

CHARACTERISTIC STUDY OF SOME ELECTRONIC SPECTROSCOPIC PARAMETERS FOR THE COMPLEX PRODUCT OF IRON(III) AND ACETYLSALICYLIC ACID LIGAND

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في هذه الدراسة، تم إجراء قياسات لحساب بعض المعاملات الفيزيو-كيميائية في تفاعل تكوين المعقد بين الحديد الثلاثي Fe(III) كمستقبل إلكترونات، والنسيقة، حمض أسيتيل الساليسال (ACSA) كمانح إلكترونات، في وسط مائي عند درجة 25°م. وقد تم قياس ودراسة أطوال حزم امتصاص مانح الإلكترونات، مستقبل الإلكترونات والمترابك الناتج من تفاعلهما. كما تم حساب ومناقشة قيم المعاملات الفيزيو-كيميائية، مثل معامل الامتصاص الجزيئي، ϵ ، للمترابك و ثابت الاستقرار لتفاعل التكوين، K، باستخدام معادلات بينيسي-هيلدبراند، سكوت، فوستر-هاميك-واردلي. بالإضافة إلى ذلك فقد تم حساب طاقة حزمة امتصاص انتقال الشحنة للمترابك (E_{CT}) و التغير في طاقة جيبس الحرة للتفاعل (ΔG^0). وأوصفت النتائج أن المترابك المتكون ثابت وأن تفاعل تكوين المترابك حساس وتلقائي. وأظهرت النتائج أن تفاعل انتقال الشحنة كان بنسبة 1:1.

In this study, UV-visible spectroscopic investigations have been carried out to determine some physico-chemical parameters of the complexation reaction between iron(III) as an electron acceptor and acetylsalicylic acid ligand (ACSA) as an electron donor in water at 25°C. The absorption band wavelengths of the electron donor, the electron acceptor and their complex were measured and studied. The values of the parameters such as the molar extinction coefficient, ϵ , of the complex and the association constant, K, of their formation reaction obtained from the Benesi-Hildebrand, Scott, Foster-Hammick-Wardley equations were evaluated and discussed. The absorption band energy of the charge transfer complex, E_{CT} , and the Gibbs energy change of the above reaction, ΔG^0 , were calculated. The results reveal that the complex was stable and the complexation reaction was sensitive and spontaneous. Furthermore, the charge transfer complex was established as 1:1 stoichiometry.

Keywords: Acetylsalicylic acid ligand, iron(III), Charge transfer, Benesi-Hildebrand, Scott and Foster-Hammick-Wardley equations, Complexation parameters, Electronic spectroscopy.

INTRODUCTION

Water pollution is the most serious problem in almost every country. Recently, there has been a general concern for decreasing the discharge or disposal of water effluents containing hazardous heavy metals [1-2]. These metals enter the environment mainly by two means: (i) natural processes (for example, erosion of rocks, volcanic activity, forest fires) and (ii) processes due to human activities. An anthropogenic activity may add considerable amounts of polluting compounds, which will influence the existing

natural aquatic system. Heavy metals are frequently released in large quantities during different processes derived from human activities and may lead to major destruction of drinking waters. Moreover, human beings located at places contaminated by heavy metals could be especially sensitive to these contaminants due to bio-accumulation [3]. Also, at high concentrations, trace of heavy metals are toxic for living organisms and can accumulate in bone, hair and in some soft tissues, such as the liver, kidney or lungs [4-10].

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In our own research laboratory, we are testing the feasibility of using complex formation reactions to determine some heavy metal ions like iron(III), copper(II) or nickel(II) in aqueous waste solutions. This can effectively be achieved by the reaction between the target metals and suitable complexing ligand, and directly analysed by UV-visible spectrophotometry technique.

The present study is focused on the determination of some complexation parameters of iron(III) in aqueous solutions prior to its analysis.

This metal is recognized as a moderately toxic element when compared with other heavy metals. However, the toxic doses of iron and its compounds can lead to serious diseases, including depression, rapid and shallow respiration, coma, convulsions and cardiac arrest [11-13].

In addition to that, iron and its compounds have widespread industrial applications (e.g. food colors, pigments in paints and plastics, coagulants in water treatment); hence, large quantities of iron are discharged into the environment. Thus, appropriate knowledge of the iron content of natural water is very desirable.

In the last decade, increasing interest has been shown in developing complexing ligand for the spectrophotometric determination of Fe(III) [14-15]. However, most of them often have absorption band in visible region because of their conjugation structures.

The aim of the present work was to propose a UV-visible spectrophotometric determination of iron ions in water by its complexation with acetylsalicylic acid as a ligand. This organic acidic complexing agent ($pK_a = 3.5$) is a colorless ligand and can be easily prepared. The absorption band wavelengths of the acetylsalicylic acid electron donor, the electron metallic acceptor and their complexes were measured and studied in water solutions.

Furthermore, several physico-chemical complexation parameters such as the molar absorptivities, ϵ , of these complexes and the equilibrium constants, K , of their formation reactions obtained from Benesi-Hildebrand [16], Scott [17] and Foster-Hammick-Wardley [18] equations were established and discussed. The absorption band energy of the complex, E_{CT} , and

the Gibbs energy changes of the complex reaction, ΔG^0 , were also calculated.

Finally, after going through the literature during the past ten years we saw no such studies have been done on iron(III) complex of acetylsalicylic as a ligand; thus it is worthwhile to investigate its complexation behavior.

EXPERIMENTAL

Materials and instruments:

$FeCl_3 \cdot 6H_2O$ was obtained from Fluka and all organic compounds were obtained from Merk and used as received.

The UV-visible spectra were measured using Perkin Elmer Lambda 20 and Shimadzu UV-1202 (Shimadzu Europa GMBH) UV-Visible spectrometers with quartz cells of 1cm path length. The infrared spectra of the donor were recorded using a Perkin Elmer Paragon 1000 FT-IR spectrometer. The 1H -NMR spectra were recorded in $CDCl_3$ by a Bruker Avance DSX-400 MHz Spectrometer. Chemical shifts are reported as δ values in ppm relative to an internal standard tetramethylsilane.

Typical synthesis of acetylsalicylic acid ligand:

To a mixture of a salicylic acid (2.76 g, 0.02 mol) and acetic anhydride (4 g, 0.04 mol) was added two drops of sulphuric acid (1M), and the resulting mixture was heated at $60^\circ C$ for 15 min. After cooling, 35 mL of distilled water was added to the reaction mixture. The white solid products obtained thus formed was collected by filtration and purified by recrystallisation from water-ethanol. The purity of final product was controlled by 1H -NMR spectra, and found to be higher than 90%. white solid, mp $136-138^\circ C$ [19], FT-IR (KBr): ν 3006, 2891, 2701, 1754, 1693, 1436, 1272, 841, 667 cm^{-1} . 1H -NMR (400 MHz, $CDCl_3$): δ 11 (s, 1H, OH), δ 7.14-8.13 (m, 4H, Arom-H), δ 2.35 (s, 3H, CH_3).

Procedure of preparation of complex solutions

The spectrometric spectra of the donor (acetylsalicylic acid), acceptor (iron (III)) and the complex were recorded in the region 200-800 nm.

The complex was prepared by mixing variable amounts of donor into a constant volume

of the acceptor solution in water at 25°C. The donor concentration in the reaction mixture was varied over the range of 5×10^{-4} M to 4.5×10^{-3} M, while the concentration of the acceptor was kept fixed at 5×10^{-4} M. The absorbencies of the mixtures at the wavelength of measurement (λ_{\max}) which are due entirely to the complex, were measured using pure solvent, water, as the blank.

The kinetics measurements were performed in water at 25°C on equimolar sample of donor and acceptor (4×10^{-3} M). The measurements were followed kinetically at the complex wavelength (λ_{\max}).

RESULTS AND DISCUSSION

Identification of Fe(III)-ACSA complex

The acetylsalicylic acid solution (electron donor) was colourless but when mixing the solutions of the donor and the electron acceptor in water a characteristic colour was developed which exhibits a new absorption band located at 520 nm in the visible region in which neither the acceptor nor the donor exhibited such an absorption band (Table 1, Figure 1). This indicates the formation of charge transfer complex Fe(III)-acetylsalicylic acid and the complete electrons transfer from the donor to the unfilled orbital of the metallic iron(III).

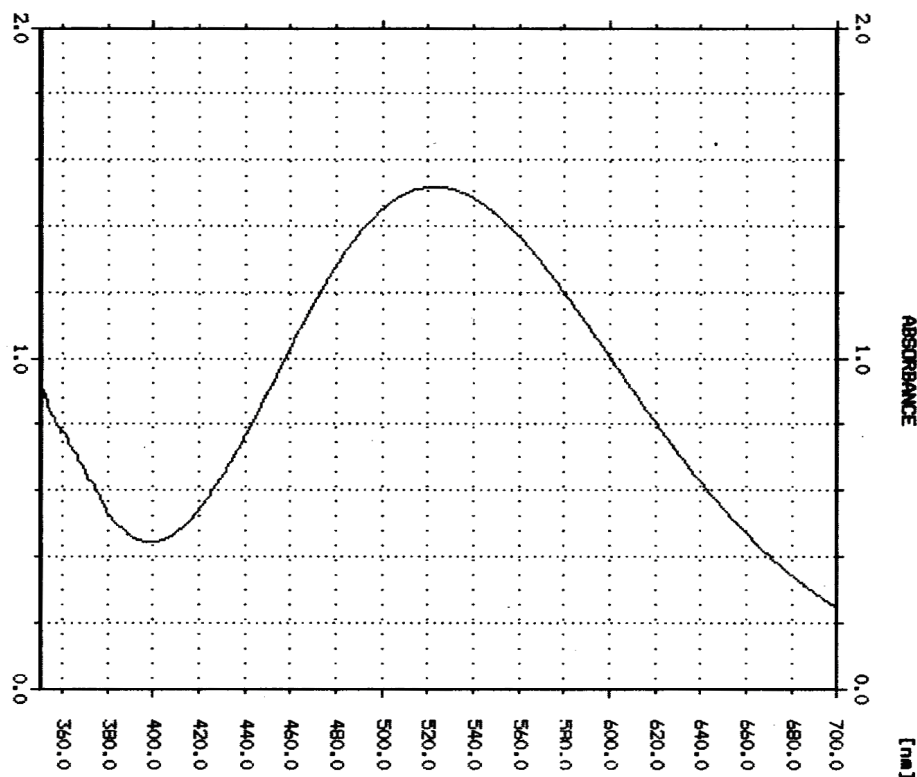


Figure 1: Visible electronic absorption spectrum of Fe(III)-acetylsalicylic acid complex in water.

Table 1: Absorption band wavelengths (nm) of the donor, acceptor and their complex in water at 25 °C.

Donor (ACSA)	Acceptor FeCl ₃ .6H ₂ O	Complex
220	210	220
300	290	290
		520

Determination of the complexation parameters

The spectrophotometric data are employed to calculate the equilibrium constant, K, and the molar absorptivity of the complex, ε, for ACSA-Fe(III) complex in methanol using the following Benesi-Hildebrand (Equation 1) [16], Scott (Equation 2) [17] and Foster-Hammick-Warley (Equation 3) [18] equations. These equations are based on the assumption of 1:1 (Acceptor-Donor) complex formation.

$$\frac{[A]_0}{A} = \frac{1}{K \epsilon [D]_0} + \frac{1}{\epsilon} \quad (1)$$

$$\frac{[D]_0 [A]_0}{A} = \frac{[D]_0}{\epsilon} + \frac{1}{K \epsilon} \quad (2)$$

$$\frac{A}{[D]_0} = -K \cdot A + K \cdot \epsilon \cdot [A]_0 \quad (3)$$

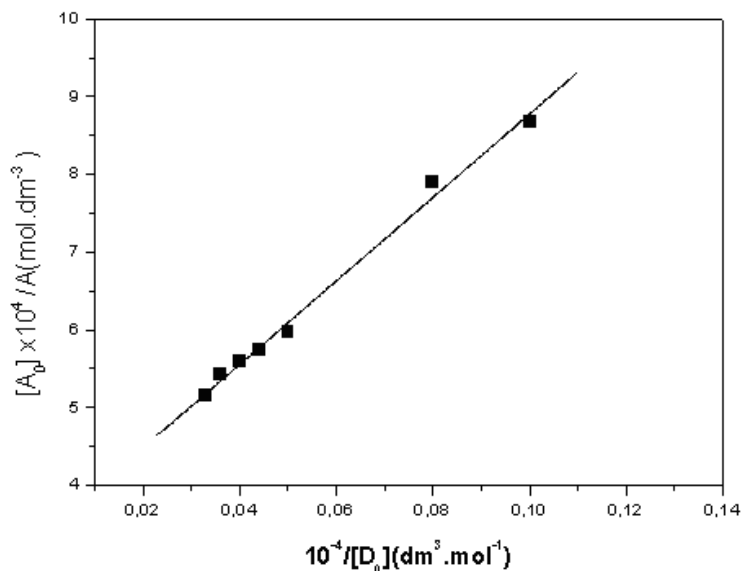
where A = absorbance of the CT band complex,
 [A]₀ = initial concentration of the acceptor,
 [D]₀ = initial concentration of the donor,
 K = association constant of the complex reaction in solution, and
 E = molar absorptivity of CT band complex.

These equations are obviously of the type:

$$y = a x + b.$$

After having determined the values of A experimentally, the corresponding y values were plotted against those of x term.

The plots reveal a good linearity between the two quantities in the three equations (Figures 2, 3 and 4) indicating the 1:1 stoichiometry of the CT complex.

**Figure 2: plot of Benesi-Hildebrand's equation.**

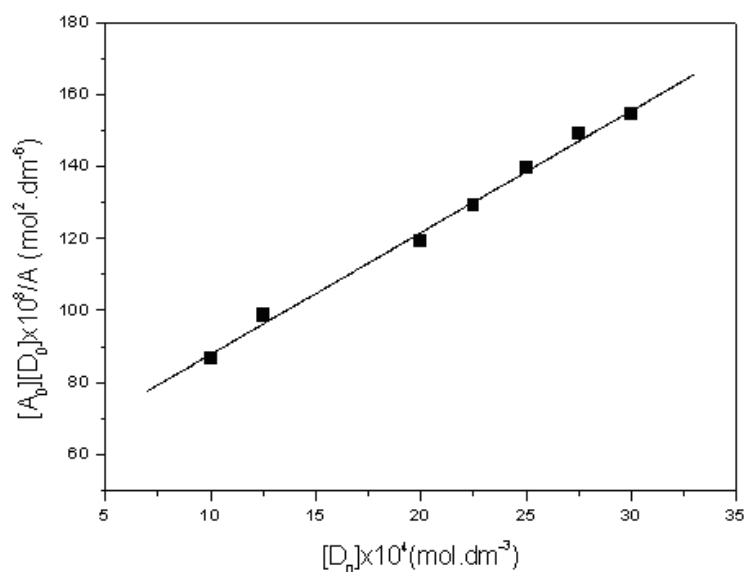


Figure 3: Plot of Scott's equation.

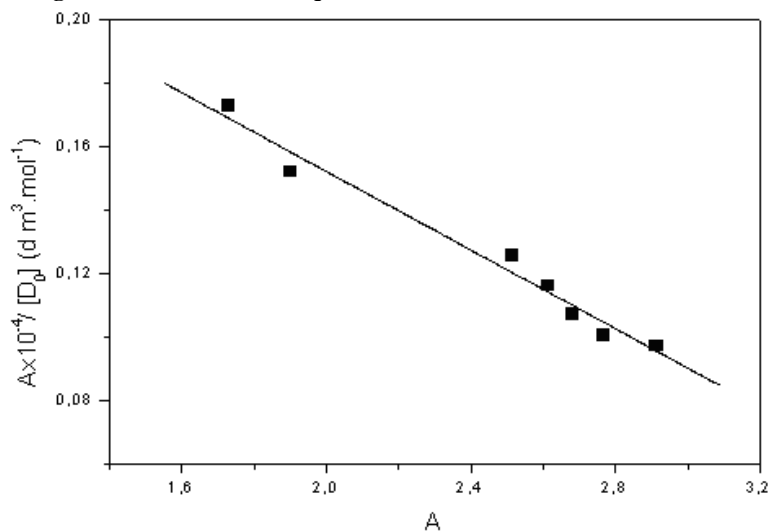


Figure 4: Plot of Foster-Hammick-Wardley's equation

The values of K and ϵ were obtained from the slopes and intercepts of the plots of the equations (1), (2) and (3) as shown in figures 2-4 and reported in table 2.

The K values are 636, 627 and 619 L mol^{-1} while the values of ϵ are 2931, 2954 and 2971 $\text{L cm}^{-1} \text{ mol}^{-1}$ from equations (1), (2) and (3), respectively, which prove the validity of these three equations for such reaction.

The charge transfer complex can also be studied by evaluating its adsorption band energy, E_{CT} and the Gibbs energy changes, ΔG^0 , calculated from λ_{max} and K values, respectively (Table 2), applying the following equations:

$$E_{CT} = \frac{1243.667}{\lambda_{max}} \text{ (e.V)} \quad (4)$$

$$\Delta G^0 = -RT \ln K \quad (5)$$

Table 2: Values of association constants, molar absorptivities, absorption band energies and Gibbs energy changes of complex formation reaction in water at 25°C.

	Equation 1	Equation 2	Equation 3	Average value
K (L.mol ⁻¹)	636	627	619	631
ε (L.cm ⁻¹ .mol ⁻¹)	2931	2954	2971	2952
E (eV)	2.392	2.392	2.392	2.392
-ΔG ⁰ (kJ.mol ⁻¹)	15.951	15.916	15.884	15.917

It is apparent that the formation of ACSA-Fe(III) complex takes place spontaneously and is energetically favored. Finally, the kinetic of the complexation between the donor ligand (ACSA) and the acceptor ferric ion was studied at 25 °C and shown to be instantaneous.

Conclusion:

In this paper, acetylsalicylic acid (ACSA) was synthesized and the coloured reaction of ACSA with iron(III) was firstly studied using Benesi-Hildebrand, Scott and Foster-Hammick-Wardley equations. The obtained results indicate the formation of 1:1 charge transfer complex.

ACSA is one of the sensitive spectrophotometric reagents for iron. The molar absorptivity of the chelate reaches 2952 L cm⁻¹ mol⁻¹. The determination of some complexation parameters shows that the reaction is instantaneous, stable for over 24 h, and spontaneous. The association constant Fe-ACSA and Gibbs free energy are 631 L mol⁻¹ and 15.917 kJ mol⁻¹, respectively.

Because the ACSA can rapidly react with iron(III) in aqueous solution at room temperature, this complexing agent can be used to determine iron spectrophotometrically without heating or extraction. This is convenient and rapid. It is a sensitive and convenience complexation method for iron.

Finally, further work is underway in our laboratory, to examine other parameters, such as pH of the solution, nature of solvent and temperature in the complexation of ACSA with Fe(III), and hence to accomplish determination of iron in real samples.

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