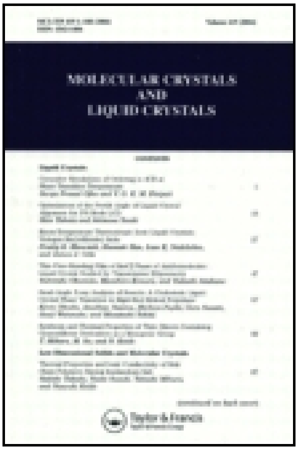

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Spectrophotometric and Thermodynamic Studies of Charge Transfer Complexes of 8-Hydroxyquinoline with π Acceptor p-Nitrophenol in Different Solvents

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Spectrophotometric and Thermodynamic Studies of Charge Transfer Complexes of 8-Hydroxyquinoline with π Acceptor p-Nitrophenol in Different Solvents

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The charge transfer complexes of the donor 8-hydroxyquinoline (8HQ) with π *acceptor p-nitrophenol (PNP) have been studied spectrophotometrically in various solvents. The results indicate the formation of CTC in less Polar solvent to be more and also* λ_{CT} *shifted to longer wavelength with increased polarity. The stoichiometry of the complex was found to be 1:1 by straight line method between donor and acceptor with maximum absorption bands. The data are discussed in terms of molar extinction coefficient (*ε_{CT}*), equilibrium constant (Formation constant), resonance energy (*R_N*), free energy (*ΔG^o*), ionization potential (*I_D*), and oscillator strengths (f). The results indicate the formation constant (*K_{CT}*) for the complex to be dependent of the nature of electron acceptors, donors, and polarity of solvents.*

Keywords: charge transfer; formation constant; 8-hydroxyquinoline; p-nitrophenol; solvent

1. INTRODUCTION

Charge transfer phenomena was first introduced by Milliken [1]. The term charge transfer gives a certain type of complex resulting from interactions of donor and acceptor with the formation of weak bonds [2] discussed widely by Foster. CT-interactions between aromatic electron acceptors and various electron donors containing nitrogen, oxygen, or sulfur atoms have attracted increased interest over the last few years [3]. Charge transfer complexes play an important role in many biological systems, e.g., the transfer of charge from one molecule to another [4–8] during drug action, enzyme catalysis, and

Address correspondence to Afaq Ahmad, Department of Chemistry, Faculty of Science, Aligarh Muslim University, Aligarh-202002, India. E-mail: drafaqahmad7@gmail.com ion transfer through lipophilic membranes. In the recent years, some of the CT complexes have been widely important for the efficiency in the field of magnetic properties, electrical conductivities, and optical properties [9–20]. In this type of reaction, some drugs can behave as electron donors, forming charge-transfer complexes by electron transfer from an occupied orbital to an empty orbital of an acceptor molecule [21]. The formation of charge transfer complexes is often characterized by an intense, broad, electronic absorption band, either in the UV visible region or in the visible region [22]. The stoichiometry, structure, spectral, thermal, and electronic properties of the complexes depend strongly on the type and nature of the donor base as well as the electron acceptors. Quinoline and its derivatives such as 8-hydroxyquinoline (8HQ) and 5-nitro-8-hydroxyquinoline exhibit strong chemical and biological activities, revealing a wide range of pharmaceutical application due to their cytotoxic, bactericide, and fungicide properties [23–27]. 8HQ is a versatile molecule because of its amphoteric and Zwitterionic properties [28]. Generally, p-Nitrophenol (PNP) is more acidic than alcohols [29] and will react with the base sodium hydroxide but alcohols will not. Electron withdrawing groups on the benzene ring increase the acidity of phenol, accordingly, phenols play role of the acceptors. This fact can be applied herein in our study between para-substituted nitrophenol (acceptor) and 8HQ as donor. The solid state reactions between 8HQ and nitrophenols have been studied [30]. However, in this article, the effect of polarity of solvents on the formation of CTC of 8HQ and PNP are investigated. The characterization of the CT complexes were carried out by several measurements including determination of association constant (K_{CT}), by fitting to the Gaussian function and molar extinction coefficient. In this article, we investigate the interaction of 8HQ with PNP in solvents of different polarity by visible spectral data of CT complex (π-n) of 8HQ with π acceptor PNP. Variation in λ_{CT} in which CT complex forms with change in polarity of solvents were also investigated. Determination were made for the formation constant (K_{CT}) and λ_{CT} for the CT complexes of 8HQ with PNP in different polarity solvents.

2. MATERIALS AND METHODS

2.1. Materials

8HQ, PNP (Qualigens Fine Chemicals, Thomas Baker, respectively) were of the highest purity and used without further purification. Double distilled water, Ethanol (Merck analytical grade) and acetone (Merck) were used without further purification.

2.2. Preparation of Standard Solutions

Solutions of different concentration of donor, 0.1 M, 0.2 M, 0.3 M, 0.4 M, were prepared by dissolving 8HQ accurately weighed in different solvents such as acetone and ethanol and their aqueous solutions in different ratios (for acetone 90:10, 8:20, and 70:30, for ethanol 95:05, 90:10, and 85:15).

A standard solution of PNP (0.01 M) was prepared by dissolving accurate weight of pure π acceptor in above solvents.

3. RESULTS AND DISCUSSION

3.1. Observation of CT Bands

The electronic absorption spectra of the donor 8HQ, acceptor p-Nitrophenol and the resulting CT complex in acetone, ethanol, and their aqueous solutions, were recorded in the visible region 340–599 nm using a spectrophotometer model spectronic 20D$^+$ (thermo-spectronic) with a 1 cm quartz cell path length were shown in Figs. 1 and 2.

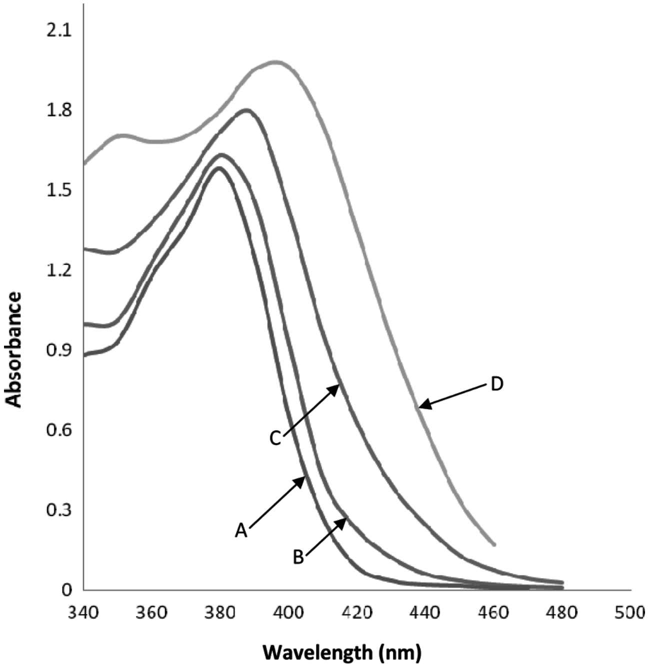


FIGURE 1 Electronic absorption spectra of charge transfer complexes of 0.1 M 8HQ–0.1 M PNP in different solvents: (A) Acetone, (B) 90:10 (Acetone:Water), (C) 80:20 (Acetone:Water), (D) 70:30 (Acetone:Water) at room temperature.

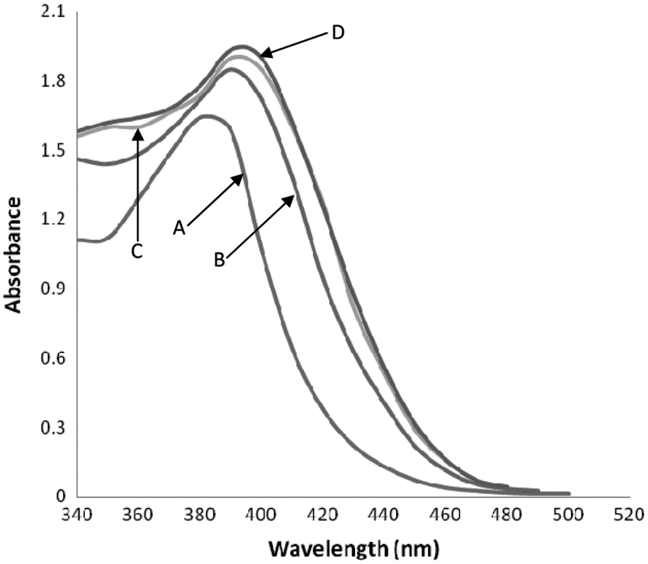


FIGURE 2 Electronic absorption spectra of charge transfer complexes of 0.1 M 8HQ–0.1 M PNP in different solvents: (A) Ethanol, (B) 95:05 (Ethanol:Water), (C) 90:10 (Ethanol:Water), (D) 85:15 (Ethanol:Water) at room temperature.

A 3 ml volume of donor and acceptor were scanned separately through a spectrophotometric titration [31] at room temperature to their wavelength of maximum absorption. When 3 ml of acceptor solution and 3 ml of donor solution were mixed, a light green color charge transfer complex was formed. The wavelength of maximum absorption of the resulting solution was determined. The complex for each of the reaction mixture standing over night at room temperature to form stable complexes before analysis at the maximum absorbance at 382 nm, 384 nm, 386 nm, 400 nm, 384 nm, 390 nm, 394 nm, and 397 nm, which were determined in different polar solvents by using spectrophotometer. The concentration of the donor in the reaction mixture was kept greater than acceptor, ($[D]_0) >> [A]_0$) [21,22] and changed over a wide range of concentration from 0.1 M to 0.4 M, while concentration of the π acceptor (p-substituted phenol) was kept fixed [21] at 0.01 M in each solvents, these produced solutions with donor: acceptor molar ratios varying from 10:1 to 40:1, these concentration ratios were used to straight line diagram for determination of formation constant of CTC were shown in Tables 1 (a and b). To obtain the CT bands, the spectrum of solution of 0.1 M 8HQ and 0.1 M PNP in different solvents were recorded using above mentioned solvents

Table 1 The Electronic Absorption Spectral Data for Charge Transfer Complex of 8HQ with PN in Different Solvent Having Different Polarity at Room Temperature

Solvent (Acetone:Water)	[Acceptor]:[Donor]	
(a)		Absorbance at 382 nm
100:00	0.01:0.1	0.502
	0.01:0.2	0.512
	0.01:0.3	0.516
	0.01:0.4	0.527
		Absorbance at 384 nm
90:10	0.01:0.1	0.760
	0.01:0.2	0.792
	0.01:0.3	0.801
	0.01:0.4	0.808
		Absorbance at 386 nm
80:20	0.01:0.1	0.855
	0.01:0.2	0.955
	0.01:0.3	1.035
	0.01:0.4	1.040
		Absorbance at 400 nm
70:30	0.01:0.1	1.120
	0.01:0.2	1.420
	0.01:0.3	1.580
	0.01:0.4	1.740

Solvent (Ethanol:Water)	[Acceptor]:[Donor]	
(b)		Absorbance at 384 nm
100:00	0.01:0.1	0.774
	0.01:0.2	0.920
	0.01:0.3	0.985
	0.01:0.4	1.045
		Absorbance at 390 nm
95:05	0.01:0.1	0.905
	0.01:0.2	1.120
	0.01:0.3	1.230
	0.01:0.4	1.350
		Absorbance at 394 nm
90:10	0.01:0.1	0.952
	0.01:0.2	1.220
	0.01:0.3	1.420
	0.01:0.4	1.620
		Absorbance at 397 nm
85:15	0.01:0.1	1.000
	0.01:0.2	1.380
	0.01:0.3	1.640
	0.01:0.4	1.800

as a reference, these concentration ratios were used for electronic absorption spectra of the CTC in said solvents. It is observed that new absorption peak appear in the visible region due to n→π^* transition by the formation of radical ion pairs. In some cases multiple peaks were obtained; the longest wavelength peak was considered as CT peak [32]. The change of the absorption intensity to higher side for all complexes when adding the donor are reported in Table 1 (a and b). These measurements are based on the CT absorption bands exhibited by the spectra of the systems are shown in Figs. 1 and 2. The CT absorption spectra were analyzed by fitting to the Gaussian function $y = y_0 + [A/(w\sqrt{(\pi/2)})]\exp[-2(x - x_c)^2/w^2]$, where x and y denote wavelength and absorbance, respectively. The results of the Gaussian analysis for all system under study are shown in Table 2. The wavelength of the absorption maximum ($\lambda_{max} = x_c$) and the corresponding transition energies (hv) are summarized in Table 3. It has been observed that the λ_{CT} of CTC increases and $h\nu_{CT}$ decreases with increasing polarity of the solvents due to the change in dative structure [1].

3.2. Ionization Potentials of the Donor

The ionization potentials of the donor in the charge transfer complex in different solvents are calculated using empirical equation derived by Aloisi and Piganatro [33]

$$I_D(\mathrm{ev}) = 5.76 + 1.53 \times 10^{-4}\nu_{CT}, \tag{1}$$

where I_D is the ionization potential of the donor molecule.

TABLE 2 Gaussian Curve Analysis for the CT Spectrum of 8HQ with PNP in Different Polar Solvents

Solvent	Area of the curve (A)	Width of the curve (w)	y_0
Acetone:Water			
100:00	91.17 ± 10.10	48.39 ± 4.54	0.01 ± 0.06
90:10	103.92 ± 11.33	52.71 ± 4.69	−0.005 ± 0.07
80:20	154.86 ± 25.56	70.88 ± 8.28	−0.03 ± 0.13
70:30	408.57 ± 35.54	117.32 ± 27.84	−0.83 ± 0.77
Ethanol:Water			
100:00	121.92 ± 14.67	60.53 ± 5.66	−0.01 ± 0.08
95:05	231.24 ± 61.56	90.33 ± 13.98	−0.25 ± 0.27
90:10	1163.97 ± 102.61	173.90 ± 51.93	−3.48 ± 8.17
85:15	1241.66 ± 152.45	177.80 ± 72.43	−3.69 ± 9.14

TABLE 3 The Ionization Potentials (I_D) of Donor, Resonance Energies (R_N), $h\nu_{CT}$, Oscillator Strength (*f*), and Transition Dipole Strengths (μ_{EN}) of the Charge Transfer Complex of 8HQ with PNP in Different Solvents

Solvent	I_D (ev)	$h\nu_{CT}$ (ev)	$\|R_N\|$	10^6 x f	μ Debye
Acetone:Water					
100:00	9.76	3.25	0.0022	5.53	0.490
90:10	9.74	3.23	0.0035	9.65	0.620
80:20	9.72	3.22	0.0046	17.20	0.714
70:30	9.58	3.10	0.0083	52.79	0.972
Ethanol:Water					
100:00	9.74	3.23	0.0048	15.20	0.726
95:05	9.68	3.18	0.0065	30.47	0.848
90:10	9.64	3.15	0.0084	78.25	0.972
85:15	9.61	3.13	0.0100	96.01	1.064

The ν_{CT} is wave numbers in cm^{-1} of the complex were determined in different solvents, viz., acetone, ethanol, and their aqueous solutions. The ionization potentials are calculated and reported in Table 3, which decrease with increasing polarity of the solvent due to change in dielectric constant.

3.3. Determination of Resonance Energy (R_N) and Free Energy (ΔG^o)

Brieglab and Czekalla [34] theoretically derived the relation

$$\varepsilon_{CT} = 7.7 \times 10^4/[h\nu_{CT}/|R_N| - 3.5], \tag{2}$$

where ε_{CT} is the molar extinction coefficient of the complex at the maximum of the CT absorption, ν_{CT} is the frequency of the CT peak, and R_N is the resonance energy of the complex in the ground state, which obviously is a contributing factor to the stability constant of the complex (a ground state property). The values of R_N for the complexes under study have been given in Table 3.

The standard free energy of the CT complexes (ΔG^o) were calculated [35] from the formation constant using the following equation:

$$\Delta G^o = -2.303\ RT \log K_{CT}, \tag{3}$$

where ΔG^o is the free energy of the CT complexes ($kJ\,mol^{-1}$). R the gas constant ($8.314\,J\,mol^{-1}K^{-1}$), T the temperature in Kelvin (273+°C), and K_{CT} is the formation constant of donor-acceptor

TABLE 4 The Adsorption Maxima (λ_{CT}, ν_{CT}), Formation Constant (K_{CT}), Molar Extinction Coefficient (ε_{CT}), and Free Energy (ΔG^o) of the Charge Transfer Complexes of 8HQ with PNP in Different Solvents at Room Temperature

Solvent	λ_{CT} (nm)	K_{CT} (l mol^{-1})	ε_{CT} (l mol^{-1} cm^{-1})	$-\Delta G^o$ (kJ mol^{-1})	$\bar{\nu}_{CT}$ (cm^{-1})
Acetone:Water					
100:00	382	182.70	52.91	12.905	26178
90:10	384	70.80	84.74	10.556	26041
80:20	386	33.37	112.35	08.692	25906
70:30	400	11.36	208.33	06.021	25000
Ethanol:Water					
100:00	384	20.36	116.28	07.464	26041
95:05	390	13.55	158.73	06.460	25641
90:10	394	8.26	208.33	05.232	25380
85:15	397	6.66	250.00	04.698	25188

complexes in different solvents at room temperature. The values are calculated and reported in Table 4. It is found that the R_N and the ΔG^o increase with increasing polarity of the solvent may also be due to the dative structure be destabilized in polar solvent.

3.4. Spectrophotometric Study of Formation Constant of the Charge Transfer Complexes of 8-HQ/PNP

Stoichiometry and the formation constant of the charge transfer complexes of 8HQ with PNP have been determined in different polar solvent at room temperature using the Benesi–Hildebrauid [36] equation. The spectrophotometric data were employed to calculate the values of formation constant, K_{CT} of the complexes. The changes in the absorbance upon addition of 8HQ to a solution of PNP of fixed concentration follow the Benesi–Heldebrand [36] equation in the form

$$[A]_o/A = 1/K_{CT}\varepsilon_{CT}1/[D]_o + 1/\varepsilon_{CT}, \tag{4}$$

where $[D]_o$ and $[A]_o$ are the concentration of the 8HQ (donor), and PNP (acceptor), respectively, A is the absorbance of the donor–acceptor mixture at λ_{CT} against the solvents as reference; K_{CT} is the formation constant and ε_{CT} is the molar extinction coefficient. The above equation is valid [36] under the condition $[D]_o >> [A]_o$ [21,22] for 1:1 donor–acceptor complexes. The concentration of the donor was changed over a wide range from 0.1 M to 0.4 M while concentration of the π acceptor PNP was kept fixed at 0.01 M in each of the reaction mixture. These produced solution with donor: acceptor molar ratio varying from 10:1 to 40:1. The data are given in Table 1 (a and b).

The Benesi–Hildebrand [36] method is an approximation that have been used many times and gives decent results. But the extinction coefficient is really a different one between the complex and free species that absorbs at the same wavelength. The intensity in the visible region of the absorption bands, measured against the solvent as reference, increases with increased in the polarity and addition of 8HQ. The typical absorbance data for charge transfer complexes of 8HQ with PNP in different polar solvents at room temperature are reported in Table 1 (a and b). In all the cases, very good linear plots according to equation [36] are obtained, one typical case is being shown in Fig. 3 (a and b). Formation constant for the complexes of 8HQ with PNP in different solvents having different polarity at room temperature are summarized in Table 4. Plots of $[A]_o/[A]$ against $1/[D]_o$ were found to be linear in all cases. Figure 3 (a and b) shows 1:1 charge transfer complex, i.e., the straight lines are obtained. These result prove the formation of the 1:1 CTC. From the slope and the intercept, K_{CT} and ε_{CT} of the complex were calculated.

The K_{CT} values increases significantly with decreasing polarity of the solvents. Moreover, the increases in K_{CT} value with decreasing solvent polarity may also be due to the fact that, for a very strong CTC, the dative structure D^+–A^- should be stabilized in a less polar solvent [1]. Dissociation of the complexes into D^+ and A^- radicals has been found to occur in the ground state [37]. The experimental data given in Table 4 reveals that formation constants of resulting CTC in different solvent decreases with increasing polarity of the solvent from acetone, ethanol, and to their aqueous solutions which were used as a solvents. In the present study, the formation constants are highest in less polar solvents.

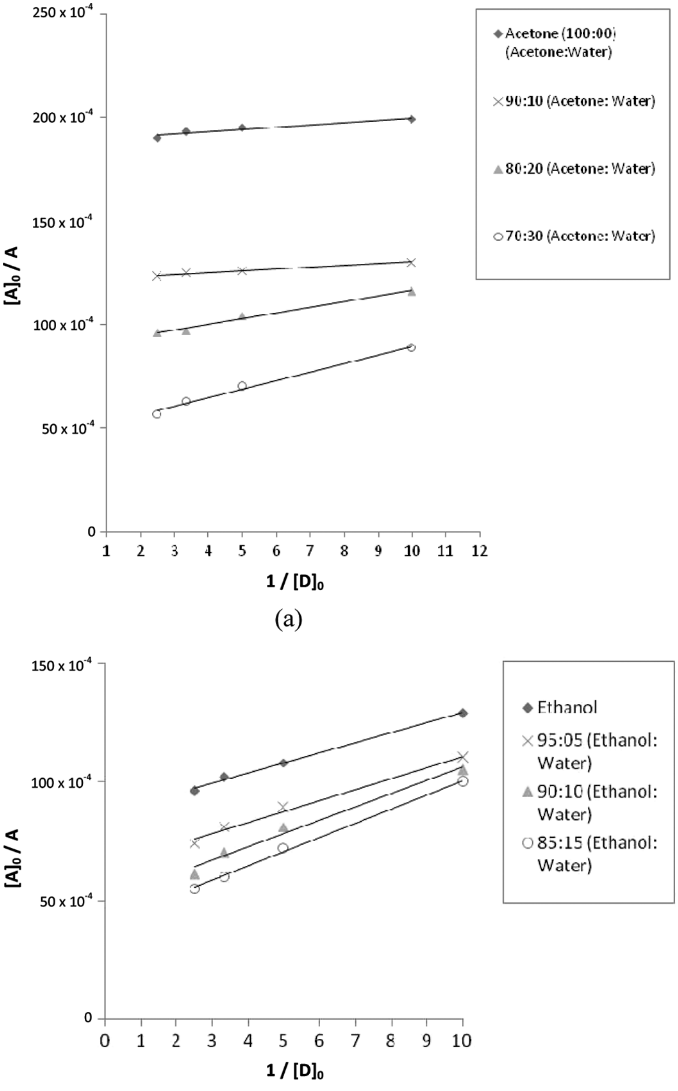
3.5. Determination of Oscillator (f) and Transition Dipole Strengths (μ_{EN})

The oscillator strength (*f*), which has a dimensionless quantity used express the transition probability of the CT bands [38] and the transition dipole strengths (μ_{EN}) of the CT complex. From the absorption spectra, we can extract an oscillator strength; the oscillator strength (*f*) is estimated using the formula

$$f = 4.32 \times 10^{-9} \int \varepsilon_{CT} d\nu, \tag{5}$$

where $\int \varepsilon_{CT}\, dv$ is the area under the curve of the extinction coefficient of the absorption band in question vs. frequency. To a first approximation

$$f = 4.32 \times 10^{-9} \varepsilon_{CT} \Delta\nu_{1/2}, \tag{6}$$



(a)

(b)

FIGURE 3 (a) Benesi–Hildebrand plots of charge transfer complexes of 8HQ with PNP $[A]_0/A$ vs $1/[D]_0$ in different solvents having different polarity at room temperature. (b) Benesi–Hildebrand plots of charge transfer complexes of 8HQ with PNP $[A]_0/A$ vs $1/[D]_0$ in different solvents having different polarity at room temperature.

where ε_{CT} is the maximum extinction coefficient of the band and $\Delta\nu_{1/2}$ is the half-width, i.e., the width of the band at half the maximum extinction. The observed oscillator strengths of the CT bands increases with increasing solvent polarity are summarized in Table 4.

The extinction coefficient is related to the transition dipole by

$$\mu_{EN} = 0.0952\ [\varepsilon_{CT}\Delta\nu_{1/2}/\Delta\nu]^{1/2}, \tag{7}$$

where $\Delta\nu \approx \nu'$ at ε_{CT} and μ_{EN} is defined as $-e\int \Psi ex \sum_i r_i \Psi_g d\tau$ μ_{EN} for the complex of 8HQ with PNP are calculated and reported in Table 4. The μ_{EN} increases with increasing polarity of the solvent.

CONCLUSIONS

From the foregoing discussion, it may be concluded that the 8HQ (donor) form charge transfer complex of 1:1 (donor:acceptor) stiochiometry with PNP in acetone, ethanol, and their aqueous solutions. It has been found that the values of the CTC decreases with increasing solvent polarity due to destabilization of the dative structure D^+A^- of CTCs in polar solvents and then the dissociation of the complexes into D^+ and A^-. The interaction between the donor and acceptor was found to be $n\rightarrow\pi^*$ transition by the formation of radical ion pair. Oscillator strength (*f*) transition dipole strengths (μ_{EN}), resonance energies (R_N), and free energy (ΔG^o) have been estimated for the 8HQ/PNP system in different polar solvents which change with variation in polarity of the solvent due to change in the dative structure. It was observed that spectrophotometric and thermodynamic parameters of the complexes are solvent dependent. The result shows that the investigated complexes are stable, exothermic, and spontaneous.

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