



Determination of Stability Constant of 1:1 Complex Formed By Fe (III) With 5-Nitrosalicylic Acid By Graphical Methods Using Spectrophotometric Data

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ABSTRACT

The composition and stability constant of the complex formed by Fe (III) with 5-nitrosalicylic acid was studied in the acid range of the pH. In this acid range of pH (1-3) only 1:1 complex is formed. For the determination of stability constant, a number of graphical methods, reported in the literature, were used for the determination of value of stability constant. These five methods give different values of stability constant. On close examination of these methods it was revealed that in order to evolve the linear equations authors have omitted certain terms in the expression of stability constant that is why there is discrepancy in the results. Retaining all the terms, a method of successive approximations was used for the determining the stability constant of 1:1 complex formed by Fe ((III) with 5-nitrosalicylic acid at pH 2.4 and ionic strength 0.1 using the same data. This method gave the value of log K as 5.09.

Keywords: Ferric chloride, 5-Nitrosalicylic acid, Stability constant, Graphical methods.

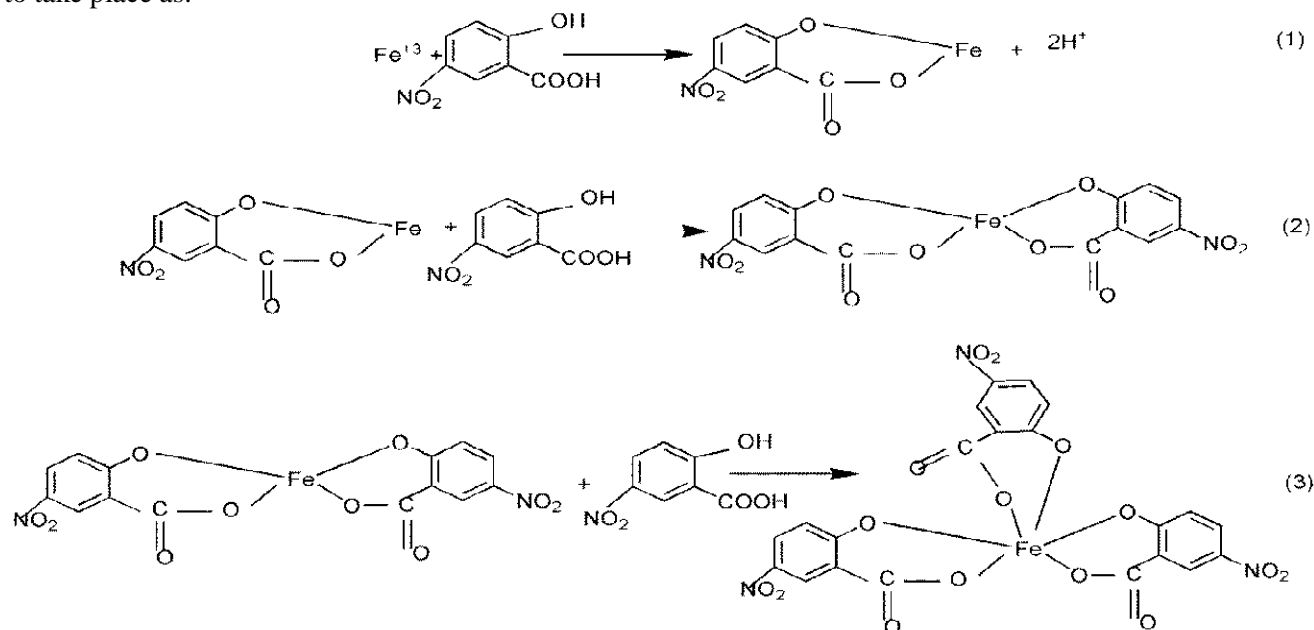
INTRODUCTION

Spectrophotometry is a popular method of analysis, employed due to its precision, sensitivity and availability of commercial instruments. As a result of metal ligand complex formation, either the spectrum of the ligand undergoes a change or new spectral lines appear. The changes in the spectra as well as appearance of new spectral lines help in following the course of metal-ligand equilibria. If Beer's law is valid, absorbance measurement can be utilized in the determination of the equilibrium concentration of metal complexes under investigation. Consequently one can calculate the stability constant under specified conditions.

