POTENTIOMETRIC AND SPECTROSCOPIC STUDIES OF NICKEL(II), COPPER(II) AND ZINC(II) COMPLEXES WITH SALICILIDEN 2-AMINOTHIAZOLE

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Abstract

Metal complexes of the divalent ions Ni, Cu and Zn with a Schiff base obtained through condensation of salicylaldehyde with 2-aminothiazole has been investigated potentiomerically and spectrophotometrivally. The stoichiometric formula of the obtained complexes are: $Ni(SAT)_2$, $Cu(SAT)_2$ and Zn(SAT) where: SAT = saliciliden 2-aminothiazole. The formation constants of proton-ligand and metal-ligand complexes have been determined at 25 ºC and 0.1 M (NaClO4) ionic strength in 50% (V/V) ethanol - water solution. The formation constants values obtained from spectrophotometric studies are found to be consistent with those obtained from potentiometric studies. The complexation reaction in the systems investigated were demonstrated and characterized using graphical logarithmic analysis of the absorbance versus pH graph. The binary systems obeyed beer's law up to 0.21, 0.19 and 0.24 µg/ml and the molar absorptivity $\varepsilon = 3.12 \times 10^3$, 2.16×10^3 3.80×10^3 l mol^{-1} cm^{-1} for Ni^{2+}, Cu^{2+} and Zn^{2+} respectively.

Keywords: Nickel(II), Copper(II) and Zinc(II); Schiffbase; stability constants; stoichiometry; potentiometric titrations; spectrophotometric study

1. Introduction

Thiazole ring structure is a useful element in medicinal chemistry. This structure has found application in drug development for treatment of allergies, hypertension, inflammation, schizophrenia, and bacterial and HIV infections [(1)]._The prepared Schiff bases from thiazole derivatives with salicylaldehyde have been screened on some stains of fungai [(2)] and Rhizoctonia solani [(3)]. The metal chelates have been shown to possess more antibacterial activity than the uncomplexed Schiff-bases for their biological activity against Escherichia coli [(4)], Staphylococcus aureous, Pseudomonas aeruginosa and Klebsiella pneumonae [(5)] and antifungal activity [(6)]. Various applications of Schiff bases and their metal complexes have been evaluated over the last 50 years as catalysts in biological systems [(7)], anticancer [(8)], antitumor, [(9)], anthelmintic [(10)], and antimicrobial [(11)] activities. Several Schiff bases [(7)] were synthesized from salicaldehyde and their metal complexes containing Cu, Ni, Zn and Co are effective chemicals to kill *Tetranychus bimaculatus* [12] and possess antitumor [13] activity. This work aims to studing (in 50% (v/v) ethanol) the protonation equilibria, coordination modes, the stoichiometries, stability and the optimal conditions of the formation complexes of Ni^{2+}, Cu^{2+} and Zn^{2+} with saliciliden 2-aminothiazole (SAT) using spectrophotometric and potentiometric methods to throw some light on their analytical applications. No systematic of these studies have yet been reported on complexation equilibria in solution of the Ni(II), Cu(II) and Zn(II) with SAT. The ligand SAT react with Ni^{2+}, Cu^{2+} and Zn^{2+} solution in the pH range 6.1 – 8.5.

2. Experimental

2. 1. Chemical and solutions

All chemicals were Analar chemically pure grade. The chemicals 2-aminothiazole, salicylaldehyde which used for preparation the ligand saliciliden 2-aminothiazole (SAT) were purchased from Sigma- Aldrich Chemicals Co., USA and were used as received. Different metal salt Copper nitrate $Cu(NO_3)_2$, Nickle chloride hexa hydrate $NiCl_2.6H_2O$, and zinc nitrate $(Zn(NO_3)_2$ were purchased from Merck (Germany), and were used without purification. $HClO_4$, Sodium perchlorate, Sodium hydroxide, potassium hydrogen phethalate, Borax and ethanol of Analar products were obtained from Sigma- Aldrich chem. Co. Saliciliden 2-aminothiazole (SAT) was prepared by the literature (5) method. The structure of the ligand SAT ($C_{10}H_8N_2OS$) was confirmed by the elemental analyses: Analysis, C, H and N%, Required: 58.82, 3.92, 13.73, Found: 58.80, 3.91, 13.71. Mass spectrum (Fig. 1) exhibited a base peak m/z; 204, corresponding to molecular weight.

