# Stability and Structure of the Complexes of Alizarin Complexone and Iron (III) in Aqueous and Organic Solvents

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**Summary:** Spectophotometric investigation of iron (III) complexes of alizarin complexone was carried out at 25°C in three protic solvents : water, methanol and ethanol. In each solvent a mononuclear complex has been identified and the stability constants, β, have been calculated. It appears that log β decreases linearly as an inverse function of the dielectric constant of the solvents. Theoretical considerations indicate a 1:2 complex of octahedral structure.

## Introduction

Alizarin (1,2-dihydroxyanthraquinone) is an important colorant anthraquinonic. The fixation of dicarboxylamine on carbon 3 gives the compound alizarin complexone (AC) as shown in figure 1.

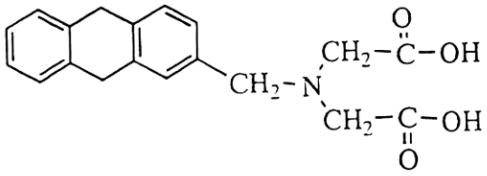

Fig. 1 Chemical structure of alizarin complexone.

This compound, acting as a good ligand, has the facility of forming complexes with several metallic ions and the coordination bonds implicate hydroxyl, carbonyl and tertiary amino groups [1], This study concerns the complexes of this compound with ferric ions in protic media.

The ferrocomplexes of alizarin complexone show electrocatalytic activity in some redox reactions, especially in the electro re duct ion of dioxygen to hydrogen peroxide. In certain reactions, the ligand to which the metallic ion is complexed adsorbs at the surface of graphite electrodes. The number of ligands so complexed influences the rate of the redox reaction. Zhang and Anson used this phenomenon to establish the stoichiometric composition of the electrocatalyser $Fe^{3+}$/AC and $Cu^{2+}$/phenanthrolin on the graphite electrode [1,2].

More and more alizarin complexone is being employed as tracers [3] especially in the medical field where it is administered at regular intervals in order to evaluate macroscopically the fusioned mass, for example of bones in intertransversal space [4].

In this study, alizarin complexone is complexed with Fe(III) cations in three different solvents, *viz.*. water, methanol and ethanol and studied spectrophotometrically. Stabilities of the species formed have been determined in order to look into the possibility of using these complexes for their chemical and their medical properties rather than the ligand alone, alizarin complexone.

## Results and Discussion

The ferric solution has a maximum at 295 nm and a shoulder peak at about 400 nm. Alizarin complexone on the other hand has several maxima of absorption. A band at 280 nm with two shoulders at about 200 and 330 nm was found in ultra violet rgion. In the visible region it shows a band centred at 430 nm.

In aqueous solutions, at low concentration of ligand, there were hardly any variations in the spectrum of Fe(III) solution. At higher ligand concentration there appears a maximum at 480 nm, which stabilises at 510 nm thus indicating the formation of a complex absorbing at this wavelength. This experimental spectrum in the visible region is presented in figure 2.