Salicylic acid (SA) and its various derivatives form an important class of hydroxy acids. These substances have outstanding antirheumatic and antifungal actions on human body. Iron (III) has a great affinity for ligands which co-ordinate via oxygen. Many complexes of Fe (III) with bidentate ligands are known in which the donor groups contain oxygen atom. With oxalate the tri-oxalato complex $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ with β^- diketones the neutral $[\text{Fe}(\text{dike})_3]$ complexes are formed. With salicylic acid, Fe (III) forms several coloured complexes and because of this salicylic acid has been used since long for the colorimetric determination of Iron (III). Like SA, 5-nitrosalicylic acid (NSA) also gives characteristic coloration with

Fe (III) ion and, therefore, in the present work the composition and stability constant of the system Fe (III)-5-NSA was studied.

The above reaction depends on the pH of the medium. The formation of various complexes can be shown to take place as:



In the pH range 1-3, the colour of the complex is violet with $\lambda_{\max} = 496$ nm as obtained from recording the electronic spectra in visible region. The colour changes, when pH is increased due to the formation of higher complexes.

MATERIALS AND METHODS

All chemicals, such as ferric chloride (BDH), 5-nitrosalicylic acid (E. Merk), sodium perchlorate (CDH) and perchloric acid (CDH) were of analytical grade (AR Grade) and used without any further purification. For making stock solution, double distilled water was used.

Following solutions were prepared- 4.0×10^{-3} M FeCl_3 solution, 4.0×10^{-3} M 5-Nitrosalicylic acid solution, 1.0 M NaClO_4 solution, 0.1 M HClO_4 solution.

A double beam UV-VIS spectrophotometer (Systronics Model-2202) with 1 cm quartz cells was used for all absorbance measurements. On recording the spectra in the visible range, λ_{\max} were observed at 496 nm for the complexes and hence in subsequent measurements of the absorbance, the wavelength used was 496 nm.

Composition of complex: The Job's method of continuous variations was used for the determining the composition of the complex.

Procedure: A set of solutions were prepared by making x mL of metal and (10 -x) mL of ligand solution to keep the total metal ion and ligands concentration constant. To each solution 2 mL of HClO_4 and 5 mL of NaClO_4 solution were added and the total volume was made upto the 50 mL by adding distilled water. The absorbance of the each solution was measured at λ_{\max} , 496 nm (Table-1) then a graph was constructed between mole fractions of metal ion against absorbance. The maximum at 0.5 reveals the formation of 1:1 complex.

Table-1 at pH = 2.4

S.N	Volume of metal FeCl ₃ (mL)	Volume of ligands 5-NSA (mL)	Volume of NaClO ₄ (mL)	Volume of HClO ₄ (mL)	Mole function of metal	Absorbance at λ _{max}
1	0.0	10.0	5.0	2.0	0.0	0.0
2	1.0	9.0	5.0	2.0	0.1	0.15
3	2.0	8.0	5.0	2.0	0.2	0.32
4	3.0	7.0	5.0	2.0	0.3	0.47
5	4.0	6.0	5.0	2.0	0.4	0.61
6	5.0	5.0	5.0	2.0	0.5	0.71
7	6.0	4.0	5.0	2.0	0.6	0.69
8	7.0	3.0	5.0	2.0	0.7	0.51
9	8.0	2.0	5.0	2.0	0.8	0.41
10	9.0	1.0	5.0	2.0	0.9	0.20
11	10.0	0.0	5.0	2.0	0.10	0.0

Determination of Stability Constant: The spectrophotometric determination of stability constant in solution has been discussed in detail by Mc Bryde [1]. He has given a number of methods of which molar absorptivity of the complex can be evaluated experimentally. By knowing the value of molar absorptivity stability constant can be calculated easily. Due to unknown equilibrium concentration of the complex, the molar absorptivity is determined with difficulties. Sometimes an excess of ligand is added to shift the equilibrium in order to convert practically the entire metal ion into complex, thus reducing the free metal ion concentration almost to a negligible amount. However, such an approach would have certain limitations, because under these conditions only the highest complex species would be formed and the intermediate species occurring in steps would not co-exist. Therefore, graphical methods are often more convenient for the determination of stability constants from spectrophotometric data because in such cases the prior knowledge of molar absorptivity is not necessary. Various authors have put forward different graphical methods. Graphical methods which were introduced in late forties [2] continue to draw attention of workers [3-7] and various regression equations and computational methods [8-9] have been developed for determination of stability constants using spectrophotometric data. In the following paragraphs the graphical methods used by different authors have been given with essential details.

1. Frank and Ostwald Method: There is greater possibility of formation of more than one complex when excess ligands are added. For instances, the thiocyanate ion forms several complexes with iron (III) depending on the concentration of thiocyanate ion concentration. At low concentration only 1:1 complex is formed.



In order to determine the stability constant of above complex, Frank and Ostwald used the following procedure:

If M° is the analytical concentration of metal ion and L° is the analytical concentration of ligand then for reaction (5).



We can write,

$$K_1 = \frac{[\text{ML}]}{(\text{M}^\circ - [\text{ML}])(\text{L}^\circ - [\text{ML}])} \quad \dots \quad (6)$$

In equation (6) charges are omitted for simplicity.

If it is assumed that only one complex 1:1 is formed and hydrolysis has been ignored, equation (6) can be rearranged as

$$[ML]^2 - (M^{\circ} + L^{\circ} + 1/K_1) ML + M^{\circ} L^{\circ} = 0 \quad \dots\dots (7)$$

From which it follows

$$[ML] = \frac{M^{\circ} L^{\circ}}{(M^{\circ} + L^{\circ} + 1/K_1)} + \frac{(M^{\circ} L^{\circ})^2}{(M^{\circ} + L^{\circ} + 1/K_1)^3} \quad \dots\dots (8)$$

If A is the absorbance of the solution under study then for 1 cm path length one can write $A = \epsilon_{ML} [ML]$. If the higher terms in equation (8) can be neglected then,

$$A = \frac{\epsilon_{ML} M^{\circ} L^{\circ}}{M^{\circ} + L^{\circ} + 1/K_1} \quad (9)$$

which on rearrangement reduces to

$$\frac{M^{\circ} L^{\circ}}{A} = \frac{(M^{\circ} + L^{\circ})}{\epsilon_{ML}} + \frac{1}{\epsilon_{ML} K_1} \quad \dots\dots(10)$$

If $M^{\circ} L^{\circ}/A$ is plotted against $(M^{\circ} + L^{\circ})$, a straight line with slope $1/\epsilon_{ML}$ and intercept $1/\epsilon_{ML} K_1$ would be obtained.

The omission of higher terms would be valid only for the systems in which $\epsilon_{ML} \gg K_1$. In that case where $K_1 \approx \epsilon_{ML}$ or $K_1 > \epsilon_{ML}$ the above equation would not be valid i.e. it would be wrong to neglect higher terms.

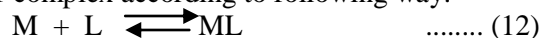
2. Ramette Method: Ramette rearranged the Frank and Ostwalt equation (10) and gave the following equation,

$$\frac{A}{M^{\circ} L^{\circ}} = \epsilon_{ML} K_1 - \frac{A(M^{\circ} L^{\circ}) K_1}{M^{\circ} L^{\circ}} \quad \dots\dots (11)$$

Thus, a plot of $A/M^{\circ} L^{\circ}$ versus $A(M^{\circ} + L^{\circ})/M^{\circ} L^{\circ}$ would be a straight line with the slope equal to K_1 and intercept as $\epsilon_{ML} K_1$. Hence, it turns out to be unnecessary to know the absorptivity of the complex ion, although this quantity can be calculated as a byproduct in the determination of K_1 .

3. Benesi and Hildebrand Method: A graphical method was developed by Benesi and Hildebrand in 1949 for determination of stability constant and molar absorptivity of a complex in solution for 1:1 type of complex.

Consider the formation of a 1:1 complex according to following way.



The stability constants for 1:1 complex is expressed as

$$K_1 = \frac{[ML]}{[M][L]} \quad \dots\dots (13)$$

If initial concentration of metal ion and ligand are M° and L° respectively, then equation (13) can be written as

$$K_1 = \frac{[ML]}{(M^{\circ} - [ML])(L^{\circ} - [ML])} \quad \dots\dots (14)$$

If the complex is very weak and the ligand is added in excess under the experimental conditions, we can assume that the complex formation does not change the concentration of the total ligand effectively and then,

$$K_1 = \frac{[ML]}{(M^{\circ} - [ML])L^{\circ}} \quad \dots\dots (15)$$

If the complex absorbs light in the region of interest then the absorbance (A) of the complex for one cm path length following Beer Lambert's law can be expressed as

$$A = \epsilon_{ML} [ML] \quad \dots\dots (16)$$

where ϵ_{ML} is the molar absorptivity of complex. Using equation (15) and (16), one can deduce,

$$\frac{M^\circ}{A} = \frac{1}{K_1 \epsilon_{ML} L^\circ} + \frac{1}{\epsilon_{ML}} \quad \dots \quad (17)$$

Thus a plot of M°/A , versus $1/L^\circ$ would be linear and the slope would be equal to $1/K_1\epsilon_{ML}$ and the intercept would be $1/\epsilon_{ML}$. This equation became very popular for evaluation of K_1 and ϵ_{ML} of the complex from spectrophotometric data. This method is valid only under the conditions that L° is $\gg M^\circ$ so that the square terms can be neglected, However, the values thus obtained will be always approximate.

4. Hammond's Method: Hammond has studied the Bensi-Hildebrand equation (17) and its modified form equation and examined the effect of errors in absorbance, concentration of ligands and metal ion on plots of Bensi-Hildebrand. From studies of series of experiments in which one of the components was in considerable excess ($L^\circ \gg M^\circ$ was chosen), equations of the form (18, 19, 20 and 21) could be developed.

$$\frac{M^\circ L^\circ}{A - A_M^\circ} = \frac{1}{K_1(\epsilon_{ML} - \epsilon_M)} + \frac{L^\circ}{(\epsilon_{ML} - \epsilon_M)} \quad \dots \quad (18)$$

$$\frac{L^\circ}{A - A_M^\circ} = \frac{1}{K_1(\epsilon_{ML} - \epsilon_M)M^\circ} + \frac{L^\circ}{(\epsilon_{ML} - \epsilon_M)M^\circ} \quad \dots \quad (19)$$

$$\frac{M^\circ}{A - A_M^\circ} = \frac{1}{K_1(\epsilon_{ML} - \epsilon_M)L^\circ} + \frac{L^\circ}{\epsilon_{ML} - \epsilon_M} \quad \dots \quad (21)$$

$$\frac{1}{A - A_M^\circ} = \frac{1}{K_1(\epsilon_{ML} - \epsilon_M)M^\circ L^\circ} + \frac{L^\circ}{(\epsilon_{ML} - \epsilon_M)M^\circ} \quad \dots \quad (22)$$

In case there is no absorption by metal ion in the region of study, the equation (18) can be written as follows

$$\frac{M^\circ L^\circ}{A} = \frac{1}{K_1 \epsilon_{ML}} + \frac{L^\circ}{\epsilon_{ML}} \quad (22. A)$$

5. Mc Connel and Davidson Method: Mc Connel et al also used similar expression for the determination of stability constant of pentacyanonickelate (II). Mc Connel and Davidson have developed an expression for determination of stability constant of 1:1 complexes when they were studying the chloro complexes in aqueous solution.

$$\frac{M^\circ L^\circ}{A - A_M^\circ} = \frac{M^\circ}{(\epsilon_{ML} - \epsilon_M)} + \frac{1}{(\epsilon_{ML} - \epsilon_M)} \quad \dots \quad (23)$$

In equation (10) the term A/ϵ_{ML}^2 was omitted by Frank and Ostwalt.

$$\frac{M^\circ L^\circ}{A} + \frac{A}{\epsilon_{ML}^2} = \frac{M^\circ + L^\circ}{\epsilon_{ML}} + \frac{1}{\epsilon_{ML} K_1} \quad \dots \quad (24)$$

The method of successive approximations (7) could be used to determine the value of K_1 using equation (24). For this a trial value of ϵ_{ML} could be selected and LHS of equation (24) could be plotted against $(M^\circ + L^\circ)$ to obtain slope and intercept by method of least squares. This will give a new value of ϵ_{ML} which is different from the trial value. In the next iteration this value of ϵ_{ML} was put in LHS of equation (24) and again a new plot can be constructed to obtain a third value of ϵ_{ML} . This process can be continued till the final trial value and value calculated became same.

RESULTS AND DISCUSSION

Determination of stability constant by graphical methods: A set of solution of Fe (III) and 5-NSA were prepared in which the ionic strength was fixed at 0.1 with the help of NaClO_4 and fixing the pH at 2.4 with the help of dilute hydrochloric acid. The absorbance values were measured at wavelength 496 nm (Table - 2).

Table -2

Fe(III)-5-NSA Complex			
S N	$M^{\circ} \times 10^4$	$L^{\circ} \times 10^4$	Abs
1	1.2	1.2	0.1938
2	1.6	1.6	0.2688
3	2.0	2.0	0.3438
4	2.4	2.4	0.4250
5	2.8	2.8	0.4969
6	3.2	3.2	0.5656
7	3.6	3.6	0.6438

Using the data from the table, various graphs were drawn, using the equations (10, 11, 17, 21 and 23, respectively). From these graphs (Fig. 1-5), slope and intercepts were found out using the method of least squares and then value stability constant was calculated (Table-3)

Table-3

SN	Method	Slope	Intercept	K	log K
1	Frank and Ostwalt Method	2.651×10^{-4}	1.004×10^{-8}	2.640×10^4	4.42
2	Ramette Method	-22410×10^4	8.58×10^7	2.611×10^{-4}	4.42
3	Benesi and Hildebrand Method	1.09×10^{-8}	5.264×10^{-4}	1.597×10^4	4.20
4	Hammond Method	1.085	6.790×10^{-8}	6.258×10^5	4.80
5	Mc Connel and Davidson Method	5.310×10^{-4}	9.757×10^{-9}	5.442×10^4	4.74

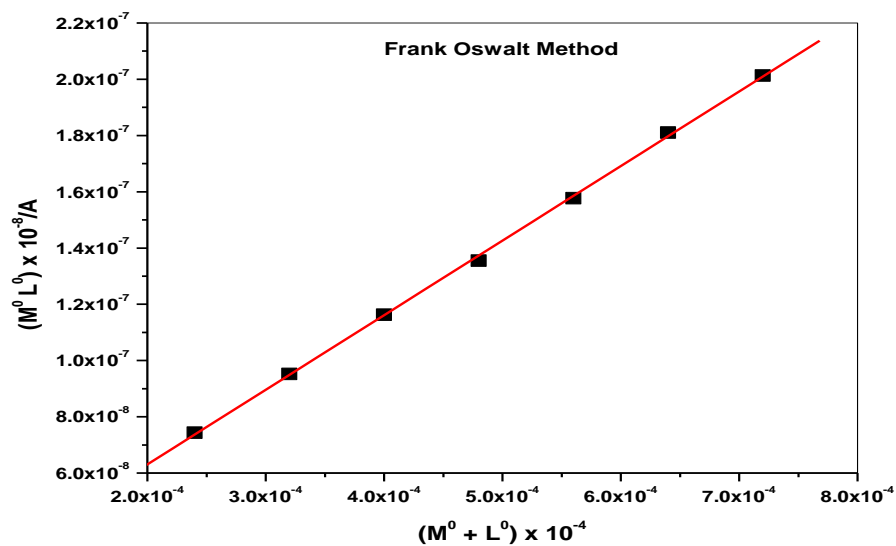


Fig. 1 Construction of graph using the equation (10)

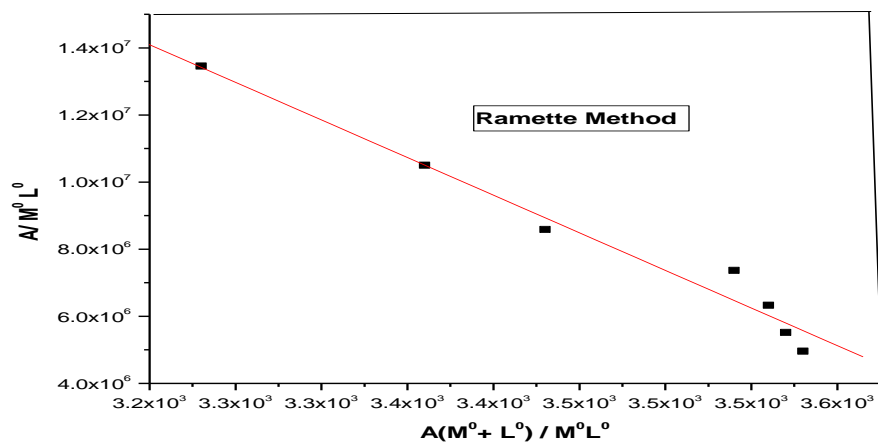


Fig.2 Construction of graph using the equation (11)

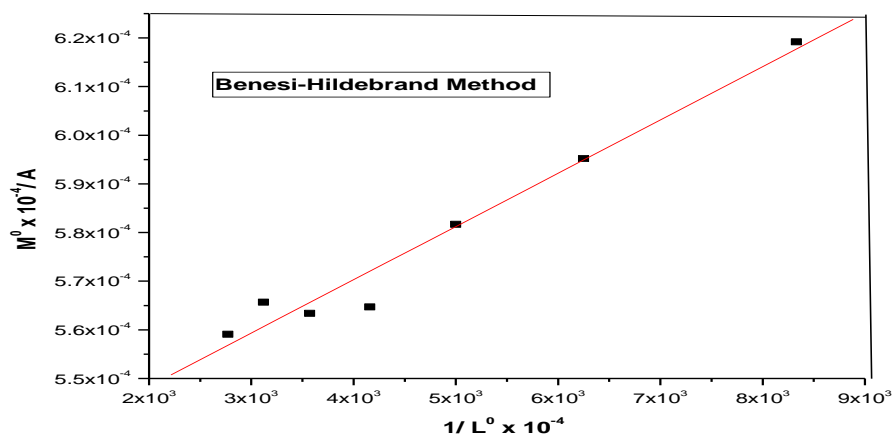


Fig. 3 Construction of graph using the equation (17)

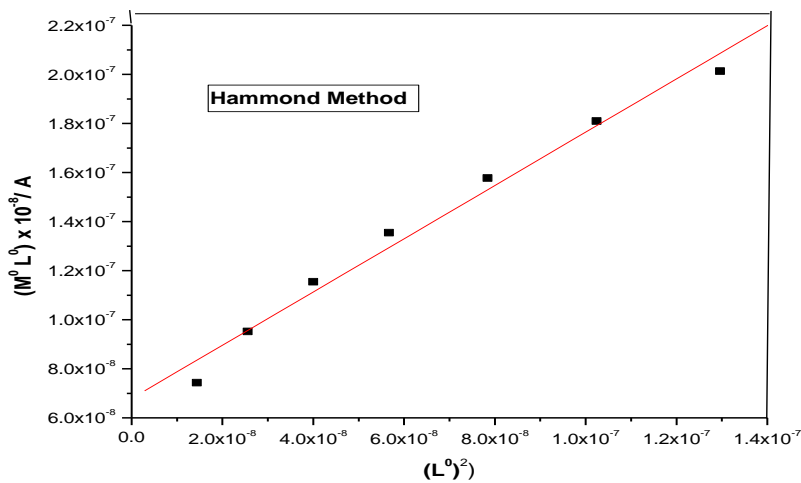


Fig.4 Construction of graph using the equation (22.A)

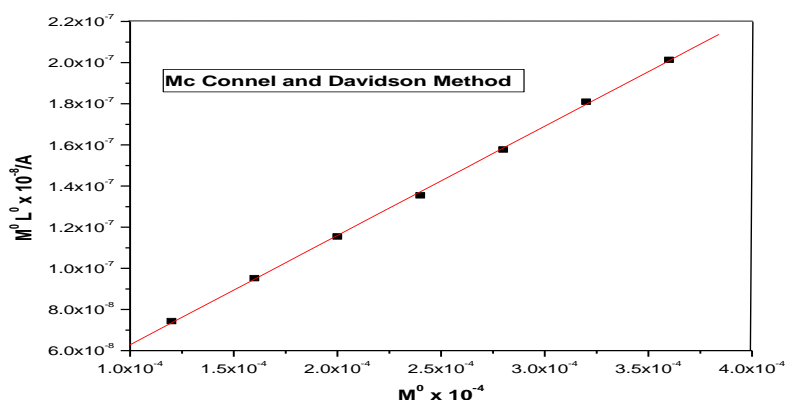


Fig. 5 Construction of graph using the equation (24)

The difference in value of K obtained may be due to the fact that in order to develop linear equation certain terms were omitted. However all the values indicate the extent of the complex formation between Fe (III) and 5-NSA. From Table-2, using same data and equation (24) the graph was constructed assuming the value of ϵ_{ML} as 1×10^5 . This trial value was refined by the method of successive approximations [10]. Using the final value of ϵ_{ML} , the $\log K_1$ works out to be 5.09.

APPLICATIONS

The method of successive approximations developed during the work does not require prior knowledge of molar absorptivity nor any term omitted to obtain the linear equation for the determination of stability constant of coloured complexes using spectrophotometric data.

CONCLUSIONS

The graphical methods are generally used for determining stability constant of metal-ligand complex using spectrophotometric data. However, in order to derive a linear equation authors have made different approximations. Therefore, when these methods were applied for the determination of stability constant of 1:1 complex formed by Fe(III) with 5-NSA in the acid range of the pH, different values of stability constant were obtained. However, when no parameter was neglected in the linear equation but a method of successive approximations was applied, correct value of stability was obtained.

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