β-Cyclodextrin Inclusion Complexes of Aromatic Amines and Nitrocompounds and their Photoinduced Electron Transfer Reaction with the Tris(2,2′-bipyridine)ruthenium(II) Complex

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Abstract

The formation of β-cyclodextrin (β-CD) inclusion complexes of aromatic amines and nitrocompounds have been studied by absorption and emission spectral methods. Among the different compounds studied, *p*-nitrobenzoic acid showed the smallest K_f value. 3,5-dinitrobenzoic acid showed the highest K_f value due to the formation of a hydrogen bond between the nitro group and the hydrogen in the hydroxyl group of CD, and this is not possible with *p*-nitrobenzoic acid. The lower K_f values in the range 60–70 observed for ortho substituted compounds indicate the steric effect imposed by the ortho substitution of the compound. The para substituted compounds showed higher K_f values in the range 110–130 due to the hydrophobic effect and also due to the absence of a steric effect. The lifetime of the Ru(II) complex is not affected by the presence of β-CD. When the aromatic amines and nitrocompounds are used as quenchers for the excited state $[Ru(bpy)_3]^{2+}$, the quenching rate constant (k_q) values are not significantly affected by the presence of β-CD. This indicates that the electron donor or electron acceptor groups are not included into the cavity of β-CD.

Introduction

Photoinduced electron transfer reactions have been extensively investigated both in homogeneous and micro-heterogeneous media [1–3]. Although the driving force dependence of such reactions is well characterized in homogeneous solutions [4–6], similar studies in micro-heterogeneous systems are not common. In studying the photoinduced electron transfer reactions in micro-heterogeneous environments, micelles, polyelectrolytes, charged colloids, micro-emulsions, vesicles and cyclodextrins have been utilized to assist charge separation and to retard the recombination reactions [1–3, 7–11]. Recent studies show that the photophysical, photochemical and electrochemical properties of the molecules are influenced by the presence of cyclodextrins in the reaction medium [12]. The three most commonly studied cyclodextrins (CDs) are α, β and γ which are comprised of six, seven and eight glucose units with a hydrophobic cavity with inner diameters of 4.4, 7.8 and 9.2 Å, respectively [12, 13]. The most important characteristics of CD is that they form inclusion complexes with guest molecules having proper size [14]. The absorption spectra of different guest molecules have been studied by forming CD complexes [13, 15, 16]. When a guest molecule is complexed with CD a shift in the absorption band has been observed. In principle one could apply the association properties of cylcodextrins for controlling the re-

combination process between photoproducts by the selective binding of one of the electron transfer products.

The transition metal complex, $[Ru(bpy)_3]^{2+}$, (Ru(II), bpy = 2,2′-bipyridine) is one of the most extensively studied photosensitizers in solar energy conversion [17–19]. Demas *et al.* [20] have studied the binding interaction of Ru(II)-substituted diimine photosensitizers with β-CD in aqueous solution by using the excited-state lifetime method. Only the complexes possessing phenyl-substituted ligands exhibited significant interaction with cyclodextrin. The inclusion of the phenyl group into the CD cavity has been observed. In such case, the binding of cyclodextrin to the Ru(II) complexes shields the complexes from oxygen quenching. The shielding increases as the number of bound CDs increases. Willner *et al.* [21] have reported the photosensitized reduction of $N, N′$-dioctyl-4,4′-bipyridinium (octylviologen) C_8V^{2+}, using $[Ru(bpy)_3]^{2+}$ as the sensitizer in the presence and absence of β-CD. In the absence of β-CD, photoreduction of C_8V^{2+} yields a dimer aggregate of the reduced photoproduct C_8V^{+}. This study revealed that the cyclodextrins stabilize effectively the intermediate photoproducts formed in different reactions against the back-electron transfer and other side reactions.

In the present investigation, the interactions of β-CD with different water soluble aromatic amines and nitrocompounds have been studied by absorption and emission spectral methods. The amines and nitrocompounds have been used as quenchers for the reductive and oxidative elec-
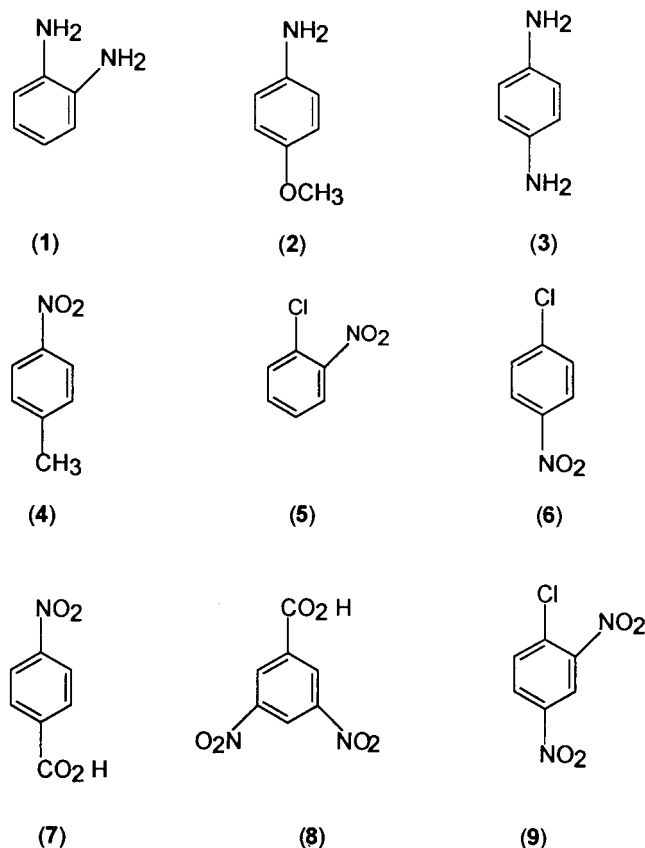
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Figure 1. Structures of *o*-phenylenediamine (**1**), *p*-anisidine (**2**), *p*-phenylenediamine (**3**), *p*-nitrotoluene (**4**), 1-chloro-2-nitrobenzene (**5**), *p*-chloronitrobenzene (**6**), 4-nitrobenzoic acid (**7**), 3,5-dinitrobenzoic acid (**8**) and 1-chloro-2,4-dinitrobenzene (**9**).

tron transfer quenching of the excited state $[Ru(bpy)_3]^{2+}$ to understand the influence of β-CD on the electron transfer mechanisms. The large $[Ru(bpy)_3]^{2+}$ complex cannot form an inclusion complex with CDs whereas the quencher molecules (aromatic amines and nitrocompounds) can form inclusion complexes with CDs.

Experimental

The aromatic amines and nitrocompounds were obtained from Merck and purified. The structures of the quencher molecules are shown in Figure 1. β-Cyclodextrin was purchased from Aldrich and was used as received. Cyclodextrin solutions were prepared immediately prior to use. The $[Ru(bpy)_3]Cl_2$ complex was prepared according to the reported procedure ($\lambda_{max} = 452$ nm and $\epsilon_{452} = 14600$ $M^{-1}cm^{-1}$) [22]. Water used in this study was doubly distilled over alkaline potassium permanganate in an all-glass apparatus.

Absorption spectral studies were carried out by using a JASCO 7800 UV/VIS spectrophotometer. Emission spectral measurements were carried out by using a Hitachi F4500 fluorescence spectrophotometer. The lifetimes of the Ru(II) complex with different quenchers in aqueous medium were measured by using an Arcon A500 laser flash photolysis spectrometer. The sample solutions used for lifetime studies were de-aerated thoroughly by purging pure Ar gas for

30 min. All the measurements were carried out at room temperature (25 °C).

The formation constant (K_f) for the inclusion of a guest molecule into the cavity of β-CD was calculated from the absorption and emission spectral data by using Benesi–Hildebrand Equations (1) and (2) [23, 24].

$$1/\Delta A = 1/K_f \cdot 1/\Delta\epsilon \cdot 1/[CD] + 1/\Delta\epsilon \qquad (1)$$

$$1/(I - I_0) = 1/K_f \cdot 1/(I_1 - I_0) \cdot 1/[CD] + 1/(I_1 - I_0), \quad (2)$$

where ΔA is the change in the absorbance, K_f is the formation constant, I_0 is the emission intensity of the guest molecule in the absence of β-CD, I_1 is the emission intensity of the inclusion complex and I is the emission intensity of guest at a particular concentration of β-CD. The formation constant (K_f) value was calculated from the absorption and emission spectral data by plotting ($1/\Delta A$) vs. ($1/[CD]$) or ($1/\Delta I_f$) vs. ($1/[CD]$). From the slope and intercept of the straight line plots, the K_f values were calculated. The Stern–Volmer constants (K_{sv}) were calculated from the Stern–Volmer plots (Equations (3) and (4)).

$$I_0/I = 1 + K_{sv}[Q] \qquad (3)$$

$$\tau_0/\tau = 1 + K_{sv}[Q], \qquad (4)$$

where K_{sv} is the Stern–Volmer constant and $[Q]$ is the concentration of the quencher. Here, I_0 and I are the emission intensities of the Ru(II) complex in the absence and presence of $[Q]$ and τ_0 and τ are the excited state lifetimes of the Ru(II) complex in the absence and presence of β-CD, respectively. I_0/I or τ_0/τ was plotted against the quencher concentration $[Q]$ and a straight line was obtained with an unit intercept in all the quenching studies. The quenching rate constants (k_q) were calculated using Equation (5).

$$k_q = K_{sv}/\tau_0. \qquad (5)$$

Results and discussion

The absorption spectra of 4-nitrobenzoic acid (**7**) in the absence and presence of different concentrations of β-CD and the corresponding Benesi–Hildebrand plot are shown in Figures 2A and 2B. An increase in the absorbance at the absorption maximum was observed for compound **7** in the presence of β-CD. The observed increase in the absorbance was due to the formation of cyclodextrin inclusion complexes. A very similar observation was also seen for all other compounds. Since the cavity diameter of β-CD (~7.8 Å) [13,14] is large enough to accommodate the guest molecules, the formation of an inclusion complex is possible. The molecular dimension of the guest molecule (~4–6 Å) favors the inclusion process. The stability of the inclusion complex can be determined from the formation constant values. The absorption spectral changes observed for the compounds in

the absence and presence of β-CD are used to draw the corresponding Benesi–Hildebrand plots (Equations (1) and (2)) and the formation constant values (K_f) for the β-CD inclusion complexes of amines and nitrocompounds calculated using the absorption spectral data are summarized in Table 1. The emission spectra of p-anisidine (2) in the presence of different concentrations of β-CD were recorded and the corresponding Benesi–Hildebrand plot is shown in Figure 3. An observable increase in the emission intensity in the presence of β-CD was observed due to the formation of an inclusion complex. The fluorescence intensity enhancement of the guest molecule by CD encapsulation has been caused by a decrease in the rotational freedom of the guest molecule and the removal of water molecules from the CD cavity which can quench the excited state molecule [25]. Using the emission spectral data, the formation constants were calculated (Equation (2)). The K_f values observed for the compounds are summarized in Table 1.

Analysis of the formation constants of the different guest molecules gives more insight into the stability of the inclusion complexes. All the inclusion complexes are comparatively stable as given in Table 1. Among the different molecules studied, p-nitrobenzoic acid showed the smallest value and 3,5-dinitrobenzoic acid showed the highest K_f value. The higher value observed for 3,5-dinitrobenzoic acid could be due to the formation of a hydrogen bond between the nitro group and the hydrogen in the hydroxyl group of CD as reported earlier [26, 27] and this is not possible with p-nitrobenzoic acid. The lower K_f values in the range 60–70 observed for compounds 1, 5 and 9 indicate the steric effect imposed by the ortho substitution of the compounds. In the case of compound 7, both —NO_2 and —COOH groups are more polar and it may form a weak inclusion complex with the hydrophobic cavity of the CD. The para substituted compounds such as 2, 3, 4 and 6 show higher K_f values in the range 110–130 due to the hydrophobic effect and also due to the absence of a steric effect.

The photoinduced electron transfer quenching reactions between the excited state Ru(II) complex and the different aromatic amines and nitrocompounds were carried out in the presence of β-CD. Since the diameter of the $[Ru(bpy)_3]^{2+}$ complex is ~12 Å [28] it cannot be included into the cavity of β-CD. However, the organic quencher molecules can be included into the β-CD cavity as described earlier. If the quencher molecule is included into the cavity of β-CD, the electron transfer between the sensitizer and the quencher molecule may be hindered. Such quenching studies between the sensitizer naphthalene and the quencher iodide ion has already been reported [29]. The emission decay of the Ru(II) complex in the absence and presence of β-CD were measured and the excited state lifetimes were found to be 580 ± 10 ns. The Ru(II) complex showed similar lifetimes both in the absence and presence of β-CD. This observation shows that the lifetime of the Ru(II) complex was not affected by the presence of β-CD. Figure 4 shows the typical emission quenching spectra obtained for the Ru(II)-p-phenylenediamine systems in the absence and presence of β-CD. The emission intensity changes and lifetime changes

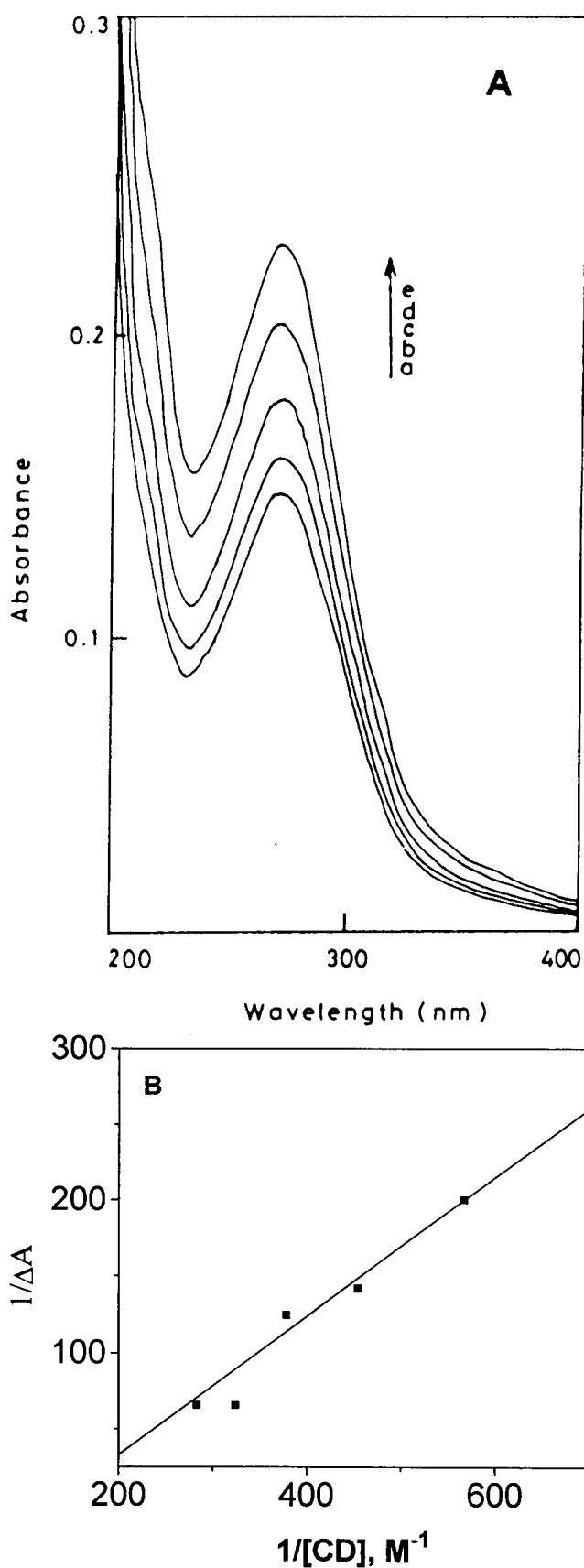*Figure 2.* A. Absorption spectra of 4-nitrobenzoic acid (1.14×10^{-5} M) in the absence and presence of various concentrations of β-CD. [β-CD]: (a) 0.0, (b) 0.88, (c) 1.76, (d) 4.40 and (e) 5.28 mM. B. Plot of ($1/\Delta A$) vs. ($1/[CD]$) for the calculation of formation constants for 4-nitrobenzoic acid (4-NBA).

Table 1. The formation constants (K_f, M^{-1}) and quenching rate constants (k_1, M^{-1} s^{-1})[a] for the quenching of excited state $[Ru(bpy)_3]^{2+}$ in the absence and presence of β-CD in aqueous solution.

Quencher	K_f, (M^{-1})	k_q,[b] absence of CD $\times 10^9$ (M^{-1} s^{-1})	k_q,[b] presence of CD $\times 10^9$ (M^{-1} s^{-1})	k_q,[b] absence of CD $\times 10^9$ (M^{-1} s^{-1})	k_q,[c] presence of CD $\times 10^9$ (M^{-1} s^{-1})
o-phenylenediamine (**1**)	71	1.04	0.46	0.88	0.77
p-anisidine (**2**)	129	0.25	0.15	0.29	0.24
p-phenylenediamine (**3**)	110	2.38	1.60		
p-nitrotoluene (**4**)	120	3.41	2.15	2.76	2.39
1-chloro-2-nitrobenzene (**5**)	79	4.01	2.65	4.05	2.90
p-chloronitrobenzene (**6**)	130	4.54	2.96	3.86	3.49
4-nitrobenzoic acid (**7**)	60	9.69	6.24	8.69	6.53
3,5-dinitrobenzoic acid (**8**)	144	9.54	7.54	9.20	9.27
1-chloro-2,4-dinitrobenzene (**9**)	63	4.90	3.66	5.14	5.23
Fe^{3+}		0.03[d]	0.02[d]		
Cu^{2+}		6.40[d]	6.80[d]		

[a] Average values of three experiments (error limit = $\sim$ 20%).
[b] Emission quenching method.
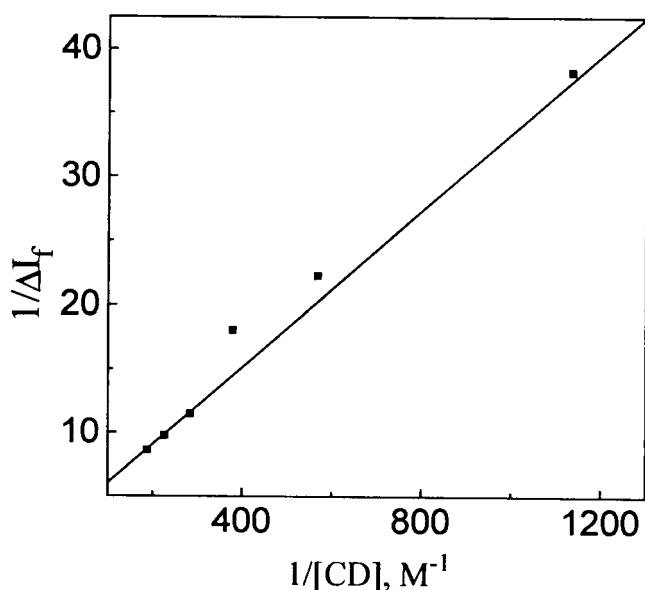[c] Lifetime quenching method.
[d] In 0.05 M H_2SO_4.

Figure 3. Plot of ($1/\Delta I_f$) vs. ($1/[CD]$) for the calculation of formation constants for *p*-anisidine (**2**).

for emission and lifetime quenching of the photoredox system were measured and used to draw the Stern–Volmer plots (Figure 5). The bimolecular quenching rate constants calculated from the linear plots obtained for different quencher molecules in the absence and presence of β-CD are given in Table 1. In all the quenching systems, the quenching rate constant (k_q) values are not significantly affected by the presence of β-CD (Table 1). It indicates that the β-CD complexation does not effectively influence the electron transfer reaction (Equation (6)).

$$^*Ru^{2+} + Q \rightarrow Ru^{3+} + Q^- \quad \text{or} \quad Ru^+ + Q^+. \quad (6)$$
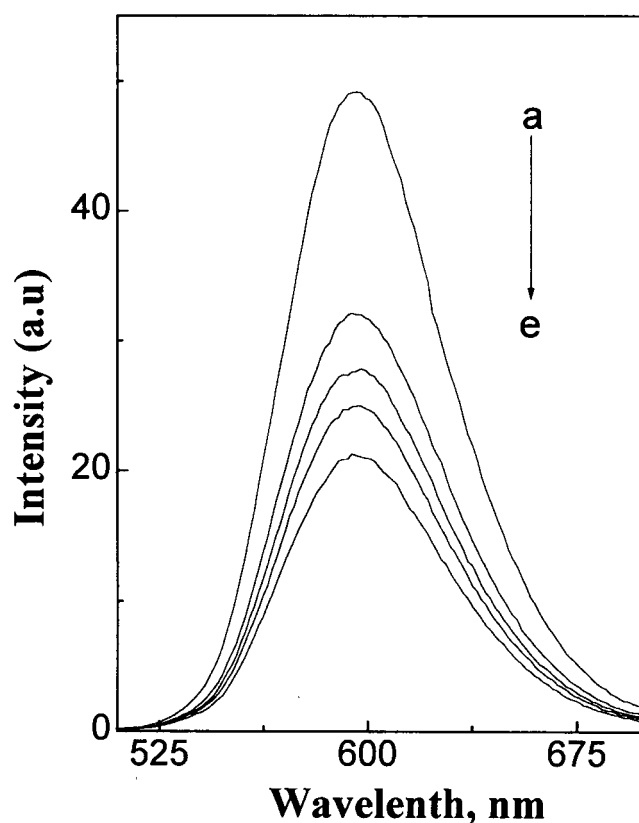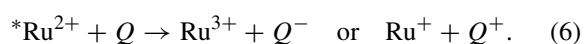

Figure 4. Emission spectra of quenching of $^*[Ru(bpy)_3]^{2+}$ in the presence of β-CD at various concentrations of *p*-phenylenediamine (PPD). [PPD]: (a) 0.0, (b) 1.38, (c) 2.77, (d) 4.16 and (e) 5.54 $\times 10^{-4}$ M.

This means that the electron donor or electron acceptor groups are not included into the cavity of β-CD. Thus we conclude that, in the present photoredox system, the β-CD is not influencing the bimolecular electron transfer quencher reaction. Bottcher and Haim [30] have studied the quench-
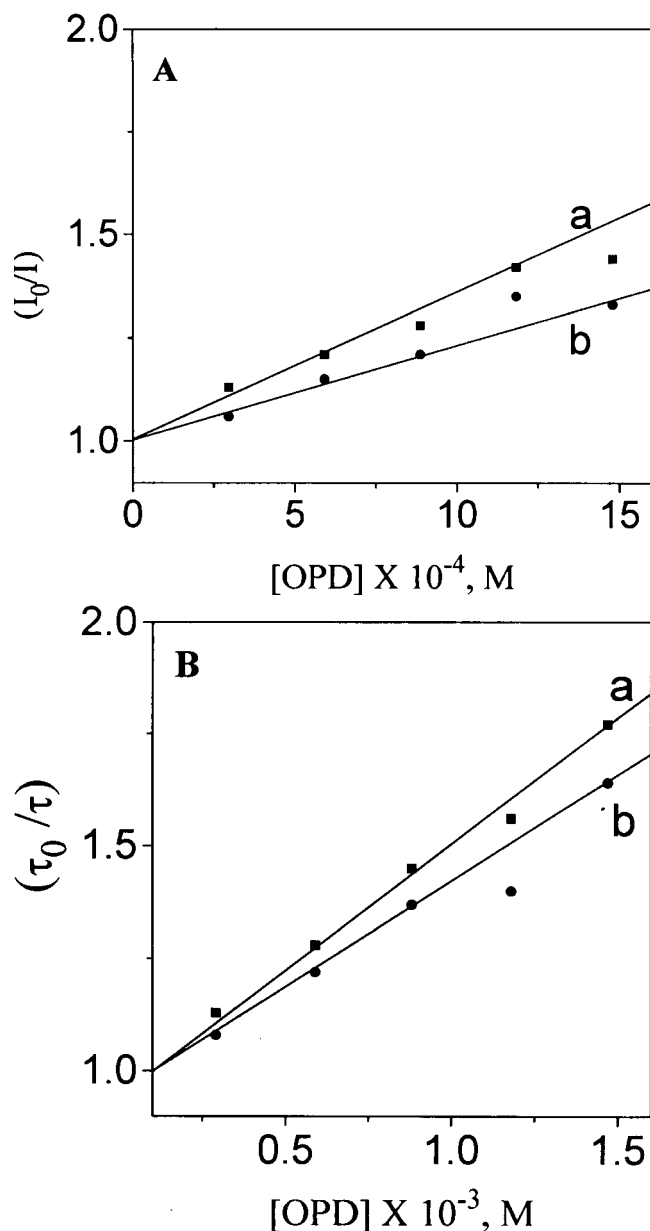
Figure 6. Hammett plot of σ vs. log k_q. (1) p-nitrotoluene, (2) p-chloronitrobenzene, (3) 1-chloro-2-nitrobenzene and (4) p-nitrobenzoic acid.

As we have used a variety of substituted nitrobenzenes we applied the Hammett equation (Equation (7)) [32] for the analysis of the k_q data to get an idea on the structure-reactivity relationship in monosubstituted nitrobenzenes.

$$\log k_q = \log k_q^0 + \rho\sigma. \tag{7}$$

In Equation (7), k_q^0 is the quenching constant observed for nitrobenzene and k_q is the corresponding values for the substituted nitrobenzenes. The term σ represents the substituent constant and ρ, the reaction constant, measures the susceptibility of the reaction to the change of substituent and medium of the reaction. We have used only four quenchers, p-nitrotoluene, 1-chloro-2-nitrobenzene, p-chloronitrobenzene and 4-nitrobenzoic acid and the results of analysis are shown in Figure 6. The Hammett plot is linear when the quenching reaction is carried out in the absence and presence of CD. The value of the reaction constant, remains constant (1.62) indicating that there is no change in the selectivity of the reaction in the presence of CD. The ρ value is positive as expected for a reaction which is facilitated by a decrease in the electron density of the reaction center.

Conclusion

The formation of cyclodextrin inclusion complexes of aromatic amines and nitrocompounds has been studied by absorption and emission spectral methods. The lower K_f values in the range 60–70 observed for *ortho* substituted compounds indicate the steric effect imposed by the *ortho* substitution of the compounds. The lifetime of the Ru(II) complex was not affected by the presence of β-CD. When the aromatic amines and nitrocompounds were used as quenchers, the quenching rate constant (k_q) values were not significantly affected by the presence of β-CD. It is concluded that the β-CD is not influencing the bimolecular electron transfer quenching reaction between the excited state Ru(II) complex and aromatic amines and nitrocompounds.

Figure 5. Stern–Volmer plots of (I_0/I) vs. [OPD] (A) and (τ_0/τ) vs [OPD](B) for the quenching of *[Ru(bpy)$_3$]$^{2+}$ by o-phenylenediamine (OPD) in the absence (a) and presence (b) of β-CD.

ing of the excited state Ru(II) complex by [Co(NH$_3$)$_5$L]$^{3+}$ complexes (L = pyridines or carboxylates) and concluded that electron transfer occurs from the excited state Ru(II) to the cobalt(III) complex through the intermediacy of the ligands. It has also been suggested [31] that the electron transfer from the excited state Ru(II) complex is transferred first to the easily reducible nitro group in the ligand of the Co(III) complex.

The electron transfer reaction between the sensitizer and the Fe^{3+} or Cu^{2+} ion was studied in the absence and presence of β-CD. It was found that the k_q values were not affected by the presence of CD (Table 1). Since the β-CD cannot form a stronger inclusion complex with hydrophilic metal ions and the Ru(II) complex the electron transfer reaction is not affected by the presence of β-CD.
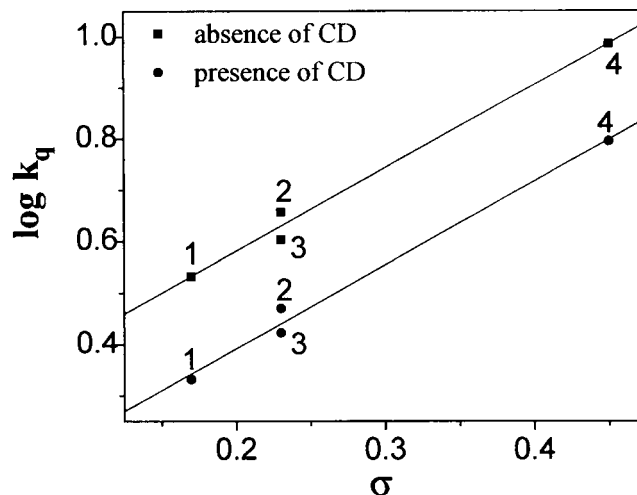
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