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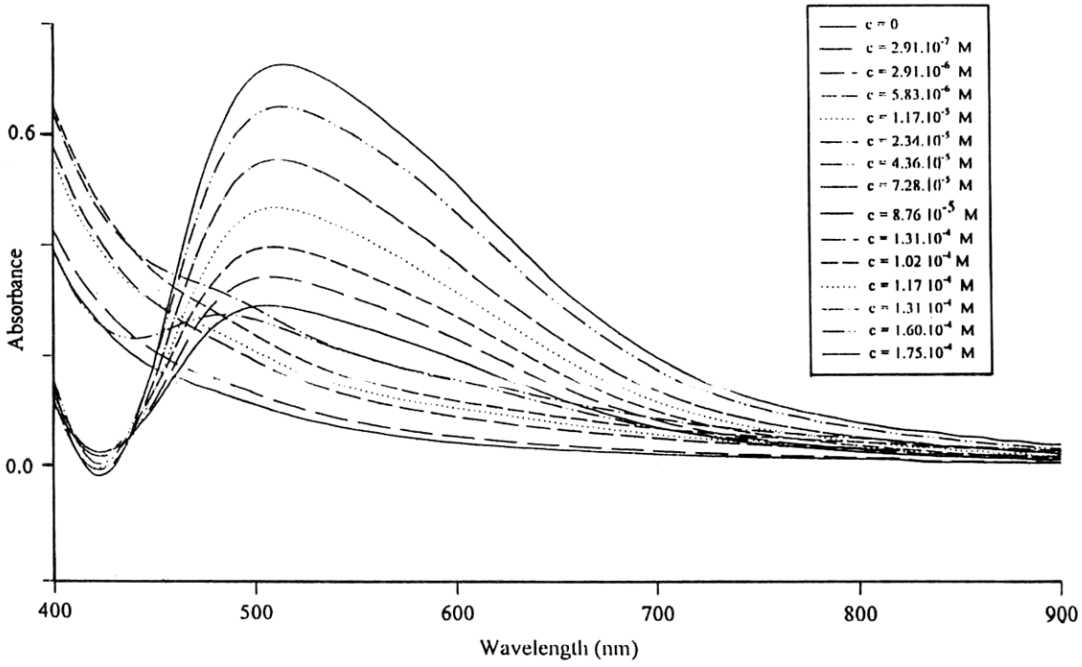


Fig. 2. Absorption spectra of aqueous solutions of Fe (III) and alizarin complexone.

The equilibrium under study is:

$$Fe^{3} + n\ AC \rightleftharpoons [Fe(AC)_n]^{3+}$$

where n is the number of ligands.

At first attempts were made to calculate the stability constants with a recent computer program Sirko [5] but without any success indicating that the constants have low values. It may be remarked that for complexes of iron (III) with tartaric and citric acids, stability constants as low as 0.21 has been reported [6] .We have therefore determined these values graphically with the method preconized by Kruh [7] based on the following equation:

$$\frac{b}{A} = \frac{1}{\varepsilon\beta c} + \frac{1}{\varepsilon}$$

where:

b = analytical concentration of $Fe^{3+}$

c = analytical concentration of AC

A == absorbance

ε = molar extinction coefficient

β = stability constant

for a plot of b/A = f(l/c), a straight line is obtained. The slope of the line gives $1/\varepsilon\beta$ and the intercept is $1/\varepsilon$. These graphs are presented in figure 3 for seven wavelengths in the visible region and the results are summarized in table 1.

Table-1: Calculated values of molar extinction coefficients and stability constants at different wavelengths in aqueous solution.

| | Wavelength (nm) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 490 | 510 | 550 | 570 | 590 | 610 | 650 |
| ε | 602 | 674 | 641 | 588 | 524 | 448 | 296 |
| β | 56.3 | 35.4 | 24.2 | 23.2 | 23.5 | 25.5 | 32.7 |

