

PHYSICOCHEMICAL STUDIES OF NICKEL AND COPPER COMPLEXES WITH TAR AND SIMULTANEOUS DETERMINATION OF THE METAL IONS IN MIXTURES BY DERIVATIVE SPECTROPHOTOMETRY

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Abstract

Nickel(II) and Copper(II) chelates of 4-(2-thiazolylazo)resorcinol (TAR) were reported. The dissociation constants of the ligand and the stability constants of the metal complexes were calculated pH-metrically and spectrophotometrically at 25 °C, in 50% (v/v) ethanol and 0.1 M ionic strength. The effects of an acid or a base on the visible absorption behaviour of the ligand and complexes has been investigated. Nickel and copper react with 4-(2-thiazolylazo)resorcinol (TAR) to form a binary complexes. The equilibria occurring in solution were established and the basic characteristics of the complexes formed were determined. The complexation reaction in the systems investigated were demonstrated and characterized using graphical logarithmic analysis of the absorbance versus pH graph. The composition of the formed complexes with the reagent have been determined. The molar absorptivity of the binary system is investigated. The binary systems obeyed Beer's law up to 0.23 and 0.25 µg/ml for Ni²⁺ and Cu²⁺ respectively. A simple and highly sensitive procedure for spectrophotometric determination of Ni²⁺ and Cu²⁺ has been developed. A method for the simultaneous determination of nickel and copper in mixtures by first-derivative spectrophotometry is described. Zero-crossing measurement technique is found suitable for the simultaneous determination of the metal ions. The method has been applied to direct determination of copper and nickel in some synthetic mixtures without any separation.

Keywords: Nickel(II) and Copper(II); TAR; stability constants; potentiometric titrations; spectrophotometry; simultaneous determination of copper and nickel

1. Introduction

4-(2-thiazolylazo)resorcinol (TAR) is the most widely used reagent in the spectrophotometric determination of metal ions due to their strong ability to form complexes with a variety of metal ions [1–3]. TAR has been frequently used for the determination of some transition and rare earth elements by reversed-phase capillary high performance liquid chromatography [4]. Optical, magnetic properties and thermal analysis of some transition metal complexes of TAR were reported [5,6]. The thiazolylazo dyes and their application, in which the heterocyclic atom involved in coordination with metal ion, in analytical chemistry have been reviewed up to the end of 1967 [7] and 2007 [8]. The dissociation constant of one proton of the two hydroxyl groups of TAR was calculated by Chalmers [9]. Derivative technique is becoming increasingly interesting popular in analytical spectrophotometry, due to it

offers a convenient solution to the overlapping of the spectra [10,11]. In this paper first-derivative spectrophotometry is applied for the simultaneous determination of copper and nickel in mixtures through the formation of the complexes using 4-(2-thiazolylazo)resorcinol (TAR) as the reagent in 50% (v/v) ethanol. The zero crossing method is evidently the most appropriate for resolving mixtures of these compounds.

2. Experimental

2.1. Apparatus and reagents. Absorption spectra were recorded on a Perkin-Elmer (Lambda 35) computerized spectrophotometer equipped with 1 cm matched quartz cells. pH measurements were carried out using a Corning 215 pH meter with a combined glass electrode. The glass electrode was calibrated before each titration with two Merck standard buffer solutions, first with the pH 7.0 followed by a pH 4.0 at 25 °C by coupling the titration cell with a thermostatic bath set at this temperature. All chemicals used of analytical grade and were purchased from Sigma-Aldrich Chemicals Co., (USA). Stock solutions (=0.001 M) of the metal ions were prepared by dissolving requisite amounts of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2$ in doubly distilled water and standardized compleximetrically [12]. The working solutions (2.5×10^{-3} M) were prepared by accurate dilution. All ligand solutions of initial concentration $C_L = 2.5 \times 10^{-3}$ M were prepared by direct weighing and dissolution in pure ethanol before use. The acidity of solutions investigated was adjusted by the addition of either HClO_4 or NaOH solution. The ionic strength was maintained constant at $I = 0.1$ M (NaClO_4).

3. Results and discussion

3.1. Potentiometric titrations. The acid-base equilibria of the ligand TAR have been investigated potentiometrically. The pH- titration technique of Irving and Rossotti [13] was employed in this study. The ligand TAR has been defined as H_2L , with two protonation sites of the phenolic groups. For samples the respective pK_a 's are 10.12 of the ortho phenolic group and 6.85 of the para phenolic group [9] in 50% (v/v) ethanol -water medium, ionic strength [$I = 0.1$ M (NaClO_4)], temp. = 25 °C. Under identical conditions the formation of binary complexes of Ni^{2+} and Cu^{2+} with TAR in 1:1, 1:2 molar ratio were studied by potentiometric pH titration. Figs. 1,2 show the titration curves for TAR, 1:1 and 1:2 copper and nickel :TAR solution. The major inflection in 1:1 and 1:2 of metal ion : TAR titrations appeared at 1.0 and 2.0 equivalents of titrant for Ni and Cu respectively. Analysis of the potentiometric data by the SUPERQUAD [14] computer program allowed the determination of the main complex species in equilibrium. Potentiometric determination of stoichiometry of the binary complexes proved that the ligand TAR form 1 : 1 M : L with Ni^{2+} and 1 : 2 Cu^{2+} : L binary complex. The complex-ligand formation curve was obtained by plotting the degree of formation complex (\bar{n}) against the negative logarithm of the concentration of non protonated ligand (pL). The \bar{n} and pL values were calculated

at different values of the pH range study. From the formation curves the stepwise stability constants of binary chelates were determined. The values of the overall formation constants of the complexes are given in Table 1. The acid-base equilibria of TAR under the experimental conditions in the pH range investigated $\geq 2.9 \leq 11.7$.

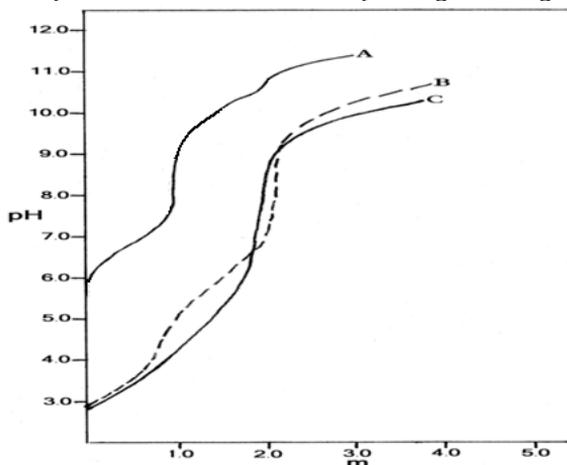


Fig. (1). Potentiometric titration curves of Binary systems of Cu^{2+} with TAR [m = moles of alkali per mole of metal ion], in 50% (V/V) ethanol, $I = 0.1 \text{ M}$ (NaClO_4) and at 25°C . A) deprotonated TAR, B) 1:2 Cu^{2+} -TAR and C) 1:1 Cu^{2+} -TAR.

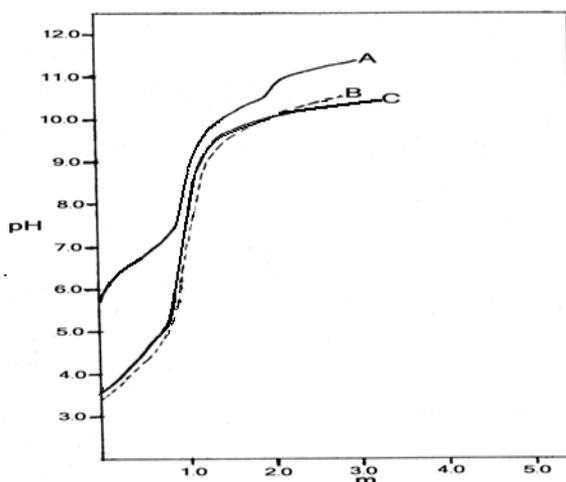
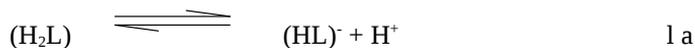


Fig. (2). Potentiometric titration curves of Binary systems of Ni^{2+} with TAR [m = moles of alkali per mole of metal ion], in 50% (V/V) ethanol, $I = 0.1 \text{ M}$ NaClO_4 and at 25°C . A) deprotonated TAR, B) 1:2 Ni^{2+} -TAR and C) 1:1 Ni^{2+} -TAR.

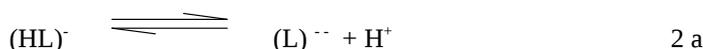
Table (1). logarithms of stability constants of Ni^{II} and Cu^{II} Complexes containing 1:2 ratio of metal ion with [TAR] [Temp. 25°C , $I=0.1 \text{ M}$ (NaClO_4) , pK_1 and pK_2 for (TAR) are 6.85 and 10.12 respectively.

Metal ion	$\log k_{ML}^M$	$\log k_{ML_2}^{ML}$	$\log \beta_{ML_2}^{ML}$
Ni ^{II}	10.5	–	10.5
Cu ^{II}	10.8	9.55	20.35

The monoanionic species of TAR (HL⁻) undergoes ionization on increasing the pH of solution according to the following protonation equilibria:



$$K \frac{H}{(H_2L)} = \frac{[(HL)^-][H^+]}{[(H_2L)]} \quad 1 \text{ b}$$



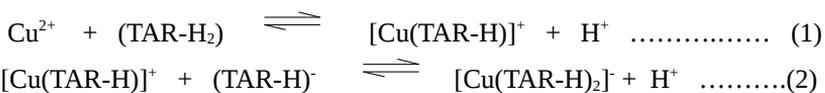
$$K \frac{H}{(HL)^-} = \frac{[(L)^{2-}] + [H^+]}{[(HL)^-]} \quad 2 \text{ b}$$

From the formation curves the stepwise stability constants of binary chelates were determined and are listed in Table 1. Copper complex is the most stable.

3. 2. Absorption spectra

3. 2. 1. *Complexation equilibria of Ni²⁺ and Cu²⁺ with TAR.* The effect of acid and base on the absorption of TAR solutions was investigated and the results are shown in Fig. 3. The absorption spectra of TAR and its Ni²⁺ and Cu²⁺ complexes measured under the same conditions used for the potentiometric measurements. The acid-base properties of TAR in ethanol-water mixtures containing 50% (v/v) ethanol and at pH 4-11, TAR exists in four different forms (LH₃⁺, LH₂, LH⁻, L²⁻), exhibiting absorption maxima at 438, 448, 475 and 490 nm respectively. The pH dependence of the absorbance at an ionic strength of 0.1 mol l⁻¹ (NaClO₄), measured at various wavelengths, indicates a gradual association of proton with heterocyclic thiazole ring at pH < 4.5. The absorption band at 448 nm is caused by the non-ionized species of the reagent (LH₂) and disappears completely at pH > 6. At a pH of approximately 6.1, the spectrum of TAR reveals an absorption band at 475 nm by the mono-ionized form (LH⁻). This band shifted to longer wavelengths on increasing the pH values of the solution medium. The absorbance versus pH graphs were interpreted according to the relationship in literature [15]. The pK values were calculated from the variation of the absorbance with pH by Phillips and Merrit [16] and Sommer [17]. The results show that TAR has two dissociation constants of the phenolic groups, the first ionization is relatively strong and is attributed to para phenolic group, the second to ortho phenolic group respectively. The solution

spectra of the reagent display a symmetrical and medium intense band at approximately 490 nm and pH=11 which corresponding to the dianionic form (L^{2-}). The variation of absorbance with pH at 448 and 490 nm reveals the existence of two acid-base equilibria in solutions of TAR (LH_2) within the pH range studied. These equilibria can be represented by equations (1a) and (2a). The final results for pK values are the average of six pairs of independent titrations. The mean pK_a values (equilibrium constants between ligand species) of the reagent are found to be $pK_{a1}(LH_2, LH^-) = 6.85 \pm 0.2$ and $pK_{a2}(LH^-, L^{2-}) = 10.12 \pm 0.02$. The solution equilibria and stability of the binary Ni^{2+} and Cu^{2+} complexes containing TAR in a 1:1 molar ratio were investigated spectrophotometrically. The spectra of Ni^{2+} and Cu^{2+} with TAR binary complex with the reagent as reference are characterized by an absorption maxima at 528 and 524 nm, in the pH range (3.5–8.5) and (3–7.5) respectively. Absorption spectral data provide evidence for the formation of Ni^{2+} and Cu^{2+} complexes. The complexation equilibria of Ni^{2+} and Cu^{2+} with TAR were studied in solutions in the pH range 3.0 - 8.5. The solution spectra were recorded in equimolar solutions and in solutions containing an excess of the reagent or the metal ions. The absorption spectra reflect the formation of one complex species and the existence of chelate equilibrium in the studying pH range. The absorption spectra for equimolar solutions and those containing a preponderance of M^{II} are analogous and exhibit an absorption band at 528 nm and 524 nm for Ni^{2+} and Cu^{2+} respectively in the pH range 3.8 – 7.5. The absorption bands characterizing the Ni^{2+} and Cu^{2+} complex species at pH 4.3 are shown in Fig. 4. The absorbance versus pH graphs for Ni-TAR and Cu-TAR (Fig. 5 (A,B)) were interpreted using relations derived by Sommer et al [18, 19]. The absorbance vs. pH graphs were analyzed graphically as described previously [20]. As shown in Fig. 5 (B), two complexation equilibria established in solutions of the complex Cu-TAR species within the pH range studied for Cu-TAR complex. The first complexation equilibrium is as a result of complexation of Cu^{2+} with the LH_2 form of the ligand. The second rising part of these graphs is assumed to be due to a stepwise complex transition with further ligand species in monoanionic form coordinated by considering values of the acid-dissociation constants for TAR. The direct and logarithmic analysis of the two rising parts of the absorbance-pH graphs were performed assuming the following equations:

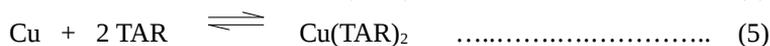


All the absorbance versus pH graphs at various wavelengths shows a rapid decrease in absorbance above pH 6.2 for Cu-TAR and at pH 6.5 for Ni-TAR complex owing to the hydrolysis of the complexed ligand. The stability constants of the complexes (Eqs. 3-5) were determined and agree well with potentiometric data. The titrations were carried out at four TAR/ M^{II} ratios. The ligand/metal ratio was varied from 4:1 to 1:1. The final results given for the overall stability constant (see

Table 1) is always the averages of at least six independent pairs of titrations. The data obtained for each method, estimation of the acidity constants of TAR and the complex formation constants were determined using the same program [14]. The program has been used to calculate acidity constants in systems previously studied [21-23]. For solution containing Ni-TAR complex the absorbance versus pH graph (Fig. 5 (A)) indicates the presence of one system only complex equilibria at wavelength 528 nm. The formation constant for the following equilibria in binary systems containing Ni-TAR was calculated considering the relevant data or the acid dissociation constants and the cumulative binary constants.



The stepwise formation constants for the following equilibria in binary systems containing Cu-TAR:



3. 2. 2. *The stoichiometry of the complexes.* Job's method of continuous variation [24,25] was applied to establish the composition of the Ni²⁺ and Cu²⁺ with TAR binary complex at pH 5.2. The mole fractions of the components were varied continuously, keeping their component in a large excess for all solutions in the series. A series of the solutions were prepared by mixing isomolar solutions of Ni²⁺ and Cu²⁺ with TAR in varying proportions while keeping the total concentration constant 2.5×10⁻⁴ M . The results confirmed the formation of complex species having the stoichiometric ratio 1:1 for Ni²⁺ but form 1:2 for Cu- TAR binary complexes. The stoichiometry of the binary complex was also determined by applying the molar ratio method [26].

3. 2. 3. *Effect of diverse ions and masking agents.* The effect of diverse ions on the determination of M²⁺ as a binary complex was studied by a known quantity of the desired ion to a solution containing 0.05 mg of M²⁺ which was determined by the procedure described above. The determination of M²⁺ as a binary complex can not performed in the presence of 15 mg of Li⁺, Na⁺, k⁺, Ca⁺, Mg²⁺, Sr²⁺, Ba²⁺, Sn²⁺, Pb²⁺, As³⁺, La³⁺, SO₄²⁻, NO₃⁻, ClO₄⁻, B₂O₇²⁻, Cl⁻, Br⁻, F⁻, acetate, tartarate, and citrate. The determination of M²⁺ was not possible in the presence of Cr³⁺, Mn²⁺, Co²⁺, Cd²⁺, Hg²⁺, Fe³⁺, Th⁴⁺, and U⁶⁺ (8 mg). Under our experimental conditions, it was observed that could be determined in the presence of appreciable amounts of cyanide or fluoride ions (~ 6 fold excess) as a masking agent. The tolerance criterion for a given ion was taken as the deviation of the absorbance value by more than ± 3% from the value expected for M²⁺ alone.

3. 2. 4. *Calibration Graph and reproducibility.* The binary system obeyed beer's law up to 0.23, 0.24 and 0.25 µg/ml of Ni²⁺ and Cu²⁺ respectively. The molar absorptivity of binary complexes at λ_{max} = 528 and 524 nm is 1.56×10³ and 2.28×10³

$l \text{ mol}^{-1} \text{ cm}^{-1}$ respectively. The sensitivity of the reaction was calculated according to sandell [27] and was found in the range $3.8 - 9.3 \times 10^{-4} \text{ ng cm}^2$ of Ni^{2+} and Cu^{2+} . The reproducibility of the method was checked by means of two series of solutions having Ni^{2+} and Cu^{2+} concentration of 3.0 and 5.0 μg per 10 ml. The relative standard deviation obtained was found in the range 0.04 - 0.06.

3. 2. 5. Simultaneous Determination of Nickel and Copper with TAR in mixtures.

Figure 4 shows the zero-order absorption spectra of Cu^{2+} -TAR (curve a), with a maximum absorption at 524 nm and Ni^{2+} -TAR (curve b), with a maximum absorption at 528 nm. The total absorption spectrum of a mixture is represented in curve c. Because of the large overlap of the spectra of the two complexes, the determination of nickel and zinc in their mixture by normal spectrophotometry is frequently difficult. This disadvantage has been overcome by using derivative spectrophotometry [28]. The first-order derivative spectra of two sets of solutions, one containing an increasing amount of Ni^{2+} or Cu^{2+} and each containing fixed amounts of TAR. Fig (6) shows the first-derivative spectra of Cu^{2+} -TAR (curve a) and Ni^{2+} -TAR (curve b) and the mixture of both of them (curve c). Fig. (7) shows a series of first-derivative spectra of mixtures of 15.88 $\mu\text{g ml}^{-1}$ of Cu^{2+} -TAR and increasing concentrations of Ni^{2+} -TAR from 1.47 to 11.73 $\mu\text{g ml}^{-1}$. The first derivative spectra gave results of high accuracy and low detection limits. Fig. (8) shows a series of first-derivative spectra of mixtures of 14.67 $\mu\text{g ml}^{-1}$ of Ni^{2+} -TAR plus increasing the concentration of Cu^{2+} -TAR from 1.59 to 12.7 $\mu\text{g ml}^{-1}$. The derivative spectrum was recorded in the range 440-650 nm against a reagent blank. The amplitude value of the first-derivative signal of the mixture was measured at 528 nm (zero-crossing point of Ni complex) and the absolute value of the second-derivative was determined at 524 nm (zero-crossing point of Cu complex). Measurement made at the zero-crossing of the derivative spectra of one of the two components would be a function only of the concentration of the other component. The calibration graphs by the recommended procedure are linear over the ranges 1.47 to 11.73 $\mu\text{g/ml}$ of nickel in the presence of 15.88 $\mu\text{g/ml}$ of copper and 1.59 to 12.7 $\mu\text{g/ml}$ of copper in the presence of 14.67 $\mu\text{g/ml}$ of nickel (Figs. 7,8). In order to test the accuracy and precision of the method, five successive measurements were carried out with the standard solution containing 2.7 $\mu\text{g/ml}$ and 4.0 $\mu\text{g/ml}$ of any metal ion.

3. 2. 6. Calibration graphs and statistical treatment of results.

The amplitude of the derivative signal of the mixture, made at the zero-crossing of the derivative spectrum of one of the two components, is a function of the concentration. The recovery study conducted by the absorbance of the first and second order derivative spectrophotometric method. Calibration graphs for the determination of nickel and copper, prepared according to the data taken from Figs. 7,8 (zero-crossing method) are straight lines in the range 1 - 13 $\mu\text{g/ml}$ of Ni^{II} or Cu^{II} as metal -TAR complex in solution. The heights h_1 and h_2 in the first- derivative spectra of mixtures are proportional to Ni and Cu concentrations, respectively. Regression equations were

calculated as reported in literature [29], regression coefficient = 0.9999. It can be seen that the zero-crossing method is superior as far as accuracy is concerned, especially when minor amounts of copper in mixtures with the excess of nickel are determined. In order to test the validity of the method, several synthetic mixtures of copper were prepared and tested between 0.1 and 10 mg L⁻¹ for copper and nickel in the complex mixture. Also, the high values of correlation coefficients (99.93%) and the intercepts on the axis (close to zero) indicate the good linearity of all the calibration graphs. The relative standard deviations were found 0.89 for copper and 0.93 for nickel with a relative error of $\leq 2.9\%$ and 3.6% for the two ions, respectively.

4. Application

The proposed method was successfully applied to the determination Copper and nickel simultaneously in different synthetic samples. The results obtained are in good agreement with the certified amounts. Simplicity, sensitivity besides accuracy are the main advantages of the proposed method. The method saves time and effort, as well as many chemicals and is less complicated.

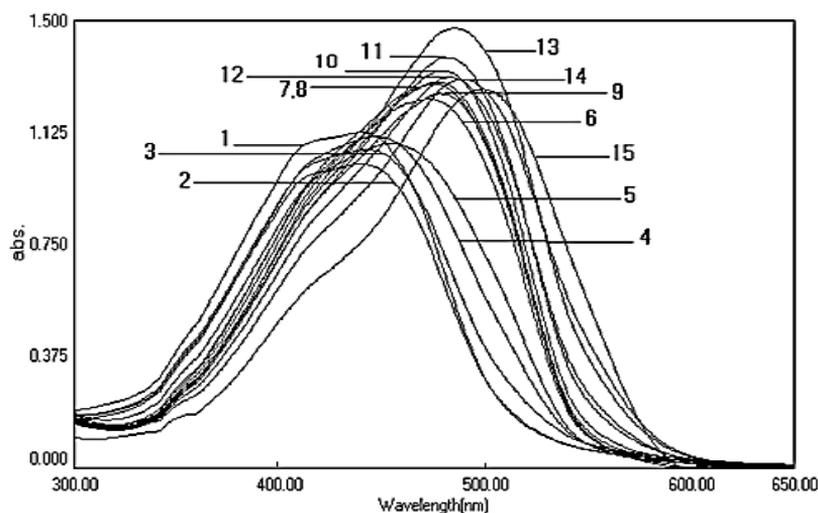


Fig. (3). Absorption spectra for 0.5×10^{-4} M of TAR at different pH values in the presence of 50% ethanol, pH: 4.0 (1), 4.5 (2), 5.0 (3), 5.5 (4), 6.0(5), 6.5 (6), 7.0 (7), 7.5 (8), 8.0 (9), 8.5 (10), 9.0 (11), 9.5 (12), 10 (13), 10.5 (14), 11 (15).

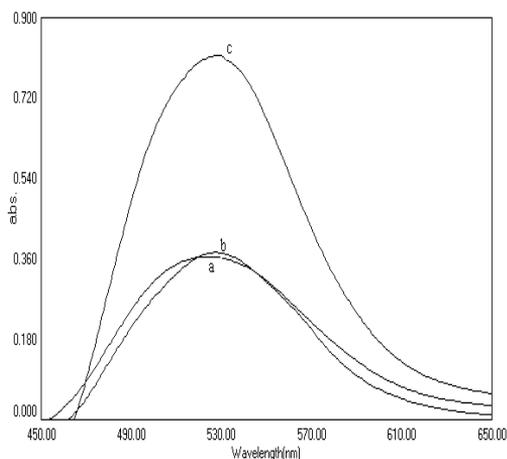


Fig. (4). Zero order absorption spectra of (a) Cu^{2+} -TAR (b) Ni^{2+} -TAR and (c) mixture of Ni^{2+} and Cu^{2+} complexes.

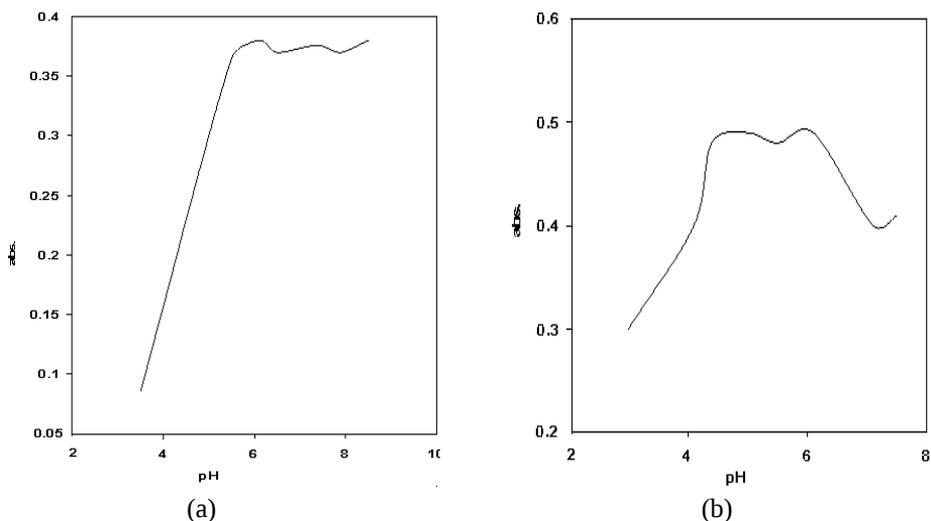


Fig. (5), a) absorption versus pH graph for binary of Ni^{2+} -TAR system: $C_L = C_M = 2.5 \times 10^{-4}$ M, $I = 0.1$ M (NaClO_4), 50% (v/v) ethanol, $\lambda_{\text{max}} = 528$ nm; b) absorption versus pH graph for binary of Cu^{2+} -TAR system: $C_L = C_M = 2.5 \times 10^{-4}$ M, $I = 0.1$ M (NaClO_4), 50% (v/v) ethanol, $\lambda_{\text{max}} = 524$ nm.

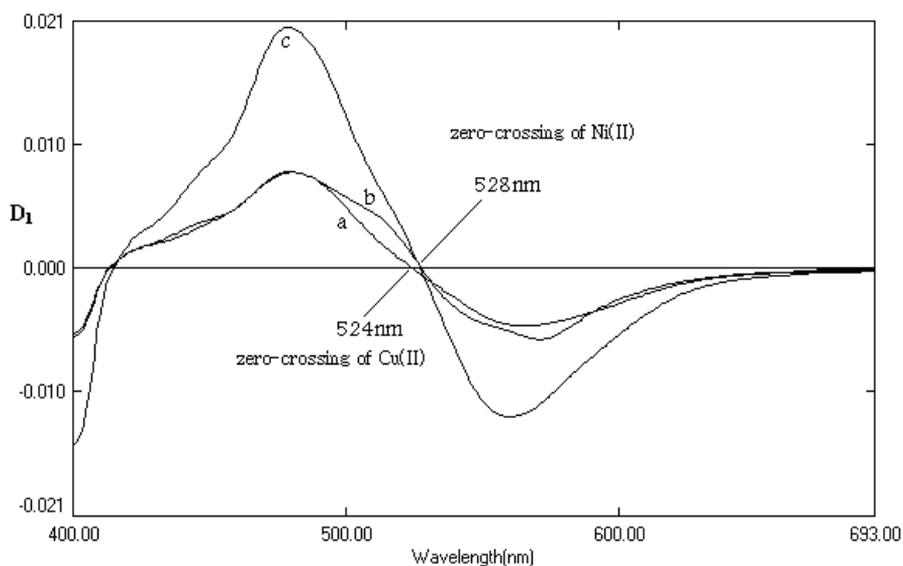


Fig. (6). First derivative absorption spectra of: (a) Cu^{2+} -TAR, (b) Ni^{2+} -TAR and (c) mixture of Ni^{2+} and Cu^{2+} complexes.

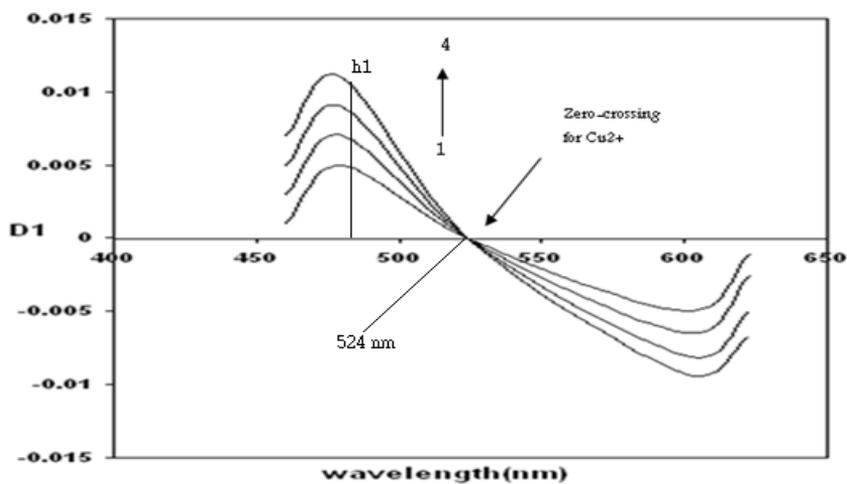


Fig. (7). First derivative spectra of the solutions containing: fixed 15.88 $\mu\text{g/ml}$ of Cu^{2+} -TAR and increasing the concentration of Ni^{2+} -TAR: 1) 1.47, 2) 5.88, 3) 8.08, 4) 11.76 $\mu\text{g/ml}$.

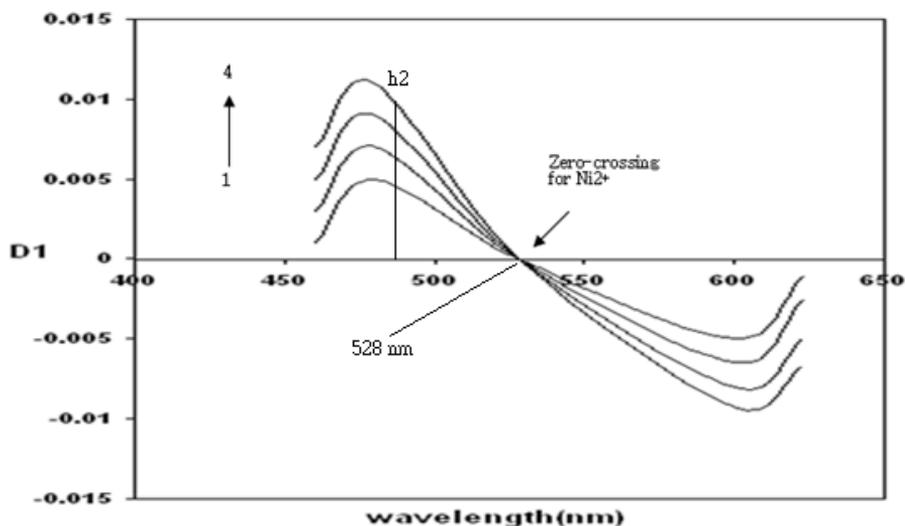


Fig. (8). First derivative spectra of the solutions containing: fixed $14.67 \mu\text{g/ml}$ of Ni^{2+} -TAR and increasing the concentration of Cu^{2+} -TAR 1) 1.58, 2) 6.32, 3) 8.69, 4) $12.64 \mu\text{g/ml}$.

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الملخص العربي

دراسات فيزيقوكيميائية على متراكبات أيونات النيكل والنحاس الثنائي مع صبغة TAR وفي نفس الوقت تقدير الأيونات المعدنية في خلطات بواسطة القياس الطيفي المشتقة

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اسيوط

تم في هذا البحث دراسة حالات الاتزان القائمة بالمحلول عند تكوين متراكبات فلزية النيكل والنحاس الثنائي مع صبغة TAR (2- ثيازول أيل أزوريسينول) ذات الأهمية البيولوجية والصيدلانية وإستخدامات الصناعية بالطرق الجهدية و الطيفية. وتم تحديد حالات اتزان التراكب الممكن تواجدها بالمحلول ونسب تكوينها و تدرج ثبات نظم التراكب المختلفة على ضوء طبيعة الكاشف الداخل في التفاعل ومقارنة ثبات هذه النظم التركيبية المختلفة في المعايرات عند تغير درجة تركيز أيون الهيدروجين بالمحلول وذلك لمعرفة الظروف المثلى لتكوين المتراكبات موضع الدراسة وكذلك استخدمت في هذه الدراسات قياس أطيايف الامتصاص المرئي و الفوق بنفسجية خلال معايرات تتبع تغير درجة تركيز أيون الهيدروجين بالمحلول عند ظروف تجريبية محددة. وتم حساب ثوابت التأيين لليجند و ثوابت تكوين المتراكبات . و أوضحت النتائج دراسة سلوك منحنيات الليجند الحر و متراكباته و أن نسبة تكوين

المتراكبات هي 1:1. وبإستخدام الكاشف الطيفي (TAR) أمكن تقدير قى وقت واحد كمية كل من النيكل والنحاس في بعض الخلائط المحضرة معمليا وذلك بإستخدام المقياس الطيفى للمشتقة الأولى عند 524 و 528 نانومتر على التوالي.