

Preparation and Spectrophotometric Determination of Cobalt, Copper and Zinc Complex with 3-(2-naphthol-4-sulphonic) azo-2-amino benzoic acid

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Abstract

In this study a 3-(2-naphthol-4-sulphonic) azo-2-amino benzoic acid was prepared and it was used to develop a sensitive spectrophotometric method for determination of cobalt, copper and zinc. The elements form pink and red complexes with this dye with maximum absorption at 340 nm with Co and gives colored chelating complex⁽⁶⁾ such as the reagent α -nitroso- β -naphthol.

Although copper (Π) ion itself gives rise to color, yet there are numerous spectrophotometric methods for its determination based on colorless reagents. Probably the most used reagent at present time is diethyl dithiocarbamic acid in the form of the sodium salt⁽⁷⁾ other reagents⁽⁸⁻¹⁰⁾ have been reported in the literature for determination of copper spectrophotometrically.

In the present work, a new ligand was prepared (NABA) and a spectrophotometric study of the complexes cobalt, copper and zinc with this ligand was done.

Experimental

1-preparation of NABA

4.8g (0.02 mole) of a 1-amino-2-naphthol-4-sulphonic acid was transferred into a beaker (100ml) and treated with HCL. To Resulting Solution, Sodium Nitrite Solution (Prepared From 1.4g(0.02mole) NaNO_2 In 16 ml Water) Was Added Dropwise With Cooling To 0 C And Stirring The Resulting Diazonium Salt Solution Was Added Dropwise With Cooling To The Basic Solution Of 2-Amino Benzoic Acid (0.02mole). A Reddish-Brown Precipitate Was Directly Formed And Left To Stand At Room Temperature For 1 Hour, Then Filtered

Washed With Cold Water,
Recrystallized From Aqueous Ethanol
And Dried In The Oven At 60 C For
About 4 Hours⁽¹¹⁾.

The Product Was Identified Using
Elemental Analysis And Ir
M.P.=245 C, Reddish Brown
Emp. Formula= $\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_6\text{S}$
M.Wt= 387.37 , $\lambda_{\text{MAX}}=490 \text{ Nm}$
Soluble In H_2O , But Slightly Soluble In
 H_2O ($\text{Ph}>7$). The I.R Spectrum,
Showing The Following Peaks 3200-
2700 cm^{-1} (Broad-Oh)
1310 cm^{-1} OH-bending
1605 cm^{-1} C=C, str. benzen ring
1580 cm^{-1} -N=N- str
740 cm^{-1} (1,2-substituted benzen)
And the elemental analysis was

	%C	%N	%H
Theoretical	52.71	10.84	3.37
Experimental	52.35	9.02	3.21

2- Determination of Cobalt, Copper and Zinc

For the determination of Co, Cu and Zn ions, a 100 ml of 0.001 M solutions of azo dye(L), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2 were prepared by using distilled H_2O . Also, solution of pH range from 2.2 to 8.0 were prepared by using Na_2HPO_4 and citric acid.

The scanned within the range 320-850 nm in H_2O , using pu 8800 u.v./vis spectrophotometer in different pH solutions.

Result and Discussion

The absorption spectra of the azo dye (L) and its complexes with Co, Cu and Zn ions were recorded within wave length range 320-850 nm. It is found from the absorption spectra of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and ZnCl_2 the absorption maxima located at 510 nm, 820 nm and 610 nm respectively. It is found also that the absorption maxima of Co and Cu complexes were located at 340 nm while of Zn complex at 460 nm, λ_{max} of the free dye is 490 nm. The absorption spectra of dye (L) and its complexes are shown in Fig. 1.

The effect of time, sequence of addition and pH on the stability of the complexes were studied in details. It is found that complexes are formed instantaneously and remain constant for more than 12 hours and there is no effect for the sequence of addition.

The suitable pH values, for complex formation were found to be in the range of 4.4-5.0 for Co-complex,

4.6-5.4 for Cu-complex and 7-7.4 for Zn-complex and the absorption at these range of pH was constant. According to above, he selected pH for the Co-complex was 5 while for Cu-complex was 5.4 and for Zn-complex was 7.4. The variations of the absorbance with the pH value are shown in Fig.2. The suitable volume of pH solution used for the three complexes is 5 ml.

Beer's law was obeyed to the complex under investigation for spectrophotometric determination of Cobalt, Copper and Zinc. It was found that Beer's law is satisfactory obeyed up to 0.16 mmol/dm^3 for Co-complex up to 0.18 for Cu-complex while up to 0.14 for Zn-complex.

The empirical formula of the colored complexes were investigated using a standard spectrophotometric methods such as mole ratio⁽¹²⁾ and continuous variation⁽¹³⁾ at the optimal pH and wave length. The results indicate the formation of 1:1 (M:L) for Co-complex and Zn-complex, while 1:2 for Cu-complex as in Figs 3 and 4. The stability of complexes are increased with the increasing of the volume of chelating ring⁽¹⁴⁾, the Cobalt and Zinc ions may be bonded with the ligand molecule through out the OH group and the two nitrogen atoms, so ligand will be terdenatate in the Co and Zn complexes as follows:

While for cooper complex, the ratio of metal to ligand is 1:2, the ligand is bidentate due to the steric

effect and due to the organic molecule, so the suggested structure is as follow:

The PH range in which the three complexes were formed in 5 to 7.4 (slightly acidic and weakly basic) so, the elimination of the acidic hydrogen from the hydroxyl group is easier than from -cooh group, because the oh group is bonded to the electron with drawing group (two phenyl), so the metal ions bonded to the ligand with the oh group⁽¹¹⁾.

Calculation of the equilibrium constant for complex formation, k_c , and molar absorption E_c , WERE BASAD

Complex	K_c	E_c
Co-Complex	3.22×10^3	2×10^3
Cu-Complex	0.918×10^3	3.3×10^2
Zn-Complex	6.75×10^3	1.4×10^3

ON THE BENESI-HILDERBRAND Equation⁽¹⁵⁾.

$$[A_0]/A = 1/(K_c \times E_c) \times 1/[D_0] + 1/E_c.$$

Where A Is The Absorbance Due To Complex Formation, $[A_0]$ And $[D_0]$ Are The Initial Concentration Of The Metal Ion And The Ligand Respectively. Values Of K_c Were Obtained From The Plot Of $[A_0]/A$ Versus $1/D_0$ As In Fig. 5, Where Slope Of The Plot Is Equal To $1/K_c \times E_c$ While Intercept Equal To $1/E_c$. The Following Table Is Shown Values Of K_c And E_c For The Different Complex.

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الخلاصة

يتضمن هذا البحث تحضير ليكاند ٣-(٢-نافثول-٤-سلفونيك)أزو-٢-امينو حامض البنزويك استخدمت طريقة سبكتروفومترية لتعيين كل من الكوبلت ، النحاس و الزنك أعطت العناصر مع هذه معقد الكوبلت ،النحاس و الزنك مستقر عند PH ٤,٤٥،٤,٥،٧ على التوالي قانون لامبرت بير ينطبق ضمن مدى تركيز ٠,٠٢ إلى ٠,١٦ للكوبلت، ٠,٠٢ إلى ٠,١٨ للنحاس و ٠,٠٤ إلى ٠,١٤ مولي دسم^{٣-} .
عينت صيغة معقدات الكوبلت و الزنك فكانت MLحيث (M = CO^{+2} ، zn^{+2} ، L=ليكاند) بينما معقد النحاس فكانت ML2 كما عينت ثوابت التكوين لهذه المعقدات.