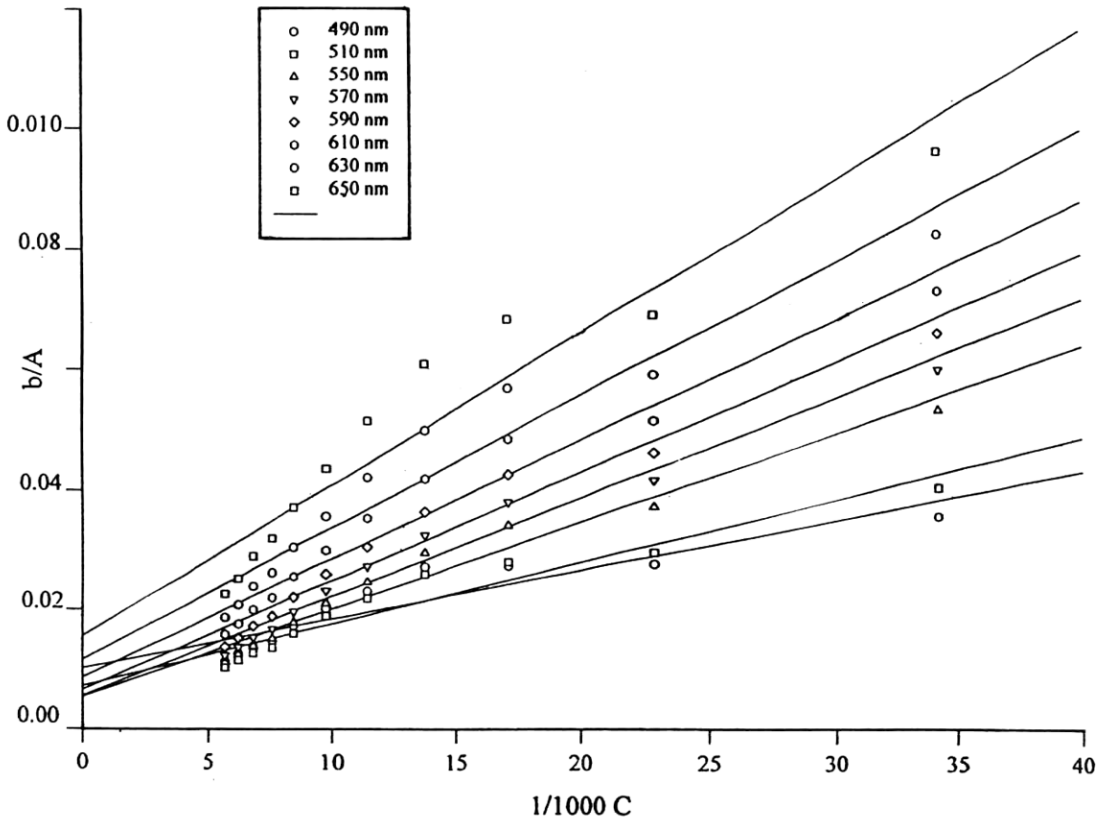


Fig. 3. Plot of b/A = f(l/C) for the determination of stability constants.

The calculated value of β are quite constant except for the one at 490 nm. The average value of p for the seven wavelengths is 31.5. However, not taking into consideration the result at 490 nm, the mean averge value was retained as 28 ± 5.

Similar experiments and calculations in methanol and ethanol led to the values of 830 ± 150 and 2600 ± 700 respectively as stability constants in these media.

Table 2: Logarithmic values of stability constants in the three solvents and their dielectric constants

| Solvent | Dielectric Constant | Logβ |
|---|---|---|
| Water | 78.5 | 1.45 |
| Methanol | 32.6 | 2.92 |
| Ethanol | 24.3 | 3.41 |

The results in the three solvents are summarized in table 2. A graph of log p *versus* the dielectric constant of the solvents show that log p is a linear function of the dielectric constant (figure 4), decreasing inversely with the permittivity of the solvent. Although the impact of this conclusion is weakened by the fact that we have only three points for the graph, yet similar results were obtained in analogous systems such as copper (II) halogeno complexes in different alcohols [8], in which the authors showed a regular decrease of stability as an inverse function of the dielectric constant of the pure solvents.

Initial results were reported earlier [9] and in addition to the relationship between stability and the dielectric constant, new ideas concerning the hypothetical structure of the identified complex are proposed. Although this study lacks structural experiments and does not permit a clear elucidation of the structure of the complex in solution, yet theoretical considerations favour a 1:2 complex where two ligands are co-ordinated to the cation with

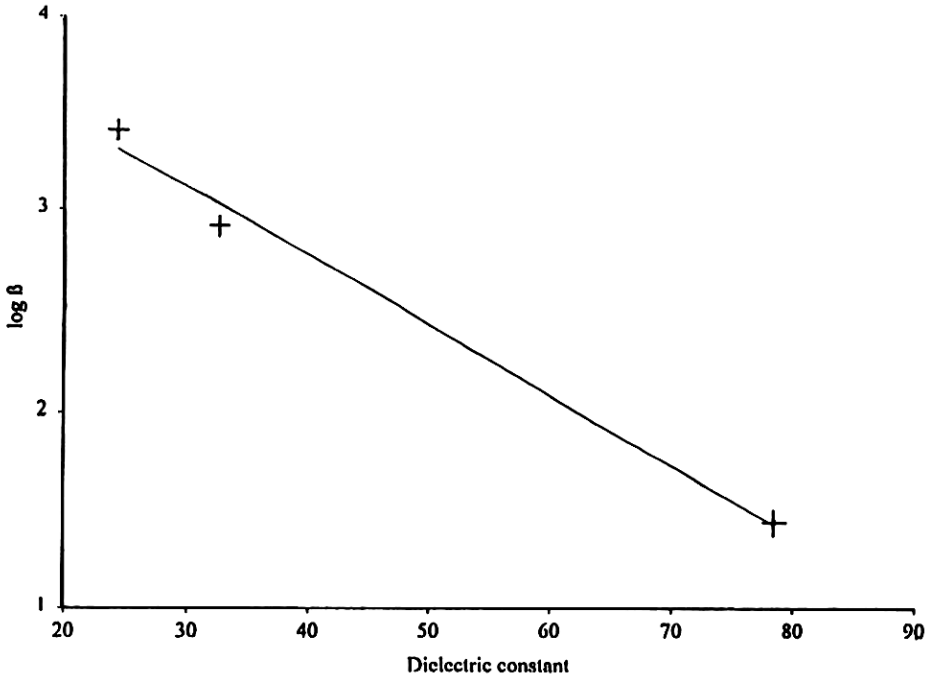


Fig. 4. Variation of the stability constant β of $Fe^{III}$/alizarin complexone complex with respect to the dielectric constant of the solvents.

solvent molecules perpendicular to the plane. It is proposed that the co-ordination is through the oxygen of the carbonyl moieties and each ligand uses its two carbonyl groups in forming a chelated complex (figure 5). These considerations are supported by the fact that the complex absorbs at 510 nm and according to Lever [10], iron (III) complexes have bands in this region, The possibility of a different structure, square planar or even tetrahedral, cannot be ruled out because the difference in stability of all these configurations in solution is low, and in most cases the structure will depend on the solvent in which the study has been carried out [11, 12].

## Experimental

A standard stock solution of alizarin complexone (M.wt. 421.35 g/m and ferric sulphate was prepared. Although alizarin complexone is sparingly soluble, a solution of $5.10^{-4}$ $mol.l^{-1}$ was prepared in water. For ferric sulphate stock solution was 0.5 $mol.l^{-1}$. As both solutions show photosensibility, they were stored in tainted flasks for

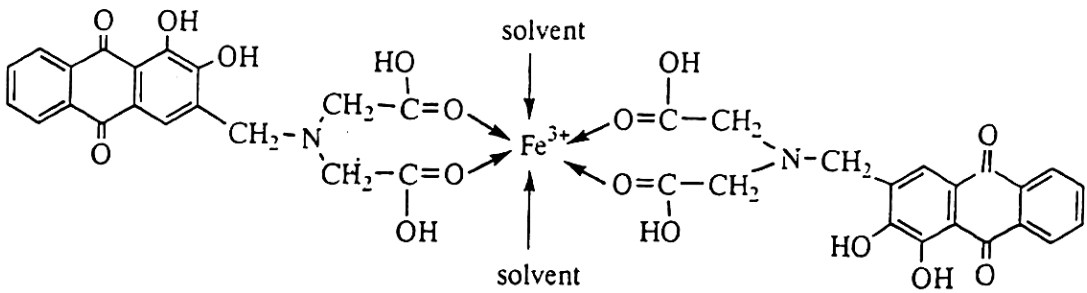


Fig. 5. Proposed structure of the alizarin complexone - iron (III) complex.

protection. The dilute solutions of iron precipitated with time and in order to stabilise them, a few drops of 0.01 mol.$l^{-1}$ $HClO_4$ solution was added to maintain the pH at about 6- The ionic strength of mixtures was kept constant at 0.01 mol.$l^{-1}$ with the help of a solution of sodium perchlorate monohydrated which did not interfere with the reaction. The spectrophotometric investigation was carried out at constant temperature of 25.0 ± 0.2°C. The analytical concentration of $Fe^{3+}$ was maintained constant at $7.5,10^{-4}$ mol.$l^{-1}$ and that of alizarin complexone varied from zero to $2.10^{-4}$ mol.$l^{-1}$

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