2. 1. a. Preparation of ligand solutions

Stock solution (2.5 mM) of ligand SAT solution were prepared by dissolving the accurate weight of each ligand in the appropriate volume solvents solution of required concentration were prepared by accurate dilution with the proper solvent.

2. 1. b. Metal salts solution

A stock Solutions (5 mM) solution of each of the investigated metal salts $Cu(NO_3)_2$, $NiCl_2.6H_2O$, and $(Zn(NO_3)_2$ content (H_2O content 1.0 mole\mole) were obtained by dissolving the accurate weight of each in the appropriate volume of bidistilled water and standardized compleximetrically [14]. More dilute solutions used for spectral measurements were obtained by accurate dilution. Doubly distilled water used for the preparation of the solutions.

2. 1. c. NaOH, $HClO_4$, $NaClO_4$ Solution

Carbonate free NaOH solution was prepared and was standardized by titration with standard solution of KH-phthalate. A stock solution of $HClO_4$ was prepared and its morality was checked by standard of NaOH solution. The working solution (1.0 molar) of $NaClO_4$ was prepared by dissolving the accurate weight of the salt in the appropriate volume of bidistilled water.

2. 1. d. Solution of Diverse Ions

Stock solutions were prepared by dissolving the calculated amounts of nitrate, chlorides or acetates of the metals to be investigated. Dilute acids were added to prevent hydrolysis whenever needed. Anions were added as solutions of their sodium or potassium salts. Standardization of solutions was performed by conventional methods.

2. 2. Instrumentation

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 standard buffer solutions, first with the pH 9.2 (0.01 M Borax) followed by a pH value 4.0 (0.05 M potassium hydrophethalate) at 25 ºC. The temperature degree was controlled by coupling the titration cell with a thermostatic bath set at 25 ºC.

The absorption spectra of ethanol solution of the ligand and SAT and its different metal complexes were recorded with derivative on a Perkin-Elmer (Lambda 35) computerized spectrophotometer equipped with 1 cm matched quartz cells.

The infrared spectra of the prepared the ligand SAT were performed by a Fourier transform infrared spectrometer (FT-IR) analysis in the region 4000-400 cm^{-1} with Jasko 480 infrared spectrometer using potassium bromide (KBr) disk technique.

Microchemical analyses were carried out by the unit of micro analyses on a perkin – Elmer 240 C instrument.

The mass spectra were performed by Shimadzu- GCMS-OP 1000 Ex using direct inlet system.

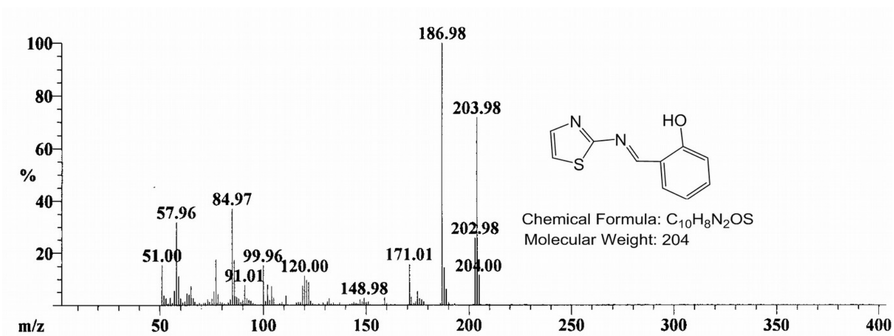
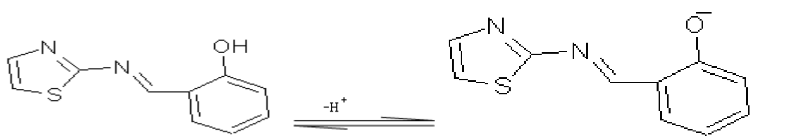


Fig.(1) Mass Spectra of saliciliden 2-aminothiazole (SAT)

3. Results and discussion:

3. 1. Equilibrium determination:

Solutions used during the potentiometric and spectrophotometric equilibrium work were prepared and titrated as previously described in the literature [15,16]. The pH- titration technique of Irving and Rossotti [17] was employed in this study. All titrations (Fig. a-c) were carried out in 0.10 M $NaClO_4$ solutions and were analysed with the SUPERQUAD [18] computer program allowed the determination of the main complex species in equilibrium. The pH-metric titration curves of the free ligand saliciliden 2-aminothiazole (SAT) (2.5 x 10^{-4} mol dm^{-3}) ligand in the absence and presence of different metal ions (2.5 x 10^{-4} mol dm^{-3}), namely Ni(II), Cu(II) and Zn(II) show distinct inflection at m = 1 (m = number of moles of alkali added per mole of ligand). The dissociation constant of SAT corresponding to the ionization of hydrogen of the phenolic group. The acid-base equilibria of the ligand SAT in 50% (v⁄v) at 25 ºC, indicated that the predominant form of a reagent within pH 8.66 is the monoanionic species $(L)^-$, which undergoes ionization on increasing the pH of solution according to the following equalibria:



[HL] **[L⁻]**

$$\mathbf{HL} \overset{pK_1}{\rightleftharpoons} \mathbf{L^- + H^+} \qquad \mathbf{(\,pk_a = 8.66\,)} \quad \ldots\ldots\ldots\ldots\ldots \mathbf{(1)}$$

The stoichiometry of the complexes formed during the interaction of Ni(II), Cu(II) or Zn(II) with SAT was established from the magntude of the proton displacement, which was determined by titrating solutions containingthe ligand against standard alkaki in the absence and presence of different molar quantities of metal ion. The formation constants of the metal(II) complexes were determined from titration of solutions containing 1:1 or 1:2 metal:ligand molar ratio assuming a fixed value of 8.66 for pK_a of the ligand SAT. The titrations were performed with a carbonate free NaOH solution over pH range 3 - 12.5. The stability constants for the binary complexes Ni^{2+}, Cu^{2+} and Zn^{2+} with SAT were computed from titration curves are given in Table (1). The titration curve for a system containing Zn-SAT in 1:1 or 1:2 molar ratio exhibits an inflection at m = 1 (m = moles of base added per mole of metal ion) indicating the formation of mono binary complexes as shown in Fig. 2 (a). The graphs for the systems containing Ni(II) or Cu(II) and SAT (Fig. 2 (b,c)) in 1:1 or 1:2 molar ratio exhibts two inflections at m = 1 and m = 2, indicating the formation of mono and bis-binary complexes, the corresponding equilibria may be represented as follows:

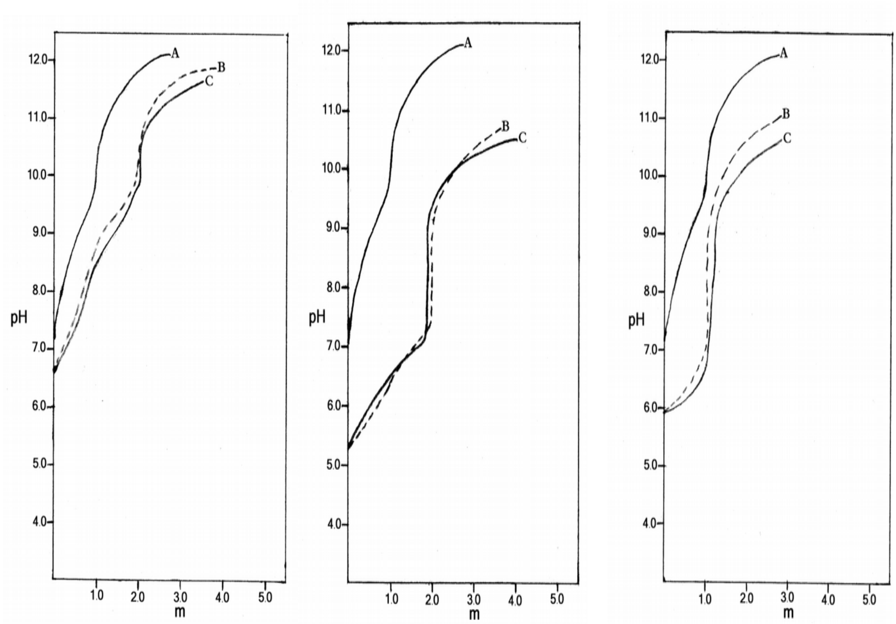
$$\text{Cu} + \text{SAT} \rightleftharpoons \text{Cu(SAT)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$\text{Cu(SAT)} + \text{SAT} \rightleftharpoons \text{Cu(SAT)2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

A comparison of the stability constants of binary complexes indicates that the order of stability in terms of metal ion is $Cu^{2+} > Ni^{2+} > Zn^{2+}$.

