Turk J Chem
24 (2000) , 223 – 230.
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Spectroscopic Studies of Charge-Transfer Complexes of 2,3-Dichloro-5,6-Dicyano-P-Benzo-Quinone

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Received 28.08.1997

Charge-transfer complexes of 2,3-dichloro-5, 6-dicyano-p-benzoquinone (DDQ) p-acetotoluidide, acetanilid, biphenyl and naphthalene were studied and their absorption spectra in solution were recorded. Absorption spectral data were obtained in CH_2Cl_2, $CHCl_3$, CCl_4 and mixture (CH_2Cl_2 + v) at different temperatures. Two charge-transfer bands were observed in each case. Spectral characterization of these complexes was determined and correlated with the ionization potential of the donor. Variation in thermodynamic parameters were also found to be due to change in donor and solvent.

Introduction

Various aromatic molecules can behave as electron donors and form molecular complexes with electron acceptor molecules such as halogens, mitrocompounds and quinones[1,2]. Extensive works have been carried out to elucidate the nature of intermolecular interactions in these molecular complexes. Mulliken has developed the theory of the intermolecular CT interactions, which has been applied successfully to the interpretation of the absorption bands characteristic of molecular complexes in various systems[3]. DDQ is a strong electron acceptor having electron affinity 1.9 e.v.[14].

In the present paper, spectrophotometric studies have been carried out for CT complexes of DDQ with p-acetotoluidide, acetanilide, biphenyl and naphthalene, special attention being paid to the appearance of two CT bands. Orgel first reported two bands in the case of methylbenzene complexes of chloranil and 1,2,5-trinitrobenzene[5]. Orgel related the two ionization potentials of the donor molecules to the frequencies of the CT bands.

Experimental

Solid materials including acceptor and donors (of Merck, BDH and Kodak) were used as such without further purification after confirmation of their purity measurement of their melting points. In solvents CH_2Cl_2 and CCl_4, the were used without further purification after measurement of their reflactive indices and comparing with reported values.

$CHCl_3$ was purified by the method reported in the literature.

It was washed with water, dried with anhydrous $CaCl_2$ and then distilled[6].

Spectrophotometric measurements were made on a Hitachi 2205 spectrophotometer. Freshly prepared solutions were used for measurements.

Results

DDQ solution in all the solvents used in the study was light yellow, and the solutions of the donors (acetanilide, p-acetotoluidide, biphenyl and naphthalene) in the solvents considered were colourless. λ_{max}. values for the solutions of acceptors and donors in the given solvents are reported in Table 1. Absorption Spectra of CT complexes of DDQ with various donors in different solvents are shown in Figs 1-4 and their λ_{max}. are reported in Table 2.

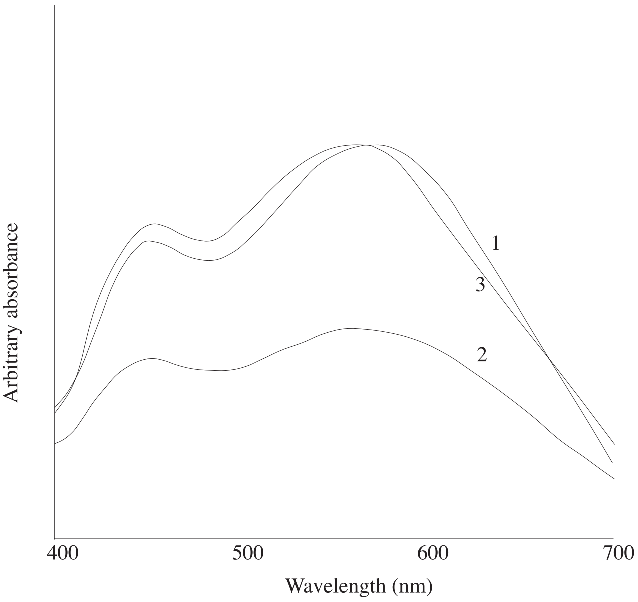

Figure 1. Absorption spectra of Acetanilide-DDQ complexes in (1) CH_2Cl_2 (2) $CHCl_3$ (3) Mixture.

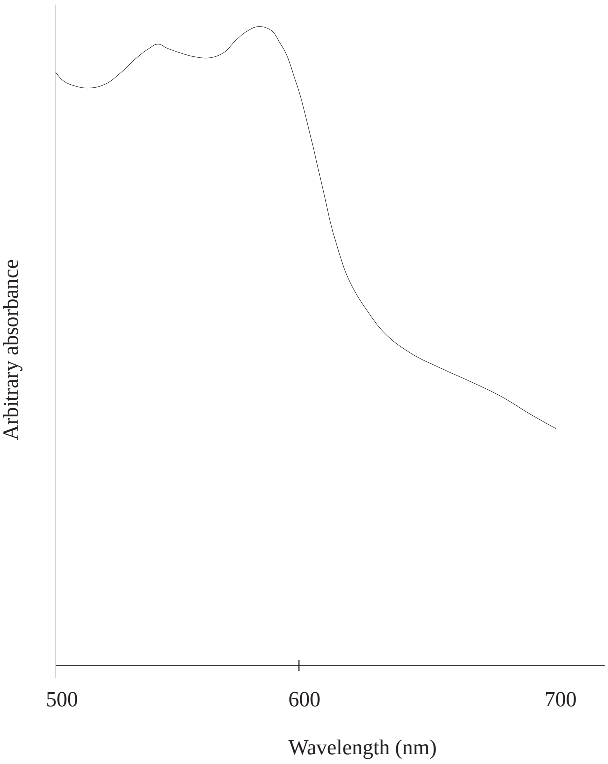

Figure 2. Absorption spectrum of P-acetotoluidide-DDQ complex in CH_2Cl_2.

Table 1. Position of Absorption maxima of Donors and acceptor-(DDQ) CH_2Cl_2 (2) $CHCl_3$ (3) CCl_4, (4) Mixture.

Compound	λ_{max} in nm CH_2Cl_2	 $CHCl_3$	 CCl_4
Acetanilide	255	252	
P-acetotoluidide	260	259	
Naphthalene	230, 277	270, 280	271, 282
Biphenyl	270	266	268
DDQ	242, 288 349	292, 352	288

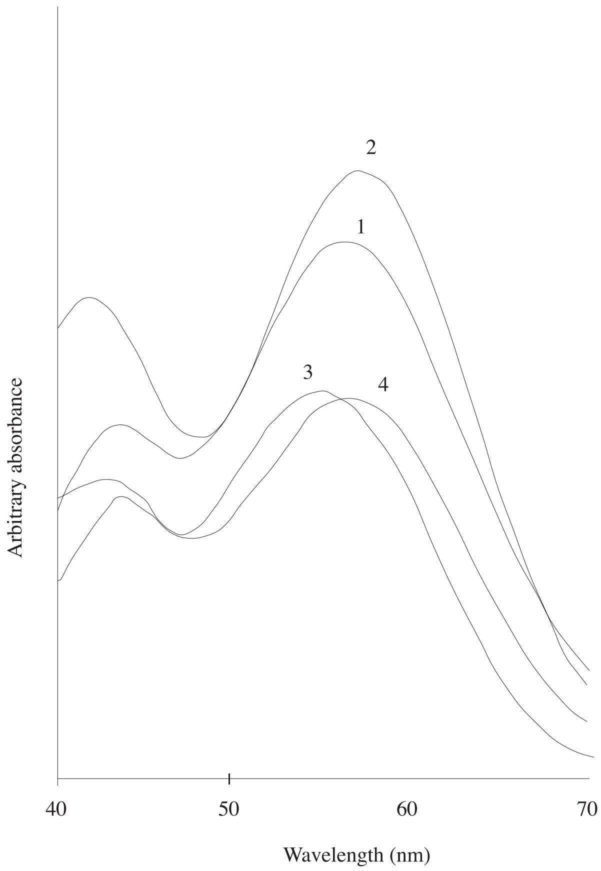

Figure 3. Absorption spectra of Biphenyl-DDQ complexes in (1) CH_2Cl_2 (2) $CHCl_3$ (3) CCl_4 (4) Mixture.

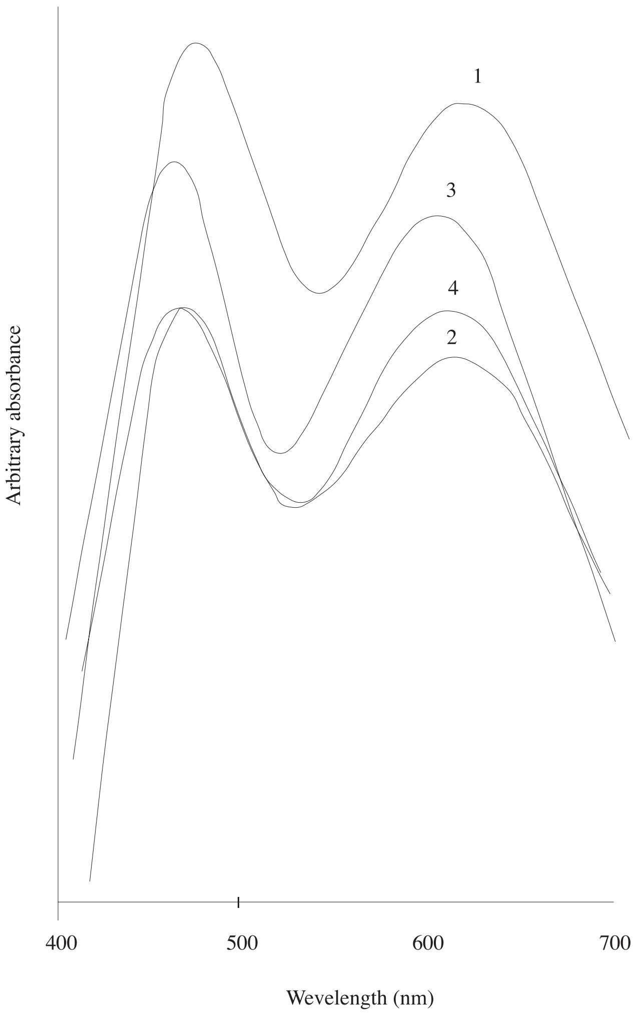

Figure 4. Absorption spectra of Naphthalene-DDQ complexes in (1) CH_2Cl_2 (2) $CHCl_3$ (3) CCl_4 (4) Mixture.

Table 2. Results of complexes of DDQ

Complex	Solvent	λ_{max} (nm)	$\bar{\nu}.10^3(cm^{-1})$		K°_{20}		K°_{25}		K°_{30}	$h\nu$ (e.v)		I°	
Biphenyl -DDQ	CH_2Cl_2	440,565	22.7	17.7	0.32,	0.30	0.84,	060		2.70,	2.10	8.93,	8.23
	$CHCl_3$	440,570	22.7	17.5	1.23,	1.24	0.97,	0.97	2.70,	2.00	8.93,	8.21	
	CCl_4	435, 555	22.9,	18.0			3.30,	3.30	1.94, 1.89	2.70,	2.10	8.96,	8.27
CH_2Cl_2+CCl_4	430, 565 1:1	23.2,	17.7			1.37,	1.20		2.57,	2.10	9.05,	8.20	
Naphthal- ene-DDQ	CH_2Cl_2	470,615	21.3,	16.3	2.43,	2.41	2.47,	1.82		2.53,	1.93	8.72,	8.03
	$CHCl_3$	470,620	21.7,	16.1	4.70,	4.70	3.38	3.26		2.53,	1.91	8.72,	8.01
	CCl_4	458,600	21.8,	16.6			10.5,	9.80	17.0,16.5	2.59,	1.98	8.46,	8.08
	CH_2cl_2+CCl_4 1:1	472,615	21.2,	16.3			4.60,	4.40		2.34,	1.93	8.70,	8.03
Acetani- -lide-DDQ	CH_2Cl_2	460,570	21.2,	17.5	0.56,	0.55	1.50,	1.20		2.50,	2.08	8.79,	8.21
	$CHCl_3$	455,560	21.9,	17.8	1.70,	1.64	1.90,	2.10		2.60,	2.10	8.82,	8.25
	CH_2Cl_2+CCl_4 1:1	452,570	22.1,	17.5			0.79,	0.83		2.70,	2.08	8.84,	8.21
P-aceto- toluidide-DDQ	CH_2Cl_2	540,580	18.5,	17.2	1.03,	1.13	2.60,	2.28		2.70,	2.00	8.34,	8.10

The association constant kass and molar absorptivity co-efficient ϵ_e were determined by the modified Benesi-Hildebrand[7] equation (1), as had been done by other workers[8,9,10] for the determination of Kass. Values of Kass. and ϵ_e are given in Tables 2 and 3 respectively.

$$\frac{C_A}{A - Ao} = \frac{1}{K(\epsilon_e - \epsilon_A)} \frac{1}{C_D} + \frac{1}{K(\epsilon_e - \epsilon_A)} \qquad (1)$$

In the determination of kass and ϵ_a from eq (1), the concentration of donor (C$_D$) was varied but that of acceptor (C$_D$) was kept constant such that C$_D$ >>C$_A$.

The plot of C$_A$/A-Ao Vs C_D^{-1} is fairly linear where Ao is the absorbance due to acceptor at the same concentration, indicating the formation of a 1:1 complex, as shown in Fig. 6 for the acetanilide-DDQ complex in CHCl$_3$.

Ionization potentials of donors were determined by eq. (2) and given in Table 2 (II)

$$h\nu_{CT} = aI^D + b \qquad (2)$$

Change in standard free energy (ΔG°), standard entropy (ΔS°) and standard enthalpy (ΔG°) are summarized in Table 4.

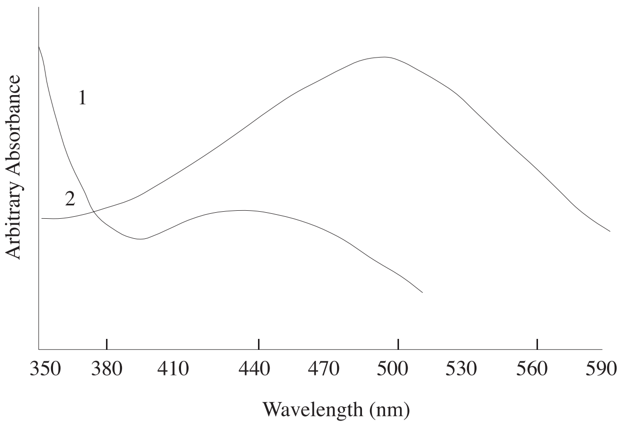

Figure 5. Absorption spectra of complexes of Chloranil in CH$_2$Cl$_2$ with (1) Acetanilide (2) P-acetotoluidide

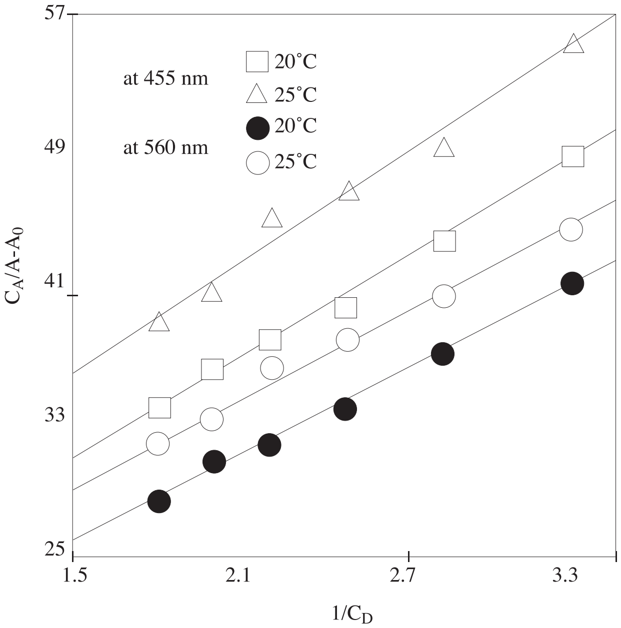

Figure 6. Plot of C$_A$/A-Ao Vs 1/C$_D$ for Acetanilide-DDQ complex in CHCl$_3$.

Discussion

Absorption Spectra

When the absorption spectra of acetanilide-DDQ complex (Fig. 1) is compared with the absorption maxima (Table 1) of acetanilide and DDQ, it is evident that the absorption bands in the region of 240-320 nm are due to the absorption of acetanilide molecule, except the absorption peaks at 242, 386 and 348 nm, which are due to DDQ. The absorption peaks at 400 nm can be attributed neither to acetanilide nor to DDQ. This is characteristic of the complex. Another absorption band characterstic of the complex is observed having a maximum at 570 nm (Fig. 1). Similarly, each complex has two characteristic bands in the DDQ system Their λ_{max}. are given in table (2).

According to the Mulliken theory (3), the wave function of the ground state of the 1:1 complex is described as follows:

$$\tau n = a\varphi_1(DA) + b\varphi(D^+A^-) \tag{3}$$

and that of the first excited state as

$$\tau E = a^\star\varphi(D^+A^-) + b^\star\varphi(C.A) \tag{4}$$

where φ(D.A) and φ(D$^+$-A$^-$) are the nobond and the dative bond wave functions respectively. For weak interacting complexes a>>b, the energy of transition, τN→ τE can be given as follows[12]:

$$h\nu = I_p - E - W \tag{5}$$

where Ip is the ionization energy of the donor, E the electron affinity of the aceptor and W the dissociation energy of the CT excited state. Foster[12] has shown that the frequencies of the CT spectra were proportional to the ionization energies of the donor (eq. 2)

$$h\nu_{CT} = aI^D + b \tag{6}$$

In the present work, a& b are equal to 0.89 and -5.15 respectively (11).

Appearance of Two CT Bands

Well defined absorption peaks of the two CT bands were observed for DDQ complexes with acetanilide, p-acetotoluidide biphenyl and naphthalene (see Figs 1-4).

Multi-CT absorption bands have been found for the CT complexes containing strong electron acceptors such as chloranil, bromanil and TCNE[13]. The origin of the multi-CT bands here observed in the case of biphenyl and naphthalene can be explained by the existence of two closely located occupied orbitals of the donor. Briegleb, Czekalla and Reuss[14] reported $\Delta\nu_{CT}$ between two peaks of naphthalene and biphenyl complexes with chloranil and TCNE as 5100 cm^{-1} and 5700 cm^{-1} respectively.

The $\Delta\nu$ct values for naphthalene and biphenyl complexes with DDQ are 5000 cm^{-1} and 5200 cm^{-1}, respectively. The $\Delta\nu$CT values for chloranil, TCNE and DDQ complexes are comparable for the respective donor. Thus, the above factor is justified for the appearance of two CT bands for naphthalene and biphenyl complexes with DDQ.

In seems that the appearance of two CT bands for complexes of acetanilide and p-acetotoluidide with DDQ can not be explained by the same mechanism as that for biphenyl and naphthalene. Acetanilide and p-acetotoluidide are considered to be non-planar molecules[15]. The orientation of these two molecules may account to some extent for the appearance of two CT bands in these two systems. Furthermore, when acetanilide and p-acetotoluidide were used as donors with chloranil, a single band is observed in both systems, as shown in Fig. 5. Thus it seems that DDQ may accept electrons at two closely located unoccupied molecular arbitals. The situation may be clarified by MO calculations to compare $\Delta\nu_{CT}$ with the energy difference of the two highest occupied levels of acetanilide and p-acetotonidide and the two lowest-unoccupied levels of DDQ.

Table 3. e_{emx} values of complexes of DDQ

Complex	Solvent	e_{emx} at 20°C (L-mol^{-1} cm^{-1})		e_{emx} at 25°C (L-mol^{-1} cm^{-1})		e_{emx} at 30°C (L-mol^{-1} cm^{-1})	
Biphenyl-DDQ	CH_2Cl_2	1859,	2941	844,	1529		
	$CHCl_3$	1096,	1652	1314	1893		
	CCl_4			1157,	1602	1513,	2096
	CH_2Cl_2+CCl_4 1:1			883,	1418		
Naphthalene-DDQ	CH_2Cl_2	1189	1098,	1152,	1212		
	$CHCl_3$	1308,	1213	1612,	1510		
	CCl_4			1175,	1602,	1198,	1137
	CH_2Cl_2+CCl_4 1:1			1129,	1057	1198,	1137
Acetanilide- CH_2Cl_2	976,	1169	363,	652			
DDQ	$CHCl_4$	61,	74	50,	58		
	CCl_4			683,	960		
	CH_2Cl_2+CCl_4 1:1						
P-acetoto-luidide-DDQ	CH_2Cl_2		3690	2146			

Association Constant Kass and Molar Absorptivity

Effect of donor on associaiton constt.

Association constant kass changes as the change of the donor changes. Kass for p-acelotoluidide DDQ complex (2.28 L mole^{-1}) in CH_2Cl_2 is larger than kass for acetanilide DDQ complex in the same solvent (1.268 L. mol^{-1}). It is expected that the presence of the methyl group may increase the value of kass in p-acelootoluidide in comparison to acetanilide. Foster, Hammick and Persons[16] reported kass values for hexamethylbenzene (HMB)-Chloranil complexes. Where each methyl group increases the kass value by a factor of 1.7, kass values for naphthalene DDQ complexes in CH_2Cl_2, $CHCl_3$,CCl_4 and mixture (CH_2Cl_2+CCl_4) are larger than kass valuesb for biphenyl-DDQ complexes in these solvents. Ianization potentials (I^D) of biphenyl and acetanilide are greater than the I^D values of p-acetotoluidide and naphthalene. This shows that ionization energies of farmers are larger than ionization energies of laters. On this basis, lower values of kass for biphenyl and acetanilide are expected, which is in agreement with our experimental results (Table 2).

Solvent Effect On Kass: Values of kass for complexes of DDQ increase with the decrease of polarity and dielectric constant, as shown in Table 2. Czekalla and Meyer[17] have reported a similar trend in the case of the tetrachlorophthalicanhydride-HMB system in a different solvent, where the kass. value increases with the decrease of the dielectric constant of the solvent. Davis and Symons[18] reported that when the solutions of donor and acceptor are mixed in non-polar solvent, the complex DA is immediately formed in high concentration. As mentioned earlier, absorbance measurements were made just after mixing the donor acceptor solution. This factor justifies the increase in kass values of DDQ complexes with the decrease of polarity.

Effect of Temp. On Kass. and ϵ_e:- Temperature affects the values of kass and ϵ_e. Generally kass for complexes of DDQ increases with the increase of temperature. but in some cases, such as complexes of DDQ with biphenyl and naphthalene in $CHCl_3$ and biphenyl-DDQ complex in CCl_4. Its value decreases with the increase of temperature (Table 2). There may be a decrease in the stability of the complex with the increases in temperature in these systems.

This trend is similar to one reported in many systems, such as TCNB-benzene complexes, where kass for CT complexes decreases with the increase of temperature[19,20,21].

Generally values of ϵ_e in a DDQ system increase with the increase of temperature, e.g., in complexes of DDA with biphenyl and naphthalene in $CHCl_3$ and in biphenyl-DDQ complex in CCl_4. This trend is similar to that reported by Tzubmura and Lange for the N,N-dimethylfoormamide iodine system[21]. The values of ϵ_e were found to decrease with the increase of temperature for some complexes of DDQ, e.g., complexes of DDQ with four donors studied in CH_2Cl_2 as shown in Table 3. Further investigation is required for the understanding of this trend.

Table 4. Thermodynamic Parameters of Complex of DDQ

Complex	Solvent	ΔG°	ΔS°	ΔH°			
		(J.mol^{-1})		(J.K^{-1}.mol^{-1})		(KJ.mol^{-1})	
Biphenyl-DDQ	CH_2Cl_2	441,	1017	457,	373	137,	112
	$CHCl_3$	74,	69	-118,	-119	-35,	-36
	CCl_4	-2966,	-2998	-258,	-278	-80,	-86
	$CH_2Cl_2+CCl_4$ 1:1	-789,	-527				
Naphthalene-DDQ	CH_2Cl_2	-2243,	-1480	16,	-134	3,	-41
	$CHCl_3$	-3023,	-2929	-150,	-170	-48,	-54
	CCl_4	-5827,	-5663	-263,	282	73,	78
	$CH_2Cl_2+CCl_4$ 1:1	-3786,	-3694				
Acetanilide-DDQ	CH_2Cl_2	-1093	-470	495,	383	147,	114
	$CHCl_3$	-1606,	-1842	62,	126	17,	36
	$CH_2Cl_2+CCl_4$ 1:1	0.557,	-467				
P-acetotoluidide-DDQ	CH_2Cl_2	-2367,	-2047	394,	341	135,	101

Table 5. Solvent Parameters.

Solvent	Z.Value	Dielectric Constant	Refective Index(n)	Dipole Moment(μ)
CH_2Cl_2	64.2	9.080	1.424	1.600
$CHCl_3$	63.2	4.806	1.446	1.150
CCl_4	54.8	2.240	1.460	
Mixture ($CH_2Cl_2+CCl_4$)		6.532		

C. Therodynamic Parameters:

Thermodynamic parameters including ΔG°, ΔH°, and ΔS°, for complexes of DDQ with different donors in different solvents are shown in Table 4. Here values of thermodynamic parameters decrease with the decrease of the polarity of the solvent (with few exceptions). As the Z-value decreases, the solvating ability of the solvent decreases and so does the stability of the complex. Most probably the decrease in solvating power is the factor responsible for the decrease in thermodynamic parameters.

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