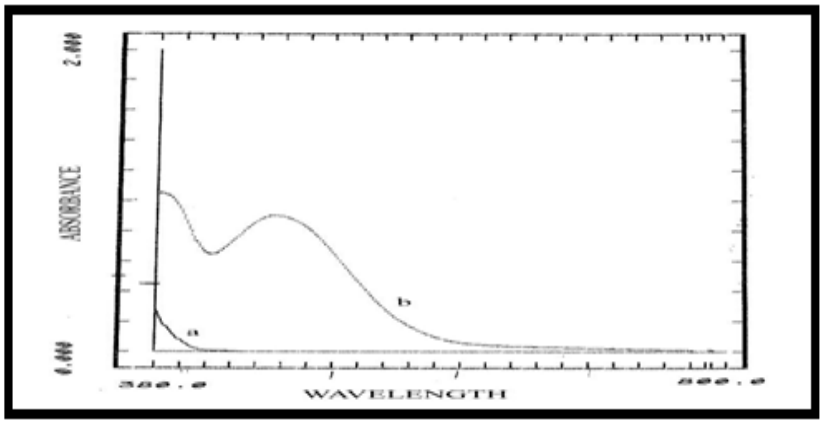


Fig. 1: Absorption spectra of a) Ofloxacin b) its molecular complex with DDQ

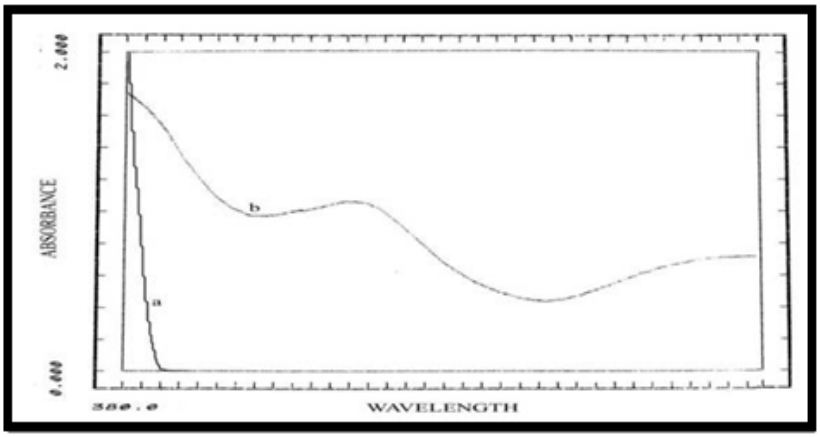


Fig. 2: Absorption spectra of a) Levofloxacin b) its molecular complex with DDQ

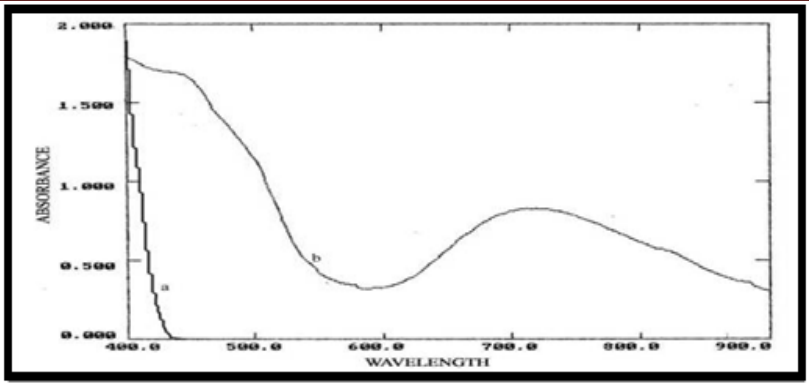


Fig. 3: Absorption spectra ofa) Ciprofloxacin b) its molecular complex with DDQ

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