COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME : 29 ANNÉE : 1983

Spectrophotometric Studies on Complexes of Ni and Cu With Some Schaffer Acid Azo Dyes.

by

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Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Universite d'Ankara

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Spectrophotometric Studies on Complexes of Ni and Cu With Some Schaffer Acid Azo Dyes.

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(Received September 5 1983, and accepted October 13 1983)

SUMMARY

A new rapid and accurate method for the spectrophotometric microdetermination of nickel and copper ions using p-nitro-(Ia), p-methoxy-(Ib) and p-ethoxy phenylazo-Schaffer acid (Ic) is given. The optimum conditions favouring the formation of the complexes are extensively investigated. The molecular structure of complexes and their obeyence to Beer's law as well as their stabilities are also studied, a spectrophotometric titration method for Ni and Cu with EDTA using Ia, Ib or Ic as indicators is also given.

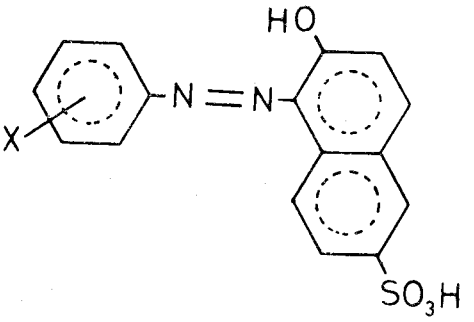
INTRODUCTION

The free electron pairs of suitably disposed oxygen and nitrogen ligand atoms in hydroxy azo dyes coordinate with the metal ion, forming stable five or six membered chelate rings. Absorption spectra studies show a shift in absorption maximum due to the formation of these rings. This change lies within the practical limits reached by change of pH; that is to say that protonation and chelation have the same effect.

Hence, these properties were used to form metal indicators in acid-base determinations. The behaviour of these indicators was studied spectrophotometrically using established different methods[1]

The acid -base properties of arylazo Schaffer acid were investigated in aqueous medium. The pKa values were correlated to molecular structure[2]. The effect of organic solvents of pKa values of some p-substituted phenylazo-Schaffer acid was studied. The results were correlated to substituent effect and solvent polarity[3].

The present investigation is a systematic spectrophotometric study of Ni and Cu ions complexes with some substituted phenylazo-Schaffer acid (I).



x = p-NO_2(a), p – OCH_3 (b) and p-OC_2H_5 (c).

EXPERIMENTAL

The water used was always twice redistilled from all glass equipment. The chemicals were all of highest purity available. The dyes were prepared by coupling the corresponding amines in sodium hydroxide medium[4]. The resulting dyes were recrystallized from the apropriate solvent. The purity of the prepared dyes was confirmed by elemental analysis.

The 0.001 M solutions of Ni^{2+} and Cu^{2+} (BDH, England) were prepared by diluting a previously standardized stock 0.05 M solutions[5].

The 0.001 M solutions of Ia, Ib and Ic were prepared by dissolving the accurate weights of dyes in water.

Solutions containing 1 mg anion or cation for testing the interfering effect were prepared as recommended. The modified Britton and Robinson universal, acetate and hexamine buffer solutions were prepared as mentioned before[6].

RESULTS AND DISCUSSION

The optimum conditions for the spectrophotometric determination of Ni^{2+} and Cu^{2+} using Ia, Ib and Ic as indicators are studied. Measurements have shown that the optimum pH values for developing the red complexes of Ni-Ia and Cu-Ia and the yellow-brown complexes

of Ni-Ib Ni-Ic, Cu-Ib and Cu-Ic are 9 for Ni-Ia, Cu-Ia and Cu-Ib and Cu-Ic and 9.5 for Ni-Ib and Ni-Ic complexes. The Britton universal buffers were the most suitable media. The absorption spectra of Ia, Ib and Ic and their complexes at the recommeneded pH values against water and against ligand show that each complex has one band at longer wavelength than that of the corresponding ligand. Representative curves are shown in Fig (1). The sequence of addition buffer-metal-dye gives best results in the case of Ni-Ic, whereas it has no effect on the formation of Ni-Ia and Ni-Ib complexes. Similarly, the Cu.-Ia complexes demonstrate best behaviour for the sequence dye -buffer-metal, while for Cu-Ib the most favourable is dye -metal-buffer. Experiments on the effect of time showed that all complexes are formed instantaneously and remain stable for at least three hours. then suffer a slight decrease in absorbance; except in the case of Cu-Ia where it remains stable for about 60 minutes after which precipitation starts.

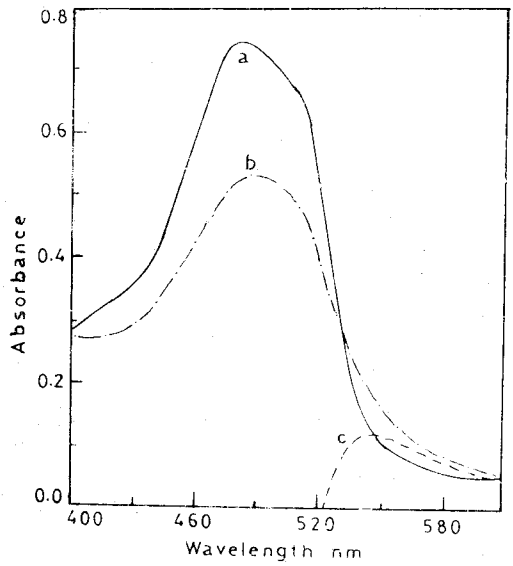


Fig (1) Absorption Spectra of Cu-Ia complex at pH 9.0
a– 3 × 10^{-5} M Ia water as blank
b– 1.5 × 10^{-5} M Cu-Ia (1:2) water as blank
c– b using a as blank.

Investigation of the molecular structure of the complexes in the light of the results obtained by the molar ratio[7] continuous variation[8] and slope ratio methods[9] reveals the formation of 1:2 Ni-Ia; 1:1, 1:2 and 1:3 Ni-Ib and 1:1, 1:2 and 1:4 Ni-Ic; 1:1 and 1:2 Cu-Ia; Cu-Ib and Cu-Ic.

The logarithmic values of the stability constants of the complexes as calculated from the molar ratio and continuous variation methods[7,8] are listed in table (I). The values for the 1:2 complex follow the order Ia $<$ Ic $<$ Ib which is in agreement with the substituent effect and the electron density on the azo linkage. The effect was very clear in case of Ni complexes than in case of Cu-complexes.

Table I

The apparent stability constants of Ni and Cu ions complexes

Complex	Molecular ratio	n	log Bn	Complex	molecular ratio	n	log Bn
Ni-Ia	1 : 2	2	9.76	Cu-Ia	1 : 1	1	7.15
					1 : 2	2	11.261
Ni-Ib	1 : 1	1	5.95				
	1 : 2	2	11.54	Cu-Ib	1 : 2	2	11.79
	1 : 3	3	14.69				
Ni-Ic	1 : 1	1	6.67				
	1 : 2	2	10.77	Cu-Ic	1 : 2	2	11.46
	1 : 4	4	19.92				

A systematic study of the influence of foreign ions can be summarized as follows:

(1) For nickel complexes: Li^+, Na^+, K^+, Rb^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Cd^{2+}, Fe^{2+}, Zn^{2+}, Th^{4+}, Zr^{4+}, Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, PO_4^{3-}, oxalate, tartrate, SO_4^{2-}, acetate and phthalate do not intefere when present in 20 folds the amount of nickel. On the other hand, Tl^+, Mn^{2+} Pb^{2+}, Ba^{2+}, Fe^{3+}, Cu^{2+}, Bi^{3+}, Cr^{3+}, CN^-; benzoate and EDTA interfere.

(2) For copper complexes: Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, Zn^{2+}, Cd^{2+}, $UO^2{}_2^+$, Al^{3+}, Th^{4+}, Zr^{4+}, Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, CH_3COO^-, SO_4^{2-} Oxalate tartrate, citrate and phthalate do not interfere (20 folds), while, Ba^{2+}, Cr^{3+}, Pb^{2+}, Fe^{3+}, Bi^{3+}, Mn^{2+}, Tl^+, Ni^{2+}, EDTA and CDTA interfere. CN^- up to 10 folds does not interfere.

Microdetermination of nickel and copper ions:

(i) Procedure:

On using Ia as the chromophoric indicator, solutions containing up to 47.2 and 51 ug of Ni and Cu respectively are used, in case of Ib, 35. 4 and 58 ug of the two cations respectively are used, while on applying Ic, solutions containing up to 29.5 and 51 ug of these ions are used. Add to each solution 6 ml Britton and Robinson universal buffer of the recommended pH value and 2 ml (10^{-3} M dye), dilute all solution mixtures up to 10 ml with water and then measure their absorbance values at 550 nm for Ni-Ia and Cu-Ia, 350 nm for Ni-Ib and Ni-Ic and 360 nm for Cu-Ib and Cu-Ic complexes against a blank containing the same ingredients except the metal ion. Compute the concentration from standard calibration curve prepared in the same manner.

Table (II) lists the limits of obeyence to Beer's law and molar absorption coefficient (ε, 1 $mole^{-1}$ cm^{-1}). The values of spesific absorptivity (a, ml g^{-1} cm^{-1})[10] and sandell sensitivity (S, ug cm^{-2})[11] are also given, the results indicate the high sensitivity of the methods and its applicability in the micro determination of Cu and Ni ions.

Table II

Nickel and Copper Complexes data.

Ligand	M	λ.nm	up to ppm M	ε*	a	S
Ia	Ni	550	4.70	5.25	0.089	0.0112
Ib		350	3.50	8.26	0.140	0.0071
Ic		350	3.00	8.70	0.148	0.0067
Ia	Cu	550	5.10	11.10	0.175	0.0057
Ib		360	5.80	10.90	0.171	0.0058
Ic		360	5.10	10.90	0.171	0.0058

*: $\varepsilon x10^{-3}$ ($l.mole^{-1}$ cm^{-1})

a: Spesific absorptivity (ml g^{-1} cm^{-1}).

S: Sandell Sensitivity (ug cm^{-2}).

The present method affords a new means for the rapid spectrophotometric microdetermination of Ni and Cu in pure solutions or in the presence of a variety of cations and anions which do not interfere with such determinations with fair accuracy, high precision

and reproducibility. The standard deviation in determining 47.2, 35.4 and 29.5 ug nickel using Ia, Ib and Ic (18 determinations) amounted to 0.0070, 0.0032 and 0.0028 respectively indicating high reproducibility.

(ii) *Spectrophotometric Titration of Ni and Cu with EDTA, using Ia, Ib or Ic as Indicator:*

Each of the above metal ions is determined by direct spectrophotometric titration with EDTA using Ia, Ib and Ic as indicators. The conditions for such determinations are summarized in Table (III). To carry out the titration, prepare a series of solutions containing 2ml 10^{-3} M dye, the metal ion within the optimum concentration range, 6 ml Britton and Robinson universal buffer of the recommended pH value and successive amounts of 0.001 M EDTA, complete with water up to 10 ml and finally measure the absorbance at 550 nm in case of Ni-Ia and Cu-Ia, 350 nm in case of Ni-Ib and Ni-Ic and at 360 nm in case of Cu-Ib and Cu-Ic complexes. Representative titration curves

Table III

Optimum Conditions for the Spectrophotometric Titrations

Metal	Indicator	pH	Optimum concentration range /10 ml (ug)
Ni	Ia	9.0	29.5—47.2
	Ib	9.5	17.7—35.4
	Ic	9.5	17.7—29.5
Cu	Ia	9.0	19.2—51.2
	Ib	9.0	19.2—57.6
	Ic	9.0	19.2—51.2

are shown in Fig (2). All titration curves show a sharp end point intersection. By the aid of the present method Ni^{2+} or Cu^{2+} can be determined accurately.

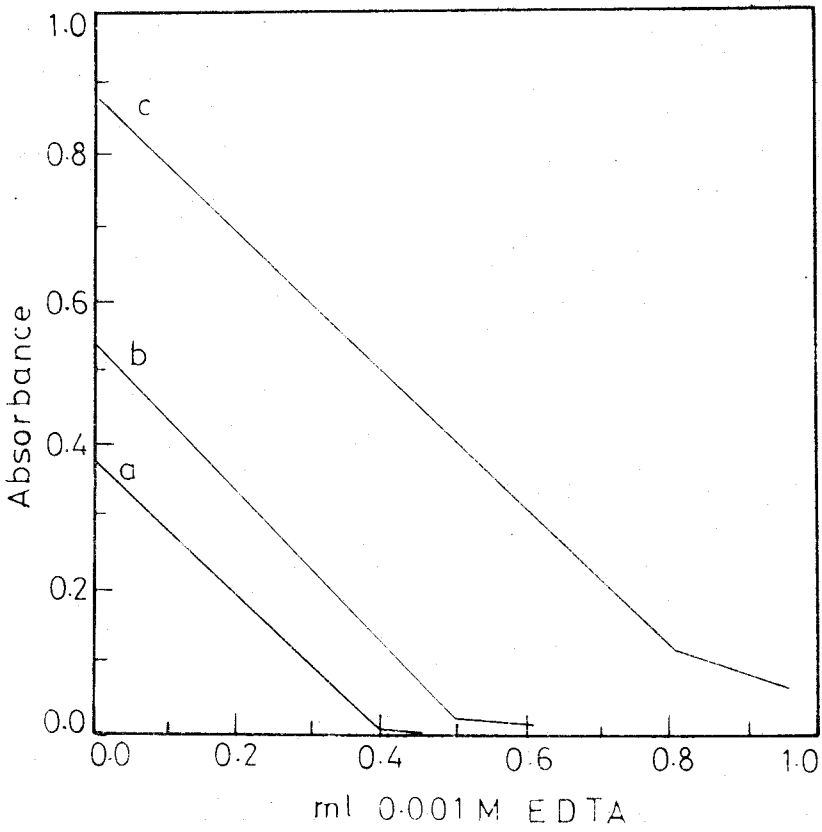


Fig (2) Spectrophotometric tiitration of Cu with EDTA using Ia (a), Ib (b) and Ic(c).

REFERENCES

1. **Szadowski, W.W.J.,** Chem. Stasowana, Ser A8 (3), 295-303 (1964); C.A. 63, 16413 g (1965).

2. **Khalifa, H., Issa, Y.M.** and **Abdel Ghani,** N.T., Rev. Roumain Chimie, 24, 1373 (1979)

3. **El-Ansary, A.I., Issa, Y.M.** and **Abdel-Rhman**, A.I; Ind. Text. J., 111 (1983)

4. **Vogel, A.I.,** "Practical Organic Chemistry" 3rd Ed. Longmans, London (1967).

5. **Welcher, F.J.,** "The Analytical Uses of Ethylene diamine, tetraacetic Acid" D. Van Norstrand Co., Inc., Princeton, N.J. (1965).

6. **Britton, H.T.S.** "Hydrogen Ions" 4th Ed. Chapman and Hall. London (1952).

7. **Yoe, J.H. and Jones, A.L.,** Eng. Chem. Anal., 16, 14 (1944).

8. **Vosburgh, W.C. and Cooper, G.R.:** J. Amer. Chem. Soc., 63, 437 (1941).

9. **Harvey, A.E. and Manning, D.L,:** J. Amer. Chem. Soc., 72, 4488 (1950).

10. **Ayers, G.H., and Narang, B.D.,** Anal. Chim. Acta, 24, 241 (1961)

11. **Sandell, E.B.,** "Colorimetric Determination of Traces of Metals", 3rd. Ed. Interscience, New York (1959).