

Interaction of metal ions with ET (30) dye in micellar media

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Abstract

Interaction between 3d-transition metal ions (Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) and the $E_T(30)$ dye, 2,6-diphenyl-4-(2,4,6-triphenyl 1-pyridino) phenolate in aqueous medium have been studied by distributing the dye between the aqueous and micellar phase formed by cationic surfactant CTAB, Cetyltrimethylammonium bromide. Values of equilibrium constant K for the dye-metal ion interaction and the partition coefficient of the dye between the micellar and the aqueous phase have been determined. K values show a systematic correlation with ionic potential of metal ions.

Keywords: $E_T(30)$ dye, Metal ions, micelles, Equilibrium constant

1. Introduction

2,6-diphenyl-4-(2,4,6-triphenyl 1-pyridino) phenolate (Fig .1), commonly known as $E_T(30)$ dye [1,2] is an example of a molecule showing strong solvent dependent ground and excited state properties [3a-e]. In the ground state the molecule has a charge separated electronic structure. The vertical photo induced electronic transition is of charge transfer character as is reflected by the strong dependence of the energy of maximum transition on the nature of the environment. As a result the dye show marked solvatochromism and the energy of maximum transition has been used to define the empirical polarity scale [4]. An aqueous solution of the dye shows halochromism. It has been observed that addition of alkali and alkaline earth metal ion in organic solvent causes a shift of the CT band to the blue [5-12]. It has been established that the observed shift is due to a change in speciation [11] rather than to non-specific electric field effect of the ion [12]. Existence of charge separation in structure of the dye lead to equilibrium of probe –electrolyte interaction involving covalent metal-oxygen bond formation [8]. Values of K, the equilibrium constant for the interaction of the dye with Li^+ ion have been determined in few organic solvents. But studies in aqueous medium have not been done as yet perhaps due to very low solubility of the dye in water [13]. Solubility of the dye in aqueous medium can however be enhanced by adding surfactants. In a micellar medium the dye distributes between the micellar phase and aqueous phase containing surfactant monomers. The objective of the present paper is to study the interaction between the dye and a metal ion in the aqueous phase of the micellar medium. In the present work we have studied the interaction of the dye with the 3d-transition metal ions e.g. Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} ions in aqueous medium containing the cationic micelle cetyltrimethylammonium bromide (CTAB). The Partition coefficient (P) of the dye between the micellar and the aqueous phase and the equilibrium constant (K) for the dye –metal ion interaction have been determined. Correlation of K values with ionic potential of the metal ions has also been studied.

2. Experimental section

2.a. Materials

A sample of the $E_T(30)$ dye was obtained as a gift from professor Ch.Reichardt, Marburg, Germany. All inorganic salts, $MnCl_2 \cdot 4H_2O$, $FeSO_4 \cdot 7H_2O$, $Fe_2(SO_4)_3 \cdot 5H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $(CH_3CO_2)_2Zn \cdot 2H_2O$ [E.MERCK](Germany) were used without further purification. Surfactants CTAB (Lancaster) and sodium dodecyl sulphate, SDS (Sigma) were purified by repeated crystallization from ethanol. Solution for spectroscopic measurements were prepared by the following procedure. At first a stock solution of the $E_T(30)$ dye was prepared in CTAB solution. To the appropriate portion of the dye solution required amount of the metal ion solution (in CTAB media) was added, the contents sonicated for a considerable period and then directly taken in the spectrophotometer cuvette.

All spectrophotometric studies were done in SHIMADZU 1601 UV-vis spectrophotometer fitted with peltier controlled thermobath (TCC controller). Concentration of the dye and metal ions in solutions were in the range 10^{-4} - 10^{-5} M and 10^{-3} - 10^{-4} M.

2.b. Methods

2.b.1. Determination of micelle –water partition coefficient (P)

In an aqueous solution the dye (D) distributes between the aqueous phase containing surfactant monomers and the micellar phase as represented by

$$D(\text{micelle}) = D(\text{aqueous}) \dots \dots \dots (1)$$

The Partition coefficient (P) is given by the following equation

$$P = [D]_m / [D]_{aq} = [n_m / v_m] / [n_{aq} / v_{aq}] \quad \dots\dots\dots(2)$$

Where n and v represent respectively number of molecules of the dye and the volume of solution phase, and the suffix 'm' and 'aq' represent respectively, the micellar and aqueous phase. The value of P has been determined by a procedure similar to that used by Fuguet et al [14,15]. As the transition energy of the $E_T(30)$ dye is dependent on the environment around the dye, the value of this parameter would be different in the two phases. The observed transition energy (E) in the solution can assumed to be given by an average of the two transition energies, averaging being done with respect to the mole -fraction of the dye in the two phases[15,16]. The transition energy in a solution containing both the micellar and the aqueous phase is thus given by the following Relation:

$$\sigma = (n_m \sigma_{aq} + n_{aq} \sigma_{aq}) / (n_m + n_{aq}) \quad \dots\dots\dots(3)$$

$$E \text{ (kcalmol}^{-1}\text{)} = 2.859 \sigma \text{ (kK)} \quad \dots\dots\dots(4)$$

In Eq(3) σ and n respectively are the wavenumbers of maximum absorbance and the number of moles of the dye. Values of n_m and n_{aq} are related to the molar based partition coefficient (p) of the solute between micellar and aqueous phase as given by Eq (2). Thus one obtains the following relation:

$$n_m / n_{aq} = Pv(C_T - CMC) / [1 - v(C_T - CMC)] \quad \dots\dots\dots(5)$$

In the above equation v is the molar volume of surfactant; C_T and CMC respectively are the total concentration and critical micellar concentration of the surfactant. Using Eqs(3) and (5) we get the Eq (6)

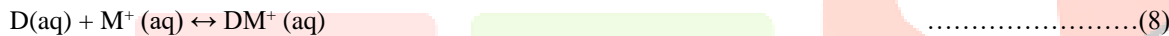
$$\sigma = [Pv C_s \sigma_m + (1-v C_s) \sigma_{aq}] / [Pv C_s + (1-v C_s)] \quad \dots\dots\dots(6)$$

$$C_s = C_T - CMC \quad \dots\dots\dots(7)$$

Measurement of wavenumber of maximum absorbance of the dye as a function of C_s , the concentration of the surfactant in the aggregated phase, allows estimation of P , σ_m and σ_{aq} if the molar volume of the surfactant is known.

2.b.2. Equilibrium constant determination

In presence of metal ions the following equilibrium also exist in the system in addition to the equilibrium (1).



$$K = [DM^+](aq) / [D]_{aq} [M^+]_{aq} \quad \dots\dots\dots(9)$$

Where k is equilibrium constant. We assumed that the metal ion does not go in the micellar phase of a cationic surfactant and process (8) takes place in the aqueous phase only. Moreover, it has been known that wavelength of maximum of the dye shifts to the blue to a large extent when bivalent cations are added to its solution (e.g. the λ_{max} for Ca^{2+} -dye complex is 450nm in acetonitrile). We have done measurements in the region 540-600nm. Hence under the experimental condition only D molecules absorb. Of the two species D (micelle) and D (aqueous), the latter is present in the solution to such a small extent (due to existence of equilibria (1) and (8) the only species contributing to the observed absorbance is D (micelle). Thus the absorbance of the solution for unit path length at a particular frequency ν is given by

$$A\nu = \epsilon \nu [D]_m \quad \dots\dots\dots(10)$$

The total stoichiometric concentration of the dye (D_T) in the system is given by Eq (11)

$$D_T = [D]_m + [D]_{aq} + [DM^+] \quad \dots\dots\dots(11)$$

Using Eqs (2),(7-9) we can write the following equation

$$[D]_T / A\nu = (P+1) / P \epsilon \nu + KM^+ / P \epsilon \nu \quad \dots\dots\dots(12)$$

Thus a plot of $[D]_T / A\nu$ versus $[M^+]$ would give a straight line. Fig 2 shows a representative plot. Values of K and ϵ can be obtained from the slope and the intercept and previously determined value of P .

3. Results and discussion

The dye is practically insoluble in water due to presence of hydrophobic group and becomes soluble only when the total surfactant composition exceeds the critical micellar concentration. The maximum wave number (σ) of the CT band of the dye shifts to the red as the concentration of surfactant increases. Plot of σ values versus $\log C_s$ gives a sigmoid curve. We have fitted the experimental data points by varying the value of P , σ_m and σ_{aq} in the Eq (6). Values of v for SDS and CTAB have been taken as 0.246Lmol^{-1} and 0.324Lmol^{-1} [16,17]. The best fit curve with values of P , σ_m and σ_{aq} as 130, 18.57kK and 19.0kK respectively for aqueous CTAB medium is shown in fig 3. Values of the equilibrium constant (K) and molar absorbance (ϵ) have been listed in Table 1. The reported value of K and ϵ are based on measurements of the maximum

wavelength of absorption of the dye in CTAB micellar medium. However, for a particular system, the value of K is independent (within experimental inaccuracy) of the wavelength of measurement (550-600nm). The value of full width at half maximum (FWHM) for the absorption spectra of the solute has been determined for the dye solution containing metal ions. Values of FWHM are independent of salt concentration. Table 1 lists the values of FWHM. Note that FWHM values are practically independent of the nature of metal ion present in the solution. The average value agrees well with that of the dye in CTAB micelle. Value of K for a particular metal ion have been found to be independent of micellar concentration in the solution. K values for the metal dye complex follows the order $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ of the metal ions. This order is the same as the Irving –Williams series of stability of metal complexes[18]. Fig 4 shows a plot of log K versus ionic potential values for the metal ions. A linear correlation for the bivalent metal ions, except Zn^{2+} , has been obtained. Values of logK for Fe^{3+} ion is slightly less than that for Fe^{2+} ion, indicating that electrostatic effects are not the only determining factor. Some experiments have also been done using SDS as surfactant. The inherent difficulty of precipitation when metal ions are added to a solution containing anionic surfactant prevented us from doing extensive studies using SDS micelles. Experiment using a limited concentration range of metal ion and surfactant indicate that the value of K obtained does not depend on the nature of the micelle used. This supports our assumption that the equilibrium with metal ion takes place in aqueous phase only.

4. Conclusion

The $E_T(30)$ dye interacts with the 3d-transition metal ions and a new chemical species involving metal-oxygen bond is formed. The equilibrium constant for the formation of the species have been determined and found to follow the Irving-williams series of stability of metal complexes. A linear relation between logK and ionic potential of metal ions have been observed.

Table1 : Values of equilibrium constant K and molar absorbance(ϵ)

Metal ions	Log K	$\epsilon(\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1})$	FWHM (cm^{-1})	Ionic radii/ Å^0	Ionic potential
Mn^{2+}	5.922	4890	2731	0.97	2.06
Fe^{2+}	6.018	4980	2931	0.92	2.17
Co^{2+}	6.112	5031	2751	0.88	2.25
Ni^{2+}	6.115	5191	2622	0.83	2.41
Cu^{2+}	6.341	5001	2581	0.87	2.29
Zn^{2+}	5.621	5072	2601	0.74	2.70
Fe^{3+}	5.632	5141	-	0.79	3.79

a Reference [19]

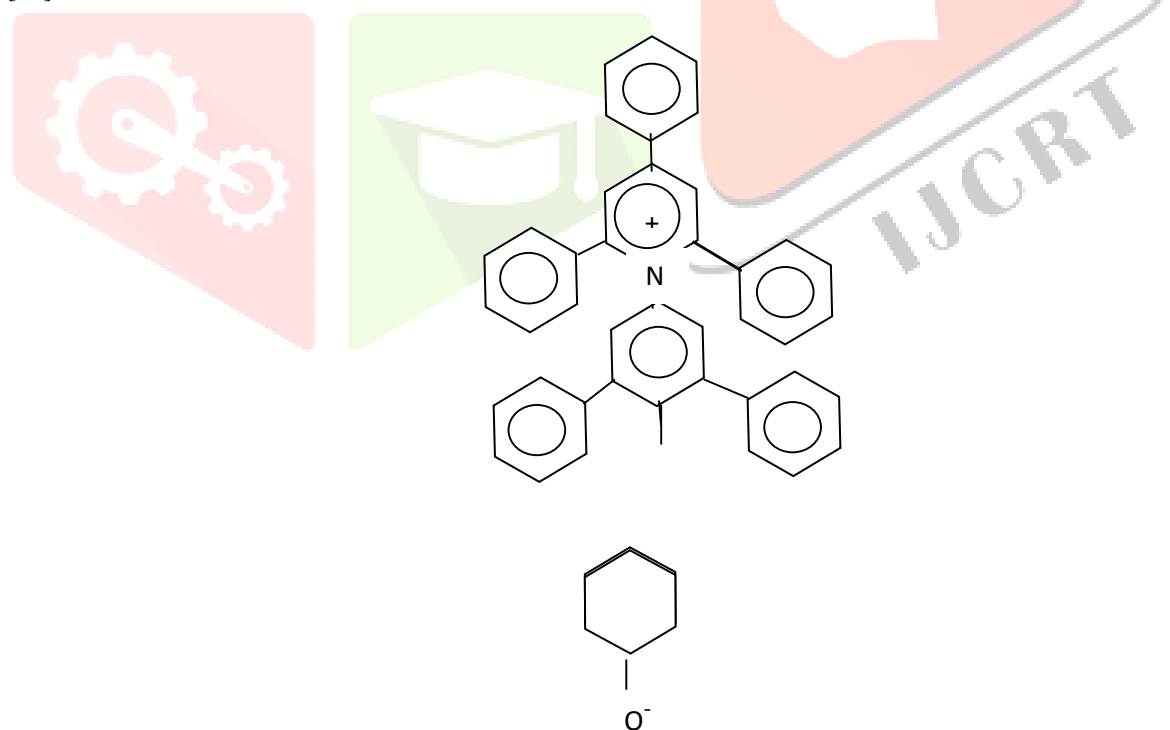


Fig 1: $E_T(30)$ dye

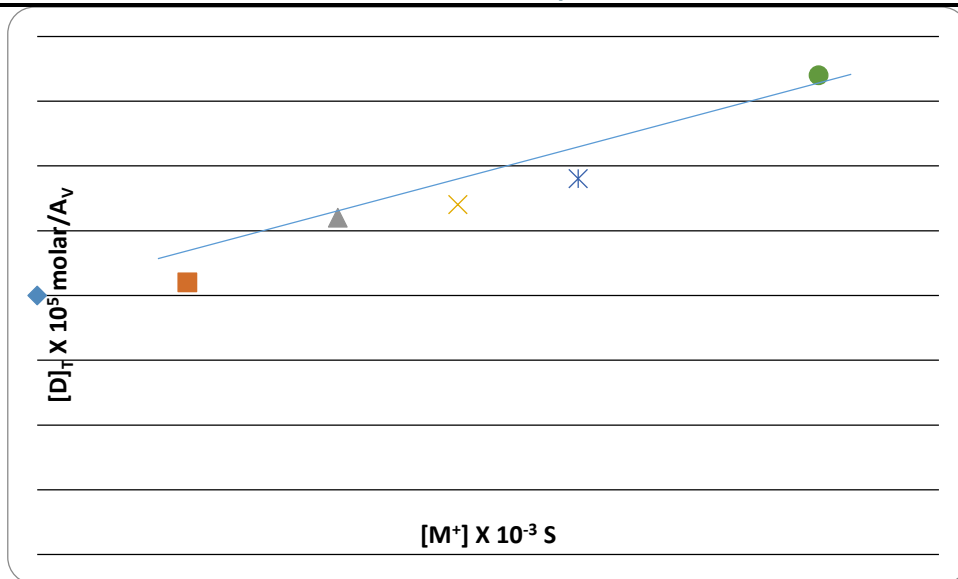


Fig 2: Representative plot of Eq (12) for $M^+ = Fe^{+3}$ in aqueous CTAB solution

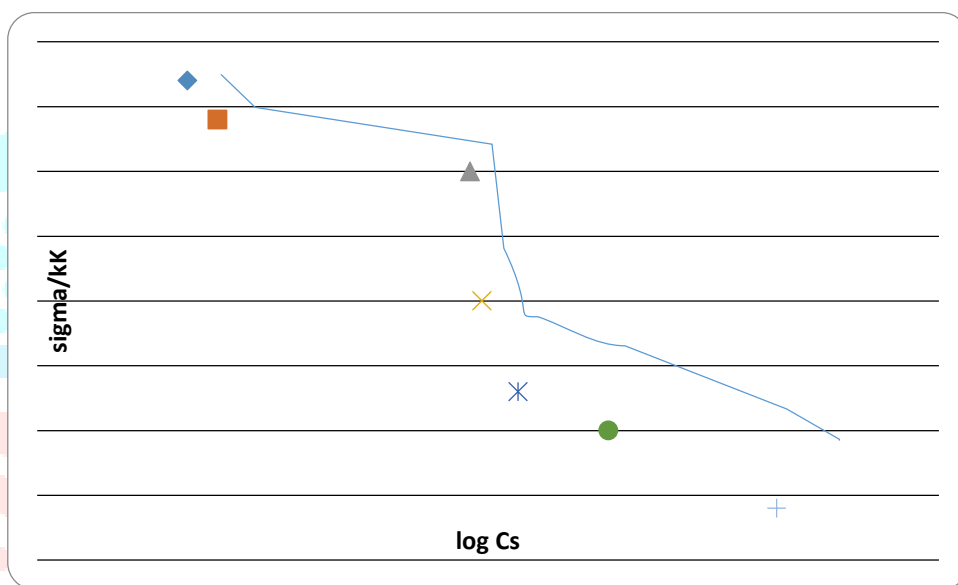


Fig 3: Plot of σ vs $\log C_s$ for E_T (30) dye in CTAB solution. The experimental points are represented by filled square.

The continuous line represents best-fit according to Eq (6) with $P=130$, $\sigma m=18.57kK$ and $\sigma aq = 19.0kK$.

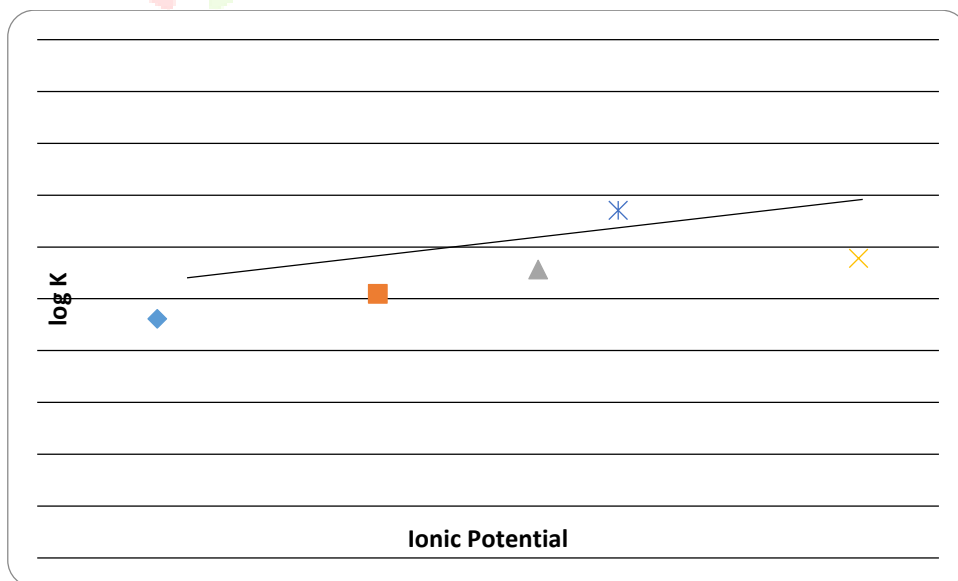


Fig 4 : Plot of $\log K$ vs Ionic potential values.

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