3. 2. Electronic Absorption Specta:

The absorption spectra of the reagent saliciliden 2-aminothiazole (SAT) of 2.5×10^{-4} M solution in ionic strength (I = 0.1 M $NaClO_4$) at 25 ºC were recorded at different pH values and in the presence of 50% (V/V) ethanol (Fig. 3). The limited wavelength values of this reagent are recorded at λ_{max}=325 nm. The graphical logarithmic analysis of the absorbance versus pH graph for the reagent AMTS is given in Fig. 4. The absorption band of SAT undergoes a reasonable shift to longer wavelengths on adding the solution of Ni^{2+}, Cu^{2+} and Zn^{2+} by about 40-100 nm. The color of a reagent undergoes a change from yellow to pink when mixed with Ni^{2+}, Cu^{2+} and Zn^{2+} solution. The effect of pH on the spectra of Ni^{2+}, Cu^{2+} and Zn^{2+} complexes with the reagent SAT measured in solution containing equimolar concentrations (Figs. 5-7). The spectra Ni(II), Cu(II) and Zn(II) with SAT complexes against reagent blank as reference ware characterized by an absorption band at λ = 430, 430 and 366 nm respectively. The maximum absorbance of the binary complexes was obtained in the pH range 7.4 - 8.3 for Ni^{2+} complex, 6.1 - 7.3 for Cu^{2+} complex and 6.5-7.5 for Zn^{2+} complex. The spectrum of the reaction mixture measured against a blank solution containing the same concentrations without metal ion. The complexation reaction in all systems investigated were demonstrated and charecterised using graphical logarithmic analysis of the absorbance versus pH and interpreted using relations derived by Sommer et al [19,20]**.** The absorbance vs. pH graphs were analyzed graphically as described previously [21]. The effect of the concentration of SAT on the formation of Ni^{2+}, Cu^{2+} and Zn^{2+} binary complexes has been investigated under identical experimental conditions. The optimum reagent concentration was concentration of 1:1 metal-ligand molar ratio 2.5×10^{-4} M.



(a) (b) (c)

Fig. (2 (a-c)). Potentiometric titration curves of Binary systems of Ni(II), Cu(II) and Zn(II) with SAT in 50% (V/V) ethanol, I = 0.1 M $NaClO_4$ and at 25 ºC. [(a): A) deprotonated SAT, B) 1:2 Ni^{2+}-SAT andC) 1:1 Ni^{2+}-SAT]; [(b): A) deprotonated SAT, B) 1:2 Cu^{2+}- SAT and C) 1:1 Cu^{2+}- SAT], [(c): A) deprotonated SAT, B) 1:2 Zn^{2+}- SAT and C) 1:1 Zn^{2+}- SAT], [m = moles of alkali per mole of metal ion].

The stoichiometry of the complexes

Job's method of continuous variation [22,23] was applied to establish the composition of the Ni^{2+}, Cu^{2+} and Zn^{2+} with SAT binary complex at pH 7.2. 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 Ni^{2+}, Cu^{2+} or Zn^{2+} 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 Zn but form 1:2 for Ni and Cu-SAT binary complexes. The stoichiometry of the binary complex was also determined by applying the molar ratio method [(24)].

Table(1). logarithms of stability constants of Ni^{II}, Cu^{II} and Zn^{II} Complexes containing 1:2 ratio of metal ion with (SAT) [Temp. 25 °C, I=0.1 M ($NaClO_4$) , pK for (SAT) is 8.66

Metal ion	$\log k_{ML}^{M}$	$\log k_{ML_2}^{ML}$	$\log \beta_{ML_2}^{ML}$
Ni^{II}	6.21	5.7	11.91
Cu^{II}	7.05	6.55	13.6
Zn^{II}	6.63	-	6.63

Effect of diverse ions

The effect of diverse ions on the determination of 0.03 mg of Ni^{2+},Cu^{2+} and Zn^{2+} were investigated. The determination of metal ion as a binary complex was possible in the presence of 6 mg of Li^{+}, Na^{+}, k^{+}, Ca^{+}, Mg^{2+}, St^{2+}, Ba^{2+}, La^{3+}, Pb^{2+}, SO_4^{2-}, ClO_4^{-}, SCN^{-}, $B_4O_7^{2-}$, Cl^{-}, Br^{-}, I^{-}, acetate, SATSATate, and citrate. Mn^{2+}, Co^{2+}, Cr^{3+}, Ni^{2+}, Th^{4+}, U^{6+}, Cd^{2+}, Zr^{4+} and Al^{3+} interference were minimized by masking with cyanide or fluride ions (20 fold excess).

Calibration Graph and reproducibility

The binary systems obeyed beer's law up to 0.21, 0.19 and 0.24 µg/ml and the molar absorptivity at λ_{max} = 430, 430 and 366 nm, ε = 3.12 x 10^3, 2.16 x 10^3 3.80 x 10^3 l mol^{-1} cm^{-1} for Ni^{2+}, Cu^{2+} and Zn^{2+} respectively. The sensitivity of the reactions was calculated according to sandell [(25)] and was found in the range 3.8- 9.3 × 10^{-4} 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 2.0 and 7.0 µg per 10 ml. The relative standard deviation obtained was found in the range 0.54 - 0.86.

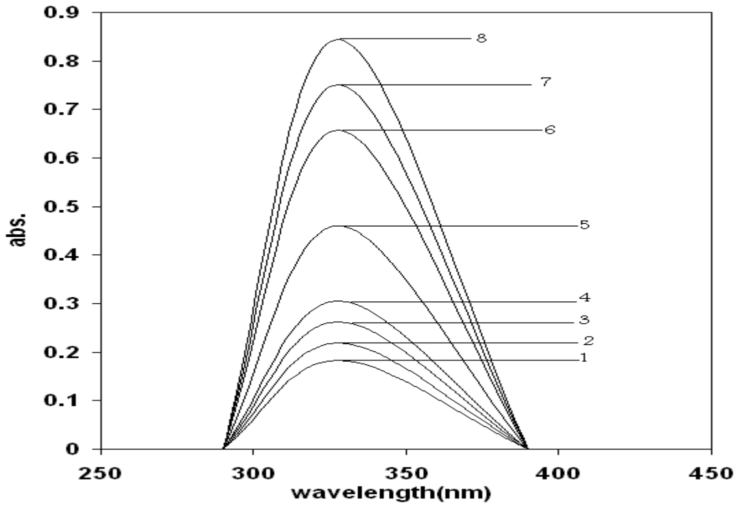


Fig. (3). Absorption Spectra of Ligand SAT, in 50% (V/V) ethanol, I = 0.1 M ($NaClO_4$), pH: 1(6), 2(6.5), 3(7), 4(7.5), 5(8), 6(8.5), 7(9), 8(9.5).

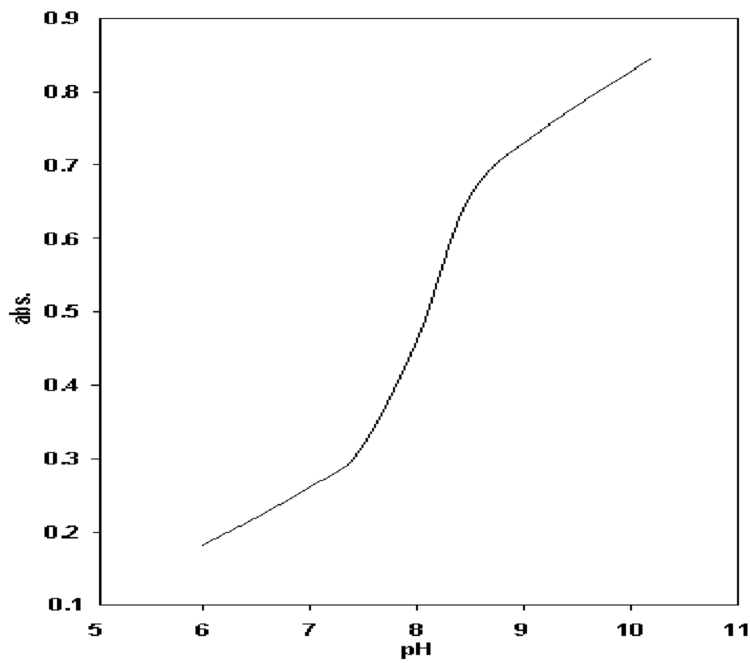


Fig. (4). Variation of Absorption spectra with pH for solution of SAT, λ_{max} = 325 nm, in 50% (V/V) ethanol.

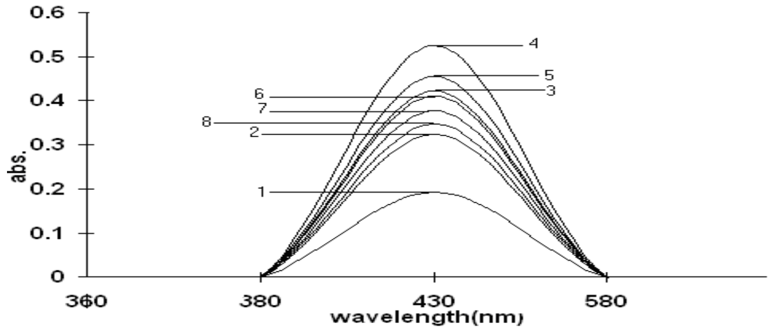


Fig. (5). Absorption spectra of Cu^{2+}-SAT complex: $C_L = C_M = 2.5\times10^{-4}$ M, I = 0.1 M ($NaClO_4$), in 50% (V/V) ethanol, pH: 1(5.32), 2(5.8), 3(6.1), 4(7), 5(7.3), 6(7.9), 7(8.2), 8(8.5).

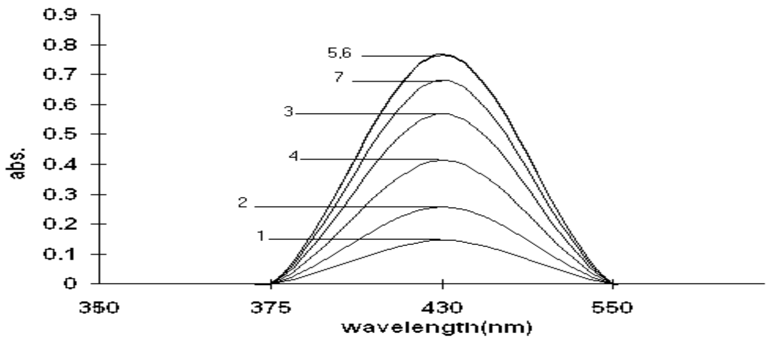


Fig. (6). Absorption spectra of Ni^{2+}-SAT complex: $C_L = C_M = 2.5\times10^{-4}$ M, I = 0.1 M ($NaClO_4$), in 50% (V/V) ethanol, pH: 1(6.5), 2(6.8), 3(7.1), 4(7.4), 5(7.7), 6(8), 7(8.3).

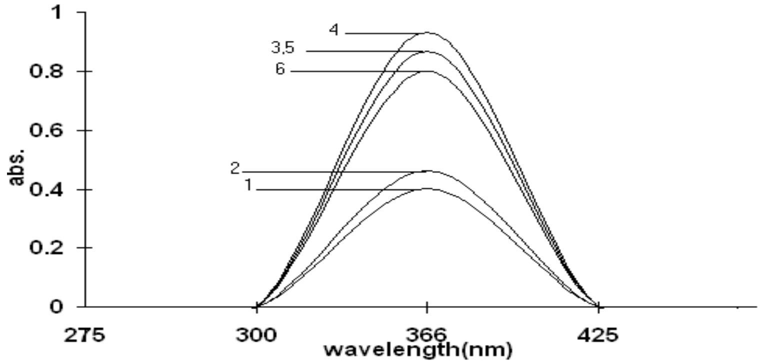


Fig. (7). Absorption spectra of Zn^{2+}-SAT complex: $C_L = C_M = 2.5\times10^{-4}$ M, I = 0.1 M ($NaClO_4$), in 50% (V/V) ethanol, pH: 1(6.05), 2(6.19), 3(6.58), 4(7.05), 5(7.5), 6(8.05).

Conclusion

Because the Schiff base saliciliden 2-aminothiazole (SAT) and their complexation with the divalent ions Ni, Cu and Zn have a range of biological activity. In this article, we have calculated the dissociation constant of the ligand and the stability constants of the complexes and the optimal conditions for the formation of the complexes were performed potentiomerically and spectrophotometrivally. The stoichiometric formula of the obtained complexes are: $Ni(SAT)_2$, $Cu(SAT)_2$ and Zn(SAT).

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الملخص العربى

دراسات جهدية و طيفية على متراكبات ايونات النيكل و النحاس و الزنك الثنائية مع سالسيلدين 2امينوثيازول

محمود حسن مصطفى و عبد الحليم مصطفى حسين و مصطفى كمال حسن و إيهاب محمود عبد الله

تم فى هذا البحث دراسة حالات الاتزان القائمة بالمحلول عند تكوين متراكبات فلزية لأيونات النيكل والنحاس و الزنك مع قاعـدة شـيف سالسـيلدين 2امينوثيـازول المشـتقة من مـركب 2امينوثيـازول و الأسـيتالدهيد ذات الأهمية البيولوجية والصـيدلية بالطرق الجهدية و الطيفيـة. وتم اثبـات الـتركيب الجزيـئى لليجند بواسطة طيف الكتلة. كذلك تم تحديد حالات اتزان التراكب الممكن تواجـدها بـالمحلول ