Complexation Equilibria Between Copper(II) and Thiosalicylic Acid. Spectrophotometric Determination of Copper in Non-Ferrous Alloys

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Summary. The complexation equilibria of Cu(II) with thiosalicylic acid (*TSA*) have been studied spectrophotometrically in aqueous ethanol (17.08 mol% ethanol) at $I = 0.1\,M$ (NaClO$_4$) and $25 \pm 0.1°C$. Analysis of the absorbance *vs.* *pH* graphs afforded the equilibria in solution and the stability constants of the complexes formed. A simple, rapid, and sensitive method for the spectrophotometric determination of trace amounts of copper is proposed. The effect of interference of a large number of foreign ions was studied. The method has been applied successfully to the analysis of some synthetic mixtures and non-ferrous alloys containing copper.

Keywords. Copper(II) determination; Thiosalicylic acid; Spectrophotometry; Complex equilibria; Non-ferrous alloys.

Komplexierungsgleichgewichte zwischen Kupfer(II) und Thiosalicylsäure.
Spektrophotometrische Bestimmung von Kupfer in eisenfreien Legierungen

Zusammenfassung. Die Komplexierungsgleichgewichte zwischen Cu(II) und Thiosalicylsäure (*TSA*) wurden spektrophotometrisch in wäßrigem Ethanol (17.08 mol% Ethanol) bei $I = 0.1\,M$ (NaClO$_4$) und $25 \pm 0.1°C$ untersucht. Analyse der Extinktions-*pH*-Kurven lieferte die Gleichgewichte in Lösung und die Stabilitätskonstanten der gebildeten Komplexe. Eine einfache, schnelle und empfindliche Methode zur Bestimmung von Spurenmengen von Kupfer wird vorgestellt. Der Einfluß einer großen Anzahl von Fremdionen wurde getestet. Die Methode wurde erfolgreich zur Analyse einiger Testmischungen sowie zur Kupferbestimmung in eisenfreien Legierungen eingesetzt.

Introduction

The complex forming ability of thiosalicylic acid (*TSA*) with many metal ions has been the subject of several investigations [1–6]. However, no detailed studies on the complexation equilibria of copper(II) with thiosalicylic acid have been reported.

In the present work, fundamental studies on the complexation equilibria of *TSA* with copper(II) in an ethanol-water mixture containing 17.08 mol% ethanol at an ionic strength of $I = 0.1\,M$ (NaClO$_4$) are presented. The aim of this investigation is to study the equilibria that exist in solution and to determine the basic charac-

teristics of the complexes formed. The optimum conditions favouring the direct spectrophotometric determination of trace amounts of copper(II) in some synthetic samples and non-ferrous alloys are established.

Results and Discussion

Acid-base behaviour of TSA

The acid dissociation constants of TSA in a water-ethanol medium containing 17.08 mol% ethanol have been determined previously [9]. The two acid dissociation constants pK_{a_1} and pK_{a_2} corresponding to the deprotonation of the carboxyl and sulfydryl groups of TSA are 4.65 and 9.40, respectively.

Complexation equilibria of Cu(II) with TSA

The complexation equilibria of Cu(II) with TSA were investigated at different pH values, in equimolar mixtures, and in solutions containing an excess of reagent or metal ion (Fig. 1). The solution spectra reflect unambiguously the formation of two complexed species in the pH range of 1.0–5.5, depending on the acidity of the medium and the concentration of the components.

It is worth mentioning that the solution spectra of (TSA) exhibit an absorption band at 355 nm within this pH range. The spectra of solutions containing an excess of metal ion and that of equimolar mixtures are analogous and exibit an absorption band with λ_{max} at 340 nm (pH 1.0–5.5). In the presence of an excess of TSA, the solution spectra display two absorption bands with λ_{max} at 340 nm (pH 3.0–5.5)
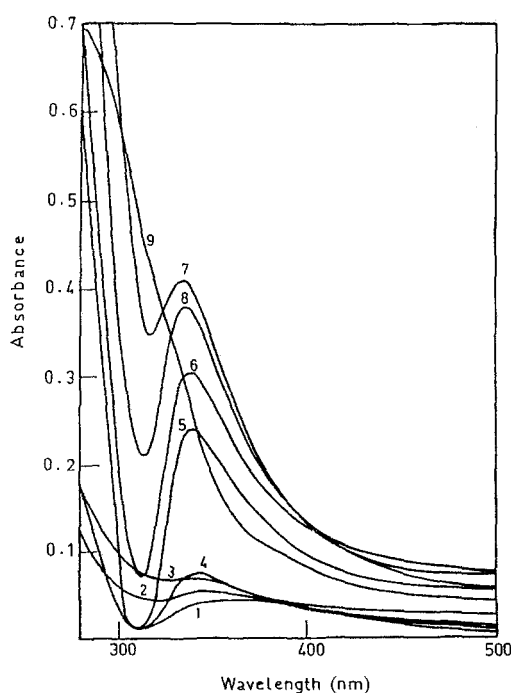

Fig. 1. Absorption spectra of Cu(II)-TSA complexes; $C_L = 1.25 \times 10^{-4} M$, $C_M = 5 \times 10^{-4} M$, $I = 0.1 M$ NaClO$_4$, 17.08 mol% ethanol; pH: (1) 1.4, (2) 1.8, (3) 2.3, (4) 3.1, (5) 4.1, (6) 5.0, (7) 5.5, (8) 6.5, (9) 7.0
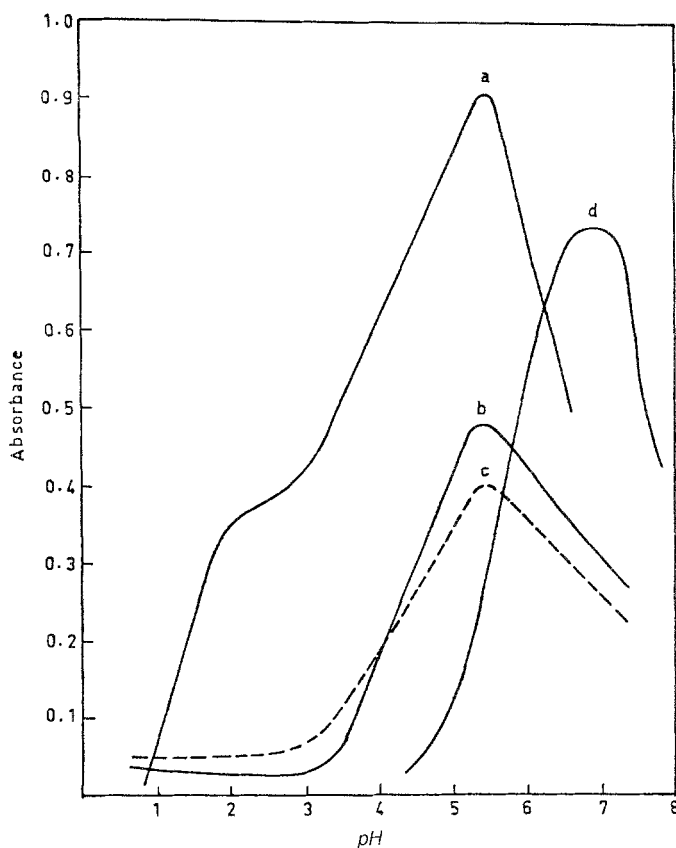
Fig. 2. Absorbance vs. pH graphs for Cu(II)-TSA (curves a, b, and c) of various component ratios together with an absorbance vs. pH graph for equimolar solutions of Cu-SA complexes (curve d) in 17.08 mol% ethanol, $I = 0.1$ M NaClO$_4$ (a) $C_L = 7.5 \times 10^{-4}M, C_M = 2.5 \times 10^{-4}M$; (b) $C_L = C_M = 2.5 \times 10^{-4}M$; (c) $C_L = 1.25 \times 10^{-4}M$, $C_M = 5 \times 10^{-4}M, \lambda = 340$ nm; (d) $C_L = C_M = 5 \times 10^{-4}$ M, $\lambda = 320$ nm

and 300 nm (pH 1.0–2.5). The variation of absorbance with pH for the above solutions shows the range of formation and the existence of the complexation equilibria within the pH range studied (Fig. 2).
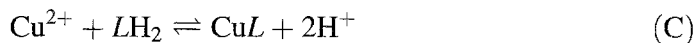
The absorbance vs. pH graph for solutions containing excess ligand at $\lambda = 340$ nm reveal the existence of two basic equilibria within the pH range of 1.0–5.5. The first ascending part of these graphs is attained in the pH range of 1.0–2.5 as a result of the interaction of Cu(II) with the LH$_2$ form of the reagent according to the following equilibrium:

$$Cu^{2+} + LH_2 \rightleftharpoons CuLH^+ + H^+ \qquad (A)$$
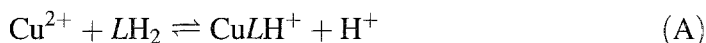
The second ascending part is attained in the pH range of 3.0–5.5 and is presumably due to the transition to a species with less protons according to the following equilibrium:

$$CuLH^+ \rightleftharpoons CuL + H^+ \qquad (B)$$

For equimolar solutions or solutions containing an excess of metal ions, the absorbance vs. pH graphs show only one inflection in the pH range of 1.0–5.5, corresponding to a single chelate equilibrium according to equilibrium (C).

$$Cu^{2+} + LH_2 \rightleftharpoons CuL + 2H^+ \qquad (C)$$

Above *pH* 5.5, the absorbance shows an apparent decrease owing to the hydrolysis of the complex formed. The absorbance *vs. pH* graphs for solutions with an excess of one component or equimolar solutions were interpreted by direct graphical and logarithmic analysis using transformations derived earlier by *Sommer et al.* [10–13].

For the logarithmic analysis of the first ascending part of the graphs for solutions containing an excess of *TSA* in the *pH* range of 1.0–2.5 (equilibrium (A)), equation (1) with $n = q = 1$ and $K = K_{1H}^*$ is valid.

$$\log\left[\Delta A/(\varepsilon_{1H}C_M - \Delta A)\right] = q\,pH + n\log C_L + \log K_{1H}^* \tag{1}$$

The second rising part of the graphs for solutions with excess reagent indicate unambiguously the deprotonation of the $[CuLH^+]$ complex. In the *pH* range of 3.0–5.5, equation (2) is confirmed for deprotonation of the $[CuLH^+]$ chelate equilibrium (B), and the slope q of the logarithmic equation equals unity.

$$\log\left[(\Delta A - \varepsilon_{1H}C_L)/(\varepsilon_1 C_L - \Delta A)\right] = q\,pH + \log K_{K_{a_1}} \tag{2}$$

Logarithmic analysis for equimolar solutions confirm the existence of equilibrium (C), and the following equation is valid:

$$\log\left[\Delta A/\varepsilon_1 C_L - \Delta A)^2\right] = q\,pH + \log K_1^* - \log(\varepsilon_1 - \varepsilon_L) \tag{3}$$

In this study, negative results were obtained for equilibrium (C) using equation (3) for equimolar solutions. On the other hand, equation (4) is valid for equilibrium (C) in solutions with an excess of metal ions.

$$\log\left[\Delta A/(\varepsilon_1 C_L - \Delta A)\right] = q\,pH + \log C_M + \log K_1^* \tag{4}$$

In the above relations, C_L is the total concentration of the ligand, C_M is the total concentration of the metal ion, ΔA is the difference in the overall absorbance and the absorbance of the reagent blank, ε_{1H} and ε_1 are the molar absorptivities of $CuLH^+$ and CuL complexes, q is the number of protons liberated during the formation of a single complex species, n is the number of ligands, K_{a_1} and K_{a_2} are the acid dissociation constants of the ligand $([LH^-][H^+]/[LH_2]$ and $[L^{2-}][H^+]/[LH^-])$, and K_{1H}^*, K_{k_a}, and K_1^* are the equilibrium constants of the corresponding complexation reactions.

The graphical and logarithmic analysis of the first part of the absorbance *vs. pH* graphs in solutions with an excess of ligand in the *pH* range of 1.0–2.5 did not prove the formation of CuL chelate according to equilibrium (C). On the other hand, a complex equilibrium involving deprotonation of the $[CuLH^+]$ complex in the *pH* range of 3.0–5.5 with release of one proton in accordance with equilibrium (A) was confirmed.

For equimolar solutions or solutions containing an excess metal ions, a graphical analysis of the ascending branch of the absorbance *vs. pH* graphs indicates the dissociation of two protons, and the formation of a CuL complex according to equation (C) is confirmed.

The calculated values of molar absorptivities, equilibrium constants, and stability constants of $[CuLH^+]$ and $[CuL]$ chelates are given in Table 1.

The stoichiometry of the Cu (II)-*TSA* complex formed was determined by the method of continuous variation [18, 19]. In solutions with $C_0 = C_M + C_L =$

Table 1. Mean values of equilibrium constants ($\log K^*$) and stability constants ($\log \beta$) of Cu(II) complexes with TSA; values are taken as averages of various component concentrations ($I = 0.1\,M$ $NaClO_4$, $25 \pm 0.1°C$, $17.08\,mol\%$ ethanol

Equilibrium[a]	Constant	log(Constant)
$[MLH][H]/[M][LH_2]$	K^*_{1H}	2.30 ± 0.01^b
$[ML][H]/[MLH]$	$K^*_{K_{a_1}}$	-1.52 ± 0.02^b
$[ML][H]^2/[M][LH_2]$	K^*_1	1.62 ± 0.02^c
		1.59 ± 0.01^d
$[MLH]/[M][LH]$	β_{1H}	6.92^e
$[ML]/[M][L]$	β_1	11.02^f

[a] Charges are omitted; [b] from the absorbance vs. pH graphs for solutions with an excess of ligand; [c] from the absorbance vs. pH graphs for solutions of equimolar concentrations; [d] from the absorbance vs. pH graphs for solutions with an excess of metal; [e] $\log \beta_{1H} = \log K^*_{1H} + pK_{a1}$; [f] $\log \beta_1 = \log K^*_1 + pK_{a_2}$

$5 \times 10^{-4}\,M$ at pH 4.5, the maximum of the *Job* plot corresponds to a component ratio of 1:1. The stoichiometry of the complex was also verified by applying the molar ratio method [20].

It would be interesting to compare the stability constants of the monoligated Cu-*TSA* complexes with those of equimolar Cu-*SA* complexes (*SA*: salicylic acid). An attempt was made to establish the conditions favouring the formation of Cu(II)-*SA* complexes at different *pH*s in equimolar solutions and to evaluate their stability constants under identical conditions. In Fig. 2, the absorbance vs. *pH* graphs for equimolar solutions of Cu(II)-*SA* complexes show only one inflection in the *pH* range of 4.5–6.5, corresponding to a single chelate equilibrium. The acidity constants of the ligands together with the calculated values of the stability constants ($\log \beta$) of the corresponding binary complexes (Cu*L*, $L = SA$ or *TSA*) are given in Table 2.

From the results of the present study and from those of previous investigations on solution equilibria of salicylic acid or its derivatives with some metal ions [14, 15] it may be stated that

a) both ligands form only monoligated complexes with copper(II). The proton released as a result of complexation with copper(II) and formation of the mono-ligand complex Cu*L* is the hydroxyl proton of *SA* or the sulfydryl proton of *TSA*, respectively.

b) a comparison of the values of the stability constants ($\log \beta$) indicates that the stability order is $SA > TSA$. This is in accordance with the basicities of the

Table 2. Acidity constants of the ligands and stability constants of their monoligated Cu complexes ($17.08\,mol\%$ ethanol, $I = 0.1\,M$ $NaClO_4$, $25 \pm 0.1°C$)

Ligand	pK_1	pK_2	$\log \beta$
SA	3.42^a	13.86_b	11.46
TSA	4.65	9.40	11.02

[a] Ref. [15]; [b] Ref. [23]

ligands [16]. On the other hand, a roughly linear relationship could be obtained between the values of the stability constants of these complexes and the second dissociation constant of their ligands [17]. The stability increases with increasing second dissociation constant of the ligand.

Beer's law, sensitivity, and reproducibility

The complex is quite stable, and the absorbance remains unchanged for at least 24 hours. At the optimum conditions (cf. Experimental), Beer's law is obeyed over a range of $0.0-15.0\,\mu g\cdot ml^{-1}$ of copper. The optimum range for accurate determinations as evaluated from a Ringbom plot [21] is $2.0-10.0\,\mu g\cdot ml^{-1}$ of copper. The molar absorptivity coefficient and Sandell's sensitivity [22] are $3.0 \times 10^4\,l\cdot mol^{-1}\cdot cm^{-1}$ and $2.25 \times 10^{-3}\,\mu g\cdot cm^{-2}$, respectively. The reproducibility of the method was checked by testing two series of solutions containing copper concentrations of 4.0 and $8.0\,\mu g\cdot ml^{-1}$. The relative standard deviation was found to be less than 1%.

Effects of foreign ions and masking agents

The effect of several ions at levels of 1.0–20.0 mg per 25 ml on the determination of 0.15 mg of Cu(II) by the given procedure was examined. The effect of each ion was tested individually. The tolerance criterion for a given ion was taken as the deviation of the absorbance value by more than 2% from the value expected for copper alone. There was no interference from 20 mg of any of the alkali metal or the alkaline earth ions, $Al^{3+}, V^{+5}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mo^{6+}, Cd^{2+}, W^{6+}, Y^{3+}, La^{3+}, Hg^{2+}, Cl^-, Br^-, F^-, NO_3^-, SO_4^{2-}, SO_3^{2-}, PO_4^{3-}, B_4O_7^{2-}$, and acetate ions; 15 mg of $Ag^+, Mg^{2+}, Pb^{2+}, Pd^{2+}, Pt^{2+}$, and Sn^{4+}; and 1mg of Th^{4+}, U^{6+}, and Fe^{3+}. Using the present experimental conditions, it was observed that Cu(II) could not be determined in the presence of EDTA or CN^-. Accordingly, the above reagents could not be used as masking agents. Interference caused by higher concentrations of Fe^{3+}, Th^{4+}, or U^{6+} up to ~ 6 mg per 25 ml could be eliminated by adding ammonium fluoride (ca. 100 fold excess) as masking agent.

Applications

The proposed method is a direct one as it involves no preliminary separation. The method has been successfully applied to the direct determination of copper in some synthetic samples and a number of non-ferrous alloys containing copper. Tables 3 and 4 report the composition of the samples, and the results obtained show that the method has a high degree of accuracy.

Experimental

Chemicals and solutions

Analytical grade reagents and deionized water were used throughout the present study. A stock solution $(5 \times 10^{-3}\,M)$ of thiosalicyclic acid (TSA) was prepared by dissolving the accurately weighed amount of the reagent in pure ethanol. A stock solution of copper perchlorate $(5 \times 10^{-3}\,M)$

Table 3. Determination of Cu(II) in synthetic samples[a]

Composition of the synthetic sample (µg/25 ml)	Cu(µg/25 ml)	
	Taken	Found
Mn(II)900, Al(III)600, Ni(II)600	150.00	149.96
	100.00	99.97
Ni(II)50, Mn(II)50, Sn(II)50, Co(II)100	150.00	149.97
	100.00	99.98
Zn(II)500, Pb(II)50, Fe(III)50	100.00	149.98
	60.00	59.95
Al(III)100, Ag(I)50, Mg(II)50	100.00	99.95
	60.00	59.97
Co(II)50, Ni(II)100, Mn(II)50	100.00	99.96
	60.00	59.95

[a] Triplicate analysis

Table 4. Determination of Cu in standard samples[a]

Sample	Composition	Copper content %	
		Reported	Found
Gun-metal alloy	Zn 4.4, Sn 5.3, Pb 6.3	83.10	82.98
Nickel-zinc alloy	Ni 18.2, Mn 0.27, Bi 0.6, Zn 25.8	55.10	54.76

[a] Triplicate analysis

was prepared from copper carbonate and perchloric acid and standardized by conventional methods [7]. A carbonate free sodium hydroxide solution was prepared and standardized by titrating with potassium hydrogen phthalate. The working solutions were prepared by accurate dilution.

The pH of solutions investigated was adjusted by addition of either dilute perchloric acid or dilute solium hydroxide solution. The ionic strength of the solutions was kept constant at $I = 0.1 M$ (NaClO$_4$). Solutions of diverse ions used for interference studies were prepared using Analar products of nitrate, acetate, or chlorides of the metal ions and potassium or sodium salts of the anions to be tested.

Apparatus

The absorption spectra of the solutions were recorded on a Perkin-Elmer (Model Lambda 3B) spectrophotometer in the wavelength range of 200–500 nm using 1 cm matched stoppered quartz cells. The pH measurements were carried out using a Radiometer pH-meter (Model M63). The pH meter was calibrated regularly before use with standard buffer solutions. All spectrophotometric measurements were performed in a water-ethanol medium containing 17.08 mol% ethanol at $25 \pm 0.1°C$. The pH readings were corrected as described elsewhere [8].

Spectrophotometric determination of copper

Into a 25.0 ml volumetric flask, a suitable aliquot of sample solution containing 75–375 μg of copper(II), 2.5 ml of 1.0 M NaClO$_4$, and the necessary amount of ethanol were transferred. After adjusting the pH to 4.0, 7.5 ml of 2.5 × 10^{-3} M TSA were added. The resulting solution was diluted to the mark with deionized water, and the absorbance was measured at 340 nm against a similarly prepared blank of the same pH.

Determination of copper in a gun metal sample and in Ni-Zn alloys

The samples (100–150 mg), were accurately weighed and treated with 3.0 ml of concentrated HNO$_3$ (gun metal) or with the minimum amount of *aqua regia* (Ni-Zn alloys), heated until dissolved, and evaporated almost to dryness. The residue was redissolved in 4.0 ml concentrated H$_2$SO$_4$ (gun metal) or 4.0–6.0 ml concentrated HCl (Ni-Zn alloy), respectively, and made up to 50.0 ml in a calibrated flask with deionized water.

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