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## RESEARCH ARTICLE

### SPECTROPHOTOMETRIC DETERMINATION OF RELIABLE ASSOCIATION CONSTANT OF WEAKLY BOUNDED CHARGE TRANSFER COMPLEX IN SOLUTION

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#### ABSTRACT

The interaction between picric acid (acceptor) and o-phenanthroline (donor) have been studied spectrophotometrically in THF solvent for the evaluation of reliable value of association constant in the formation of weakly bounded charge transfer complex. The value of association constant (K) was calculated using standard equations such as Benesi-Hildebrand, Scott, Foster Hammick Waldley, Rose Drago Ayad, El-Hati, Lang, Scatchard, Seal-Sil Mukherjee, at wavelengths 358.5, 378, 400 and 420 nm in THF solvent. The value of association constant of the 1:1 complex in solution, calculated by different standard equations ranges between 1561 and 4928. The wide range of variation of the calculated values of K led us to guess for the reliable value. The reliability of different calculated values was examined. The Benesi- and Hildebrand method was found to give most reliable value of K. The most reliable value of K for complex was found to be 1907. The stoichiometry of the complex was established spectrophotometrically by Jobs's method of constant variation.

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#### INTRODUCTION

Many standard equations have been developed for the calculation of the association constant and extinction coefficient of weakly bonded (1:1) complexes in solutions. Benesi and Hildebrand (1949), Scott (1956), Foster Hammick Waldley *et al.* (1953), Rose Drago Ayad (?), El-Hati (1962), Lang (1949), Scatchard (1982), Seal-Sil Mukherjee (1998), equations are some common equations. Each of these equations are derived from one basic equations only after some rearrangement of the parameters appearing in the equation. The value of the product of association constant and extinction constant (K $\epsilon$ ) obtained from plots of different equations give almost matching value, but separation of the two parameters – association constant (K) and the extinction coefficient ( $\epsilon$ ) by different equations give widely different equations give widely different value for the same complex with same data. B-H method has been widely used for the determination of the association constant and extinction co-efficient of loosely bounded complexes in solution by u.v. visible spectrophotometric method. This method makes certain assumptions namely, the complex is only a 1:1 complex, the solutions are ideal in behavior, so that activity coefficients of all the species may be assumed to be unity; K does not change with concentration; the complex obeys Beers law, the solvent does not interact. The value for equilibrium constant

determined by this method also varies with the unit of the concentration used; molarity has been found to be most suitable choice for the expression of the concentration. The value of the product of the association constant and the extinction coefficient is almost constants, (though may not be the correct value), but separation of the two parameters lead to quite different value of K. Some of the issues of the B-H method include different values of E with different concentration scale (Benesi and Hildebrand 1949). Lack of consistency between the B-H values and these obtained from other methods (Scott 1956), and zero and negative intercepts (J). If the concentration of the donor is not in excess of the acceptor then the plot deviates from linearity (Foster Hammick Waldley *et al.* 1953). Many modifications have been carried out in B-H equation to obviate these problems. These methods include Scott, Foster Hammick Waldley, Rose Drago Ayad, El-Hati, Lang, Scatchard, Seal-Sil Mukherjee, Wolfe and Anunziata *et al.* Each of these equations are derived from the same basic equation on which the B-H equation is based by simple rearranging the parameters or/ and interchanging the axis. But, the values of association constants of the same complex in solution calculated by different equations vary widely. So reliability of the correct value is a problem generally overlooked by researchers. Some workers including Zaini *et al.* (1998) navigated this problem and suggested certain measures to test the reliabilities of the calculated values. In the present paper we have tried to evaluate the reliable association constant of 1:1 complex formed between Picric acid and 1,10-phenanthroline in THF.

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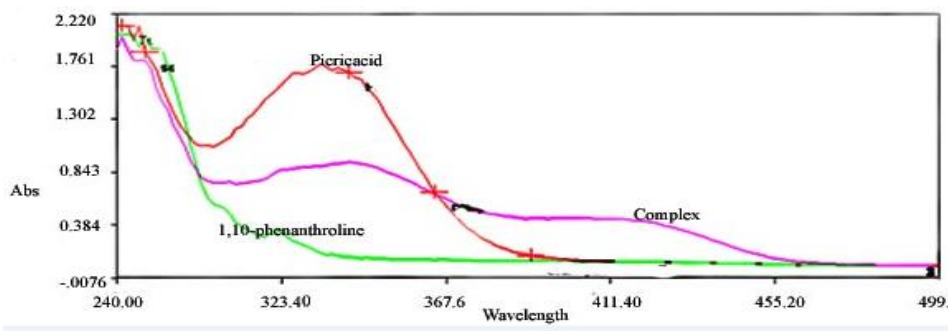


Fig 1a. Absorption spectra of D, A, and CT-complex in THF solvent at 25°C

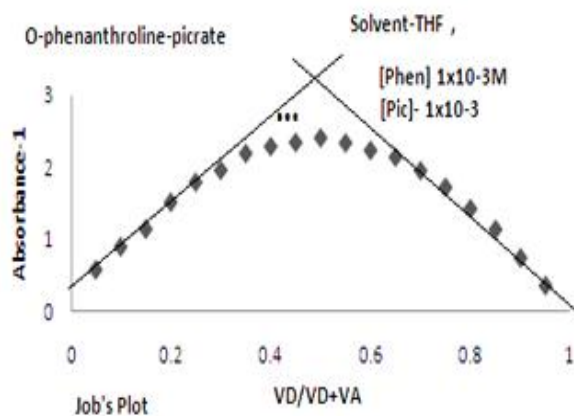


Fig 1b. Continuous variation plot of 1,10-phenanthroline-picric acid complex in THF solvent at 25°C

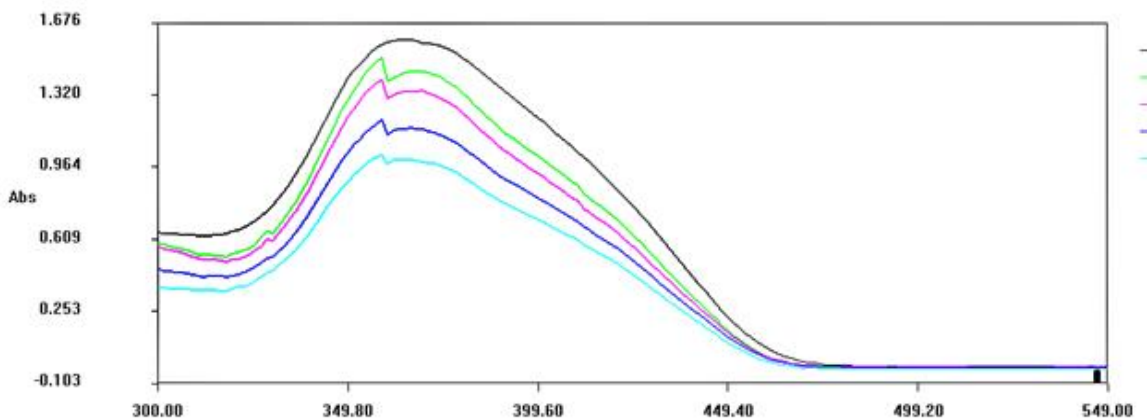


Fig 1c. Absorption spectra of Picric acid (0.0002M) in THF solvent with addition of 1, 10-phenanthroline ranging from 0.00012-0.0002M

## Theory

The equations for the determination of  $K$  and  $E$  by various methods have been listed in Table 1. Test for reliability of the value of  $K$ . If the apparent  $K_{CT}$  changes for each sample a single B-H plot may still be linear, but will give false results. To help detect this problem, data should be obtained at multiple wavelengths across the CT-band. The family of B-H plots obtained by taking data at several wavelengths across the CT-band give different intercepts at the x-axis then this is an indicator of unreliability of the  $K$  value. Therefore in B-H plot

of  $1/OD$  Vs  $1/(D_0)$  if the family of plots intercepts at the x-axis at one point then the value is reliable. In order to accurately determine the product,  $K_{CT}$ , the plot of O.D versus molar concentration of the donor should have minimal curvature. To do this we obtain the slope of the line connecting each point with the origin for all the data available. Plotting these slopes versus concentration of donor and extrapolating to infinite dilution gives us the best estimation of  $K_{CT}$ . The Scott equation would also calculate a family of lines with the same x-intercept while FHW relation yield parallel lines the evaluated value is reliable.

**Table 1. Absorption data (using wavelength-418nm) of the complex at different concentration of D and A in THF solvent at 25°C**

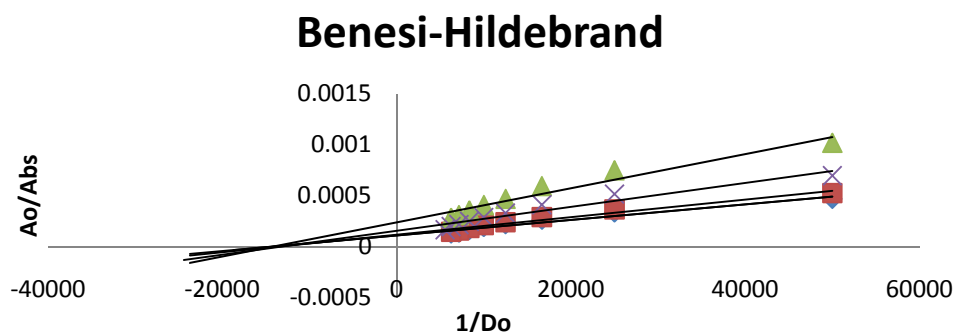
Vol D	Vol A	Total V	Abs
ml	ml	ml	
0.25	4.75	5	0.572
0.50	4.50	5	0.59
0.75	4.25	5	1.136
1.00	4.00	5	1.508
1.25	3.75	5	1.784
1.50	3.50	5	1.951
1.75	3.25	5	2.183
2.00	3.00	5	2.278
2.25	2.75	5	2.334
2.50	2.50	5	2.396
2.75	2.25	5	2.396
3.00	2.00	5	2.327
3.25	1.75	5	2.225
3.50	1.50	5	2.133
3.75	1.25	5	1.944
4.00	1.00	5	1.713
4.25	0.75	5	1.415
4.50	0.50	5	1.13
4.75	0.25	5	0.736
5.00	0.00	5	0.353

### Complex formation: Stoichiometry

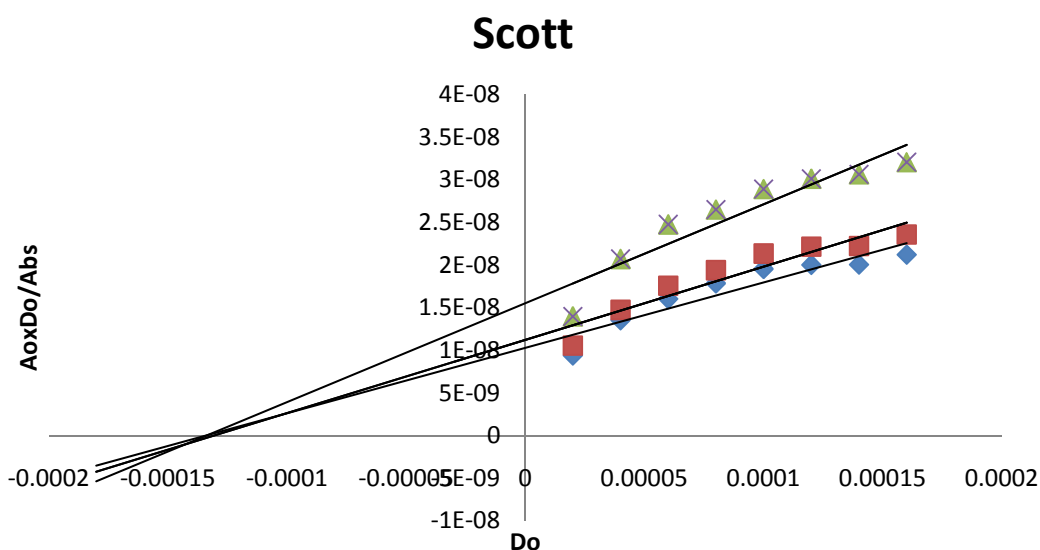
The stoichiometry of the complex formed in solution at ambient temperature was determined by Job's plot (Fig. 2) indicates the formation of 1:1 complex. Determination of association constant and molar extinction coefficient: To 1.0 ml of  $1 \times 10^{-3}$  (M) picric acid solution  $0.x$  ( $x=1,2,3 \dots 10$ ) ml of  $1 \times 10^{-3}$  (M) 1,10-phenanthroline solution was mixed in a 5.0ml measuring flask and the volume of the mixture was made 5.0 ml of THF. This solution was kept in a cuvette of 1.0 ml path length as a sample solution for absorbance measurement at different wavelengths, In a separate measuring flask 1.0 ml  $1 \times 10^{-3}$  (M) Picric acid solution alone was kept and diluted to 5.0 ml by THF. This solution was kept in another cuvette of 1.0 cm path-length for cell matching to cancel the absorbance of residual picric acid solution in the complex in sample cuvette. The absorbance of different sample solutions by matching the cell with reference cuvette were measured. The experimental data obtained appears in table .....

### RESULTS AND DISCUSSION

There was an instantaneous change to a canary yellow from yellow colour of picric acid in THF solvent upon reaction with 1, 10-phenanthroline. The electronic spectra of donor, acceptor



**Fig. 2a. Plot of Benesi-Hildebrand's equation at four wavelengths 358.5,378,400.5,420nm**



**Fig. 2b. Plot of Scott's equation at four wavelengths 358.5,378,400.5,420nm**

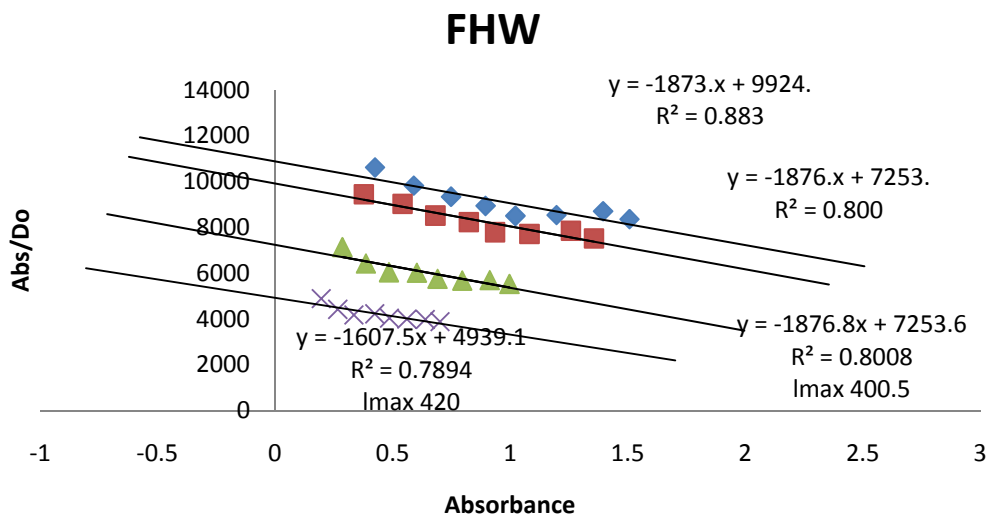


Fig. 2c. Plot of Scatchard's equation at four wavelengths 358.5,378,400.5,420nm

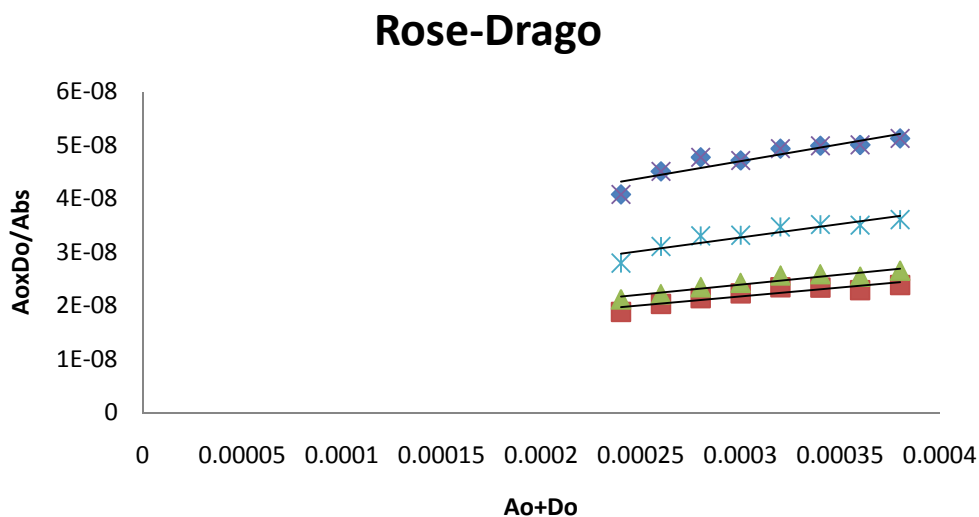


Fig. 2d. Plot of Rose Drago's equation at four wavelengths 358.5,378,400.5,420nm

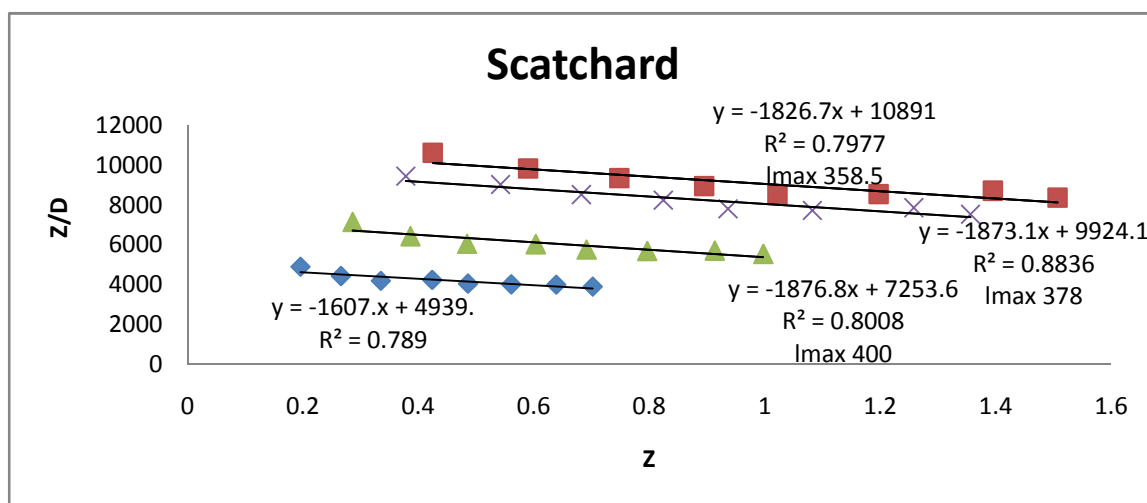


Fig. 2e. Plot of Scatchard's equation at four wavelengths 358.5,378,400.5,420nm

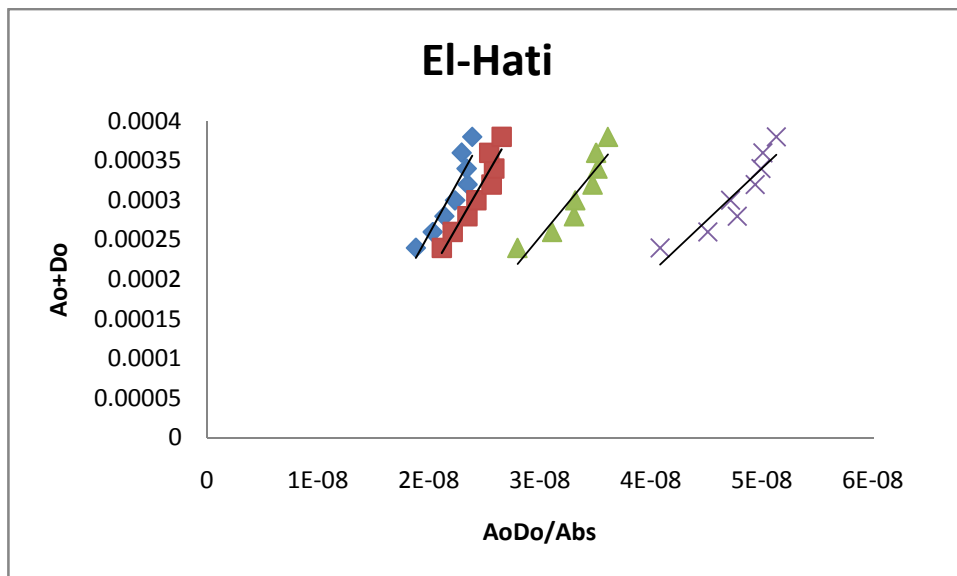


Fig. 2f. Plot of El- Hati's equation at four wavelengths 358.5,378,400.5,420nm

Table 2. Data for spectrophotometric determination of association constant at four wavelength along the CT band in THF solvent at 25°C

S.No.	Vol D	Vol A	Total V	Ao	Do	Abs	Abs	Abs	Abs
0	ml	ml	ml						Wavelength
1	0.1	1	5	0.0002	0.00002	358.4	378	400.5	420
2	0.2	1	5	0.0002	0.00004	0	0.285	0.272	0.196
3	0.3	1	5	0.0002	0.00006	0.425	0.378	0.286	0.196
4	0.4	1	5	0.0002	0.00008	0.59	0.542	0.386	0.266
5	0.5	1	5	0.0002	0.0001	0.748	0.682	0.484	0.335
6	0.6	1	5	0.0002	0.00012	0.895	0.824	0.603	0.424
7	0.7	1	5	0.0002	0.00014	1.022	0.936	0.691	0.486
8	0.8	1	5	0.0002	0.00016	1.197	1.082	0.796	0.561
9	0.9	1	5	0.0002	0.00018	1.395	1.258	0.913	0.639
10	1	1	5	0.0002	0.0002	1.507	1.356	0.997	0.702
				0.0002	0.0002	1.665	1.542	1.186	0.858

Table 3. Standard Equations for the evaluation of association constant K for CT-complexes

S.No	Plots	Year	Equation	Y-axis	X-axis	K
1	Benesi-Hildebrand	1949	$\frac{A_o}{Z} = \frac{1}{KE} + \frac{1}{E}$	$\frac{A_o}{Z}$	$\frac{1}{D_o}$	$\frac{1}{\text{slope} \times E}$
2	Inverse B-Hildebrand	1949	$\frac{1}{D_o} = KEC \frac{1}{Z} - K$	$\frac{1}{D_o}$	$\frac{1}{Z}$	-Intercept
3	Seal-Sil Mukherjee-1	1982	$Z = -\frac{1}{K} \cdot \frac{Z}{D_o} + ExA_o$	Z	$\frac{Z}{D_o}$	$-\frac{1}{\text{slope}}$
4	Seal-Sil Mukherjee-2	1982	$D_o = ExA_o \frac{D_o}{Z} - \frac{1}{K}$	D_o	$\frac{D_o}{Z}$	$-\frac{1}{\text{Intercept}}$
5	El-Hati	1991	$\frac{1}{D_o} = KEC \frac{1}{Z} - K$	Ao+Do	$\frac{A_o \times D_o}{Z}$	$-\frac{1}{\text{Intercept}}$
6	Rose Drago Ayad	1952	$\frac{A_o \times D_o}{Z} = \frac{1}{E} (A_o + D_o) + \frac{1}{KE}$	$\frac{A_o \times D_o}{Z}$	Ao + Do	$\frac{\text{slope}}{\text{Intercept}}$
7	Scott	1956	$\frac{A_o \times D_o}{Z} = \frac{1}{E} D_o + \frac{1}{K \times E}$	$\frac{A_o \times D_o}{Z}$	D_o	$\frac{1}{K \times E}$
8	FHW	1952	$\frac{Z}{D_o} = -KZ + KCE$	$\frac{Z}{D_o}$	Z	-slope
9	Lang	1962	$\frac{A_o D_o}{Z} = (A_o + D_o) \frac{Z}{E} + \frac{1}{KE}$	$\frac{A_o D_o}{Z}$	$(A_o + D_o) \frac{Z}{E}$	$\frac{\text{Slope}}{\text{Intercept}}$
10	Scatchard	1949	$\frac{Z}{A_o D_o} = KE - \frac{KZ}{A_o}$	$\frac{Z}{A_o D_o}$	Z	-slope

**Table 4. Values of association constants obtained from various studied plots at four wavelenths 358.5, 378, 400,420**

S. No	Plots	wavelength=358.5		wavelength=378		wavelength=400		wavelength=420	
		K	R	K	R	K	R	K	R
1	Benesi-Hildebrand	1906.93	0.9958	1906.93	0.9958	1906.92	0.9958	1906.93	0.9958
2	Inverse B-Hildebrand	2473	0.998	2253	0.9995	2572	0.9964	2216	0.9969
3	Seal-Sil Mukherjee-1	2289	0.8932	2120	0.9400	2343	0.8949	2036	0.8885
4	Seal-Sil Mukherjee-2	2218	0.9170	2079	0.9531	2196	0.9250	1916	0.9175
5	El-Hati	3333.3	0.917	3333.3	0.9170	3333	0.9251	3333.3	0.9175
6	Rose-Drago Ayad	2800	0.9169	2936	0.9531	2853	0.9251	2270	0.9175
7	Scott	1796	0.9170	1961	0.9504	1861	0.9251	1561	0.9175
8	FHW	1827	0.8931	1873	0.9400	1877	0.8008	1607	0.8884
9	Lang	4636	0.9205	4928	0.9546	4733	0.9203	3401	0.9187
10	Scatchard	1827	0.8931	1873	0.9400	1877	0.8008	1607	0.8884

and resulted were recorded in the region of 240-500nm shown in Fig 1. The Figure1 clearly shows the formation of two new absorption band in the range 358.5 and 420 nm indicating complex formation. The Job's method of continuous variation indicated the formation of 1:1 complex shown in Fig 2 and relevant data were tabulated in Table1, The Absorption data at four different wave length along the CT band and electronic spectra of the interaction between varying donor concentration with constant acceptor is shown in Table 2 and Fig 2. respectively. The standard equation for the evaluation of association constant is tabulated in Table 3. The values of association constant obtained from the studied standard equation have been tabulated in Table 4. From the perusal of the Table 3, it is clear that Benesi-Hildebrand gives most reliable value of association constant for the CT-complex formed between 1,10-phenanthroline and picric acid as it gives constant value of association constants along the CT band

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