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SPECTROPHOTOMETRIC STUDIES ON THE Fe (III), Co (II), Ni (II) AND Cu (II) CHELATES WITH 2- (1- HYDROXY -3- SULPHO -7- NAPHTHYLAZO)-CHROMOTROPIC ACID,

By

A.L. EL-ANSARY, S.S. BADAWY, A.I. ABDEL RAHMAN AND
L.M. SHAFIK

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SPECTROPHOTOMETRIC STUDIES ON THE Fe (III), Co (II), Ni (II) AND Cu (II) CHELATES WITH 2- (1- HYDROXY -3- SULPHO -7- NAPHTHYLAZO)-CHROMOTROPIC ACID,

A.L. EL-ANSARY, S.S. BADAWY, A.I. ABDEL RAHMAN AND L.M. SHAFIK*

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Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt.

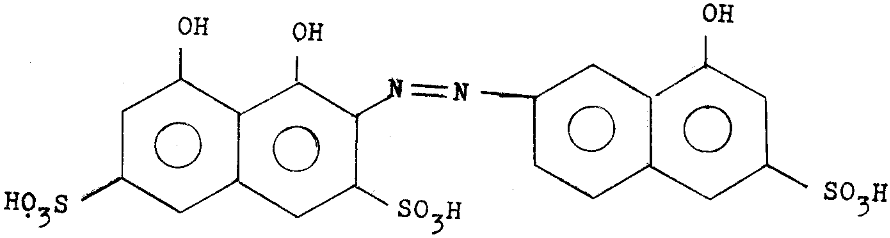
SUMMARY

A new rapid, reliable and accurate method for the spectrophotometric microdetermination of Fe (III), Co (II), Ni (II) and Cu (II) using 2- (1- OH -3- SO_3 H -7- naphythylazo) -chromotropic acid (I), is given. The optimum conditions favouring the formation of the complexes are extensively investigated. The molecular structure of the complexes and their obedience to Beer's law, as well as, their stabilities are also studied. A spectrophotometric titration method for Fe (III), Co (II) and Ni (II) with EDTA using the named reagent as indicator is also given.

INTRODUCTION

Azo dyes derived from chromotropic acid (1, 8- dihydroxynaphthalene -3,6- disulphonic acid) are of great analytical importance. They were used successfully as metallochromic and chromophoric indicators [1-6].

The present investigation deals with the use of 2- (1-OH-3-SO_3 H-7-naphthylazo) -chromotropic acid (I) for the spectrophotometric determination of Fe (III), Co (II), Ni (II) and Cu (II).



(I)

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*National Research Center, Dokki, Giza, Egypt

EXPERIMENTAL

The water used was always twice distilled. The chemicals were provided by BDH. The azo dye under investigation (I) was prepared by coupling diazotized 7- amino -1- hydroxynaphthalene –3– sulphonic acid with chromotropic acid in sodium carbonate medium and purified as recommended [3]. The purity of the dye prepared was confirmed by elemental analysis to be more than 99.5 %. A 10^{-3} M solution of the dye was prepared by dissolving an accurately weighed amount in the appropriate volume of distilled water.

Modified Britton Universal buffer series and boric acid-borax-sodium hydroxide buffers [7] were used to control the pH of solutions. The pH of the above mentioned buffers was checked by means of expanded scale Lseibold pH-meter (Austria). 0.01 M solution of Fe (III), Co (II), Ni (II) and Cu (II) were prepared and standardised by recommended methods [8]. 10^{-3}M solutions were prepared by accurate dilution. The absorption spectra were recorded by aid of SPECORD recording spectrophotometer (Carl Zeiss, Jena) using 1 cm matched silica cells.

Procedures:

1– Spectrophotometric determination of metal ions:

To solutions containing up to 5.03, 2.65, 2.94 and 3.5 ppm of Fe (III), Co (II), Ni (II) and Cu (II) respectively, add 1 ml 10^{-3}M (I) and 6ml of the recommended buffer, Table 1. Dilute all the solutions up to the mark with distilled water in 10 ml volumetric flasks, and measure their absorbances after 2 or 3 minutes at 625, 590, 600 and 570 nm for Fe–I, Co–I, Ni–I and Cu–I respectively, against a dye solution containing the same ingradients except the metal ion. Compute the concentration from a standart caliberation curve prepared in the same manner.

2– Spectrophotometric titration of Fe (III), Co (II) and Ni (II) with EDTA using (I) as indicator:

Increasing volumes (0.05, 0.1, 0.15 .... ml) of 10^{-3} M EDTA were added to (0.3–0.8) ml, (0.2–0.5) ml and (0.3–0.7) ml 10^{-3}M of Fe (III), Co (II) and Ni (II) solutions respectively, followed by 2 ml 10^{-3}M (I), then 6 ml of the recommended buffer. The absorbances were measured at 625, 585 and 590 nm for Fe (III), Co (II) and Ni (II) respectively. On plotting the absorbance against the volume of EDTA the amount of the metal ion is calculated from the intersection of the two straight lines obtained.

RESULTS AND DISCUSSION

The absorption spectra of all the Fe (III), Co (II), Ni (II) and Cu (II) complexes were investigated using the previously mentioned two types of buffers and the results showed that borax-boric acid buffer of pH 6.4, borax-boric acid buffer of pH 9.8, universal or borax-boric acid buffer of pH 9.65 and universal buffer of pH 9.8 are that most suitable buffers for developing the violet Fe (III)–I, Co (II)–I, Ni (II–)I and Cu (II)–I complexes respectively. The absorption spectra of the ligand against water and of the metal-chelates against water and against ligand have shown that the maximum absorbance of these complexes were at 625, 590, 600 and 570 nm for Fe–I, Co–I, Ni–I and Cu–I complexes respectively.

The effect of time, temperature and solvents on the stability of these complexes were also studied in detail. The colour intensity of the system was found to be time-dependant at the first one hour, but after that they give a most a steady spectra. Raising the temperature up to 50°C has no effect on the formed complexes, but boiling for one minute is suffecient for complete destruction of these complexes.

Up to 20 % methanol, ethanol or isopropanol and acetone has a very slight action upon the absorbance, while the effect was clear on addition of pyridine. In case of Fe–I, pyridine lowers the absorbance; while in case of Co–I and Ni–I the pyridine slightly shifts the the original wave (600 and 600 nm) to 618 and 630 nm with the increase of absorbance. Only in case of Cu–I the colour of the complex disappeared completely.

Beer's law was verified and found to be satisfactorily obeyed up to 5.03, 2.65, 2.94 and 3.5 ppm for Fe, Co, Ni and Cu respectively. The molar absorptivity, (ε), spesific absorptivity, (a) [9] and sandell sensitivity, (S) [10] were calculated and their values are listed in Table (1). These values indicate that the method is highly sensitive.

Table 1. Results of Fe-I, Co-I, Ni-I and Cu-I Complexes.

Complexes	pH	ε	a	S
Fe–I	6.40	7.7×10^3	0.138	0.007
Co–I	9.80	6.3×10^3	0.107	0.009
Ni–I	9.65	5.4×10^3	0.092	0.011
Cu–I	9.80	5.1×10^3	0.080	0.013

ε: Molar absorptivity ($l\ mol^{-1}\ cm^{-1}$).

a: Specific absorbance ($ml\ g^{-1}\ cm^{-1}$).

S: Sandell sensitivity ($\mu g\ cm^{-2}$).

The stoichiometry of the formed complexes was studied using the standard spectrophotometric methods such as the molar ratio [11] and continuous variation [12, 13] methods. The results indicate the formation of 1:1 and 1:3 (M:L) in case of Fe–I complexes, while in case of Co–I, Ni–I and Cu–I complexes 1:2 (metal:ligand) complexes are formed. The presence complexes was confirmed by calculating the number of absorbing species using Colemans graphical method [14] as applied to the molar ratio method.

The overall formation constants (β_n) of the complexes were calculated using the above mentioned methods [11] by aid of the relation:

$$\beta_n = \frac{(A / A_m)}{(1-A / A_m)^{n+1} C^n_L \ n^2}$$

where

A = Absorbance at ligand concentration C_L.

A_m = Maximum absorbance at full colour development.

n = Stoichiometric ratio of the complex.

The results are listed in Table (2).

Table 2. The overall stability constants of Fe–I, Co–I, Ni–I, and Cu–I complexes.

Complex	Method	Mol. ratio	log β_n
Fe–I	MR	1 : 1	5.20
		1 : 3	13.95
	CV	1 : 1	5.80
		1 : 3	13.31
Co–I	MR, CV	1 : 2	9.61
Ni–I	MR, CV	1 : 2	9.31
Cu–I	MR, CV	1 : 2	9.37

MR: Molar ratio method.
CV: Continuous variation method.

Effect of foreign ions:

In case of Fe–I complexes (27.9 μg Fe / 10 ml), data led to the conclusion that up to 20 fold of Li^+, Na^+, K^+, Rb^+, Tl^+, Ba^{2+}, Hg^{2+}, Mn^{2+}, Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, SO_4^{2-}, formate, acetate, benzoate and succinate ions do not interfere. On the other hand Ag^+, Be^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Al^{3+}, Sb^{3+}, Bi^{3+}, Y^{3+}, Th^{4+}, UO_2^{2+}, EDTA, phosphate, molybdate, tungstate, vanadate, oxalate, tartrate and citrate ions interfere. Some cations and anions do not interfere up to two fold such as Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, V^{4+}, phosphate and molybdate.

The results in case of Co–I complex (29.47 μg / 10ml) showed that up to 20 fold Li^{+}, Na^{+}, K^{+}, Rb^{+}, Ag^{+}, Zn^{2+}, Ba^{2+}, Sr^{2+}, La^{3+}, UO_2^{2+}, Cl^{-}, Br^{-}, I^{-}, NO_3^{-}, ClO_4^{-}, SO_4^{--}, phosphate, molybdate, tungstate, vanadate, acetate, formate, benzoate, succinate and tartrate ions do not interfere. On the other hand Tl^{+}, Be^{2+}, Ca^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+}, Y^{3+}, Bi^{3+}, Sb^{3+}, Th^{4+}, Zr^{4+}, V^{4+}, EDTA and oxalate interfere.

In case of Ni complex it was found that up to 20 fold Li^{+}, Na^{+}, K^{+}, Rb^{+}, Tl^{+}, Hg^{2+}, Mn^{2+}, Ca^{2+}, acetate, formate, tartrate, oxalate, vanadate, molybdate, tungstate, Cl^{-}, Br^{-}, I^{-}, ClO_4^{+}, IO_3^{-}, NO_3^{-}, and SO_4^{--}, ions do not interfere; while Ag^{+}, Be^{2+}, Ba^{2+}, Sr^{2+}, Co^{2+}, Zn^{2+}, Mg^{2+} La^{3+}, Al^{3+}, Fe^{3+}, Bi^{3+}, Zr^{4+}, Th^{4+}, V^{4+}, EDTA, benzoate, citrate and phosphate interfere.

Applying the same procedure to Cu complex it was found that Li^{+}, Na^{+}, K^{+}, Rb^{+}, Tl^{+}, Hg^{2+}, Ba^{2+}, Sr^{2+}, Zn^{2+}, Al^{3+}, Th^{4+}, V^{4+}, EDTA, Cl^{-}, Br^{-}, I^{-}, No_3^{-}, SO_4^{-}, IO_3^{-}, ClO_4^{-}, phosphate, molybdate, tungstate, vanadate, acetate, formate, oxalate, benzoate, tartrate and succinate do not interfere; while Be^{2+}, Mg^{2+}, Ca^{2+}, La^{3+}, Sb^{3+}, Bi^{3+}, Zr^{4+}, and UO_2^{2+} interfere.

Spectrophotometric titration of Fe (III), Co (II) and Ni (II) with EDTA using (I) as indicator:

Fe (III), Co (II) and Ni (II) complexes show good absorbance response on plotting the absorbance values versus the increasing volumes of EDTA; two straight lines are obtained in each case. The intersection of these two lines represents the equivalence point of the titration from which the amount of the metal ion can be computed. The titration is applicable for the concentration ranges of 16.75–44.69 μg Fe, 11.79–29.47 μg Co and 17.61–41.10 μg Ni. Higher concentrations can be titrated following the absorbance changes in the vicinity of the end point.

The present methods are accurate, rapid, versatile and reproducible for the microdetermination of Fe, Co, Ni and Cu ions spectrophotometrically; further more by aid of the presented reagent Fe, Co, and Ni can be titrated with EDTA with fair accuracy and precission.

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