Studies on Molecular Complexes of Naphthylamines

K.P. Srivastava* and Rishi Kant Shrivastava
Department of Chemistry, Jai Prakash University, Chapra-841 301, India
E-mail: kpsri@yahoo.co.in; jpukpsrichem@rediffmail.com

The stability constants and thermodynamic parameters of the electron-donor-acceptor complexes of *p*-benzoquinone, 2,6-dichlorobenzoquinone and chloranil with α- and β-naphthylamines have been calculated from the positions of the charge transfer bands using electronic absorption spectroscopy in carbon tetrachloride medium under high donor concentration. All the molecular complexes exhibit one charge-transfer band each in the wavelength region where neither donors nor acceptors have any absorption. All the molecular complexes are inferred to be of *n*-π type with 1:1 stoichiometry.

INTRODUCTION

The formation of molecular complexes or electron donor-acceptor complexes has long been recognized[1-3]. The charge transfer complexes of derivatives of quinones with different kinds of donors have been of particular interests to workers[4-8] in recent years due to their importance as potential high efficiency second order non-linear optical (NLO) materials[9]. The extensive works have been carried out to determine the stability constants (K_{AD}) and molar absorptivity of the charge transfer complexes with their stoichiometry.

In continuation[10,11] of our previous works, we have investigated the formation of 1:1 stoichiometric electron donor-acceptor complexes of quinones with some aromatic amines to get a better understanding in this field. We report herein the formation of charge transfer complexes of α- and β-naphthylamines with *p*-benzoquinone (BQ), 2,6-dichloro-*p*-benzoquinone (DCQ) and chloranil (CHL). Since the charge transfer complexes of mentioned acceptors and donors have stabilized in non-polar solvents and under high donor concentrations, so we choose carbon tetrachloride as solvent for the present study. The present work deals with the calculated stability constants and thermodynamic parameters. Further, attempts have been made to calculate the ionization potentials of the donors from the energies of the charge transfer transitions in the present investigation.

EXPERIMENTAL

The stability constant (K_{AD}) and thermodynamic parameters of charge transfer complexes were determined by spectrophotometric method using a systronics UV-Vis spectrophotometric type-119 PC based (wave length range 200-1000 nm and band width 2 nm) with 1 cm matched pair of quartz cuvettes.

The solvent carbon tetrachloride (AnalaR) was purified by distillation (b.p = 76 °C). Both α- and β-napthylamines (Fluka) were recrystallized from ethanol and their melting points were checked. *p*-Benzoquinone (BDH) was recrystallized from ethanol and chloranil (BDH) was recrystallized twice from benzene[12].

The stock solutions of each donor and acceptor compounds were prepared freshly by dissolving their appropriate amount in definite volume of carbon tetra-chloride solvent. The freshly prepared solutions of acceptor and donor compounds were mixed just before recording the spectra. The formation of charge transfer complexes was generally indicated by absorption maximum.

For quantitative studies on the formation of charge transfer complexes the spectra of a series of the mixture of each donor with mentioned acceptors were subsequently obtained (Fig. 1). The absorptions were measured with a number of initial concentrations of donors keeping always at least 10 times larger than of acceptors.
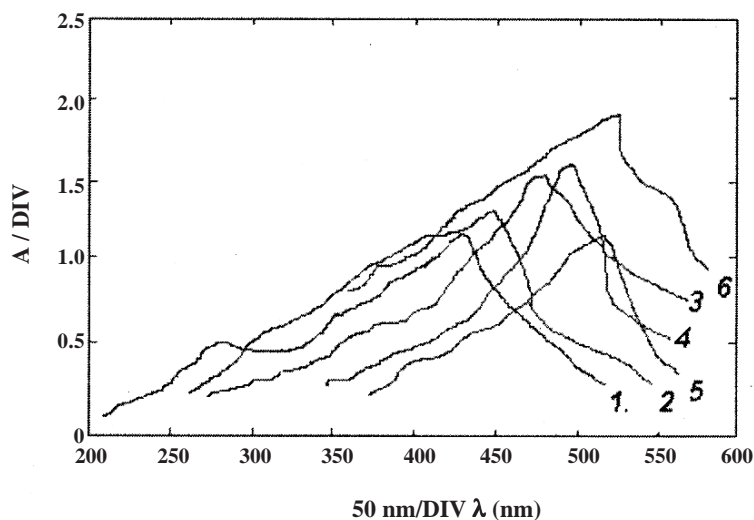

Fig. 1. Charge transfer spectra of BQ, DCQ and CHL with α- and β-Napthylamines

The formation constants or stability constants (K_{AD}) of the charge transfer complexes under investigation were determined by using Benesi-Hildebrand equation[13] (i) and also from Rose-Drago equation[14] (ii) from the absorption measurements on the charge transfer bands.

$$[A_0]/A = 1/K_{AD}[D_0]\, \varepsilon + 1/\varepsilon \qquad\qquad (i)$$

$$K_{AD}^{-1} = A/\varepsilon - \{[\,A_0] + [D_0]\} + [\,A_0][D_0]\, A/\varepsilon \qquad\qquad (ii)$$

where A is the absorbance and ε is the molar extinction coefficient of the molecular complexes, $[A_0]$ and $[D_0]$ are the initial concentrations of acceptors and donors, respectively. The stability constants for molecular complexes under investigation were obtained from the ratio of intercept to slope and e from inverse intercept of Benesi-Hildebrand plots (Fig. 2). They were also evaluated from the intersection points of the Rose-Drago plots, which agreed with the results of the Benesi-Hildebrand plots.
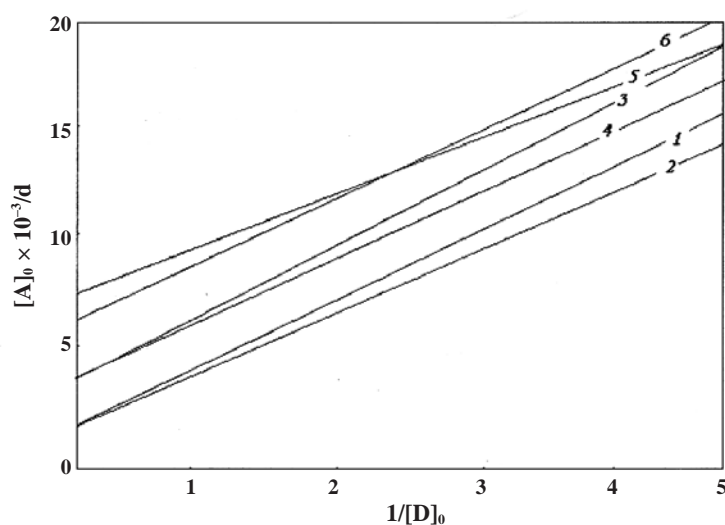

Fig. 2. Benesi-Hildebrand plot for charge transfer complexes

RESULTS AND DISCUSSION

The electronic spectra of presently studied charge transfer complexes are reported in Table-1. From the spectra a new band appears in the region 448-523 nm, for each charge transfer complex which not displayed by either component alone hence that can be attributed to a single intermolecular charge transfer transition. The charge transfer band appeared due to excitation of electron from the highest occupied molecular orbital (HOMO) of donors to the lowest unoccupied molecular orbital (LUMO) of the acceptors[15]. The examination of the data given in the Table-2 clearly indicates that the stability of charge transfer complexes of the same donor follows the order of the electron affinities of the π-acceptors as:

BQ < DCQ < CHL

On the other hand, the stability of charge transfer complexes of the electron donors with the same acceptor increases with increase in the strength of their basic strength as:
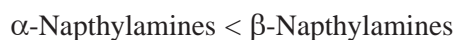
α-Napthylamines < β-Napthylamines

TABLE-1
ABSORBANCE [A] DATA OF DONOR-ACCEPTOR MIXTURES

	$[D_0]$ (mol/L)	$[A_0]$ (mol/L)	A (cm^{-1})	λ_{CT} (nm)
1.	α-Naphthylamine + *p*-benzoquinone (α-NA + BQ)			
	0.250		0.185	
	0.385	0.00245	0.269	448
	0.585		0.360	
2.	β-Naphthylamine + *p*-benzoquinone (β-NA + BQ)			
	0.300		0.260	
	0.301	0.00245	0.309	452
	0.535		0.370	
3.	α-Naphthylamine + 2,6-dichloro-*p*-benzoquinone (α-NA + DCQ)			
	0.07		0.275	
	0.14	0.00285	0.371	482
	0.21		0.607	
4.	β-Naphthylamine + 2,6-dichloro-*p*-benzoquinone (β-NA + DCQ)			
	0.107		0.277	
	0.175	0.00285	0.394	487
	0.333		0.571	
5.	α-Naphthylamine + chloranil (α-NA + CHL)			
	0.067		0.757	
	0.172	0.00297	1.113	508
	0.268		1.288	
6.	β-Naphthylamine + chloranil (β-NA + CHL)			
	0.083		0.993	
	0.140	0.00297	1.300	523
	0.400		1.700	

TABLE-2
THERMODYNAMIC PARAMETERS OF CT COMPLEXES

Charge transfer complexes	C_{AD} (Lmol^{-1} cm^{-1})	K_{AD} (L mol^{-1})	ΔH (kcal mol^{-1})	ΔS (kcal mol^{-1} K^{-1})	ΔG (kcal mol^{-1})
α-NA + BQ	555.50	0.67	14.35	-0.04742	-0.2177
β-NA + BQ	557.30	0.71	15.80	-0.05205	-0.2875
α-NA + DCQ	625.10	2.66	19.75	-0.06606	-0.6129
β-NA + DCQ	632.20	3.02	20.90	-0.06803	-0.6279
α-NA + CHL	714.20	10.47	23.40	-0.07403	-1.3997
β-NA + CHL	714.28	10.80	29.10	-0.09294	-1.4049

This behaviour strongly suggests that the formation of charge transfer complexes is mainly due to the transition of a non-bonding electron from HOMO of N atom of NH_2 of naphthylamines to the antibonding π-orbital (π*, LUMO) of the acceptors. Therefore, the investigated complexes are considered as strong n-π molecular complexes as judged by the relatively high values of K_{AD}.

The linearity of Benesi-Hildebrand plots indicated the formation of molecular complexes of 1:1 stoichiometry, which was further verified by Job's continuous variation method. The ε_{CT} values for different charge transfer complexes studied are inconsistent with the K_{AD} values, since it is theoretically expected that the higher the K_{AD} of charge transfer complex, the greater the intensity of the charge transfer band.

Thermodynamic parameters of charge-transfer complexes: The thermodynamic parameters *viz.*, ΔH, ΔS and ΔG related to the charge transfer complex formation have been determined from the temperature variation of stability constants using van't Hoff's method. These values at 298 K for charge transfer complexes under investigation are presented in Table-2. The negative values of ΔG show that the formation of the charge transfer complexes was spontaneous. Further, the decrease in the degree of formation of the components on complexation is shown by the negative values of ΔS.

Ionization potentials of electron donors: Attempts have been made to determine the ionization potentials of naphthylamines using the empirical equation derived by Aloisi and Pignataro[16]. The values of I_D obtained are recorded as:

Donor	Average I_D (eV)
α-Naphthylamines	14.1295 ± 0.1235
β-Napthylamines	14.1280 ± 0.1025

The I_D values for donors are inconsistent with the corresponding K_{AD} values of their charge transfer complexes with acceptors. However, the exact values of I_D for naphthylamines are not available in the literature. Furthermore, the I_D values of donors with three π-acceptor complexes do not differ significantly suggesting that the donor orbital involved in the charge transfer transition is the same for all 3 electron acceptor used.

Conclusion

The following conclusions were drawn from the present study: (1) All the investigated charge transfer complexes were n-π type with 1:1 stoichiometry. (2) All the charge transfer bands aroused due to excitation of electron from the HOMO of the donors to the LUMO of the π-acceptors. (3). The bathochromic shift of the charge transfer band is in the order

$$\alpha\text{-Napthylamines} < \beta\text{-Napthylamines}$$
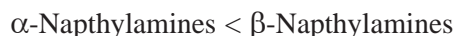
(4) The stability constants of the investigated charge transfer complexes of the same donor follow the order of the electron affinities of the π-acceptors:

$$BQ < DCQ < CHL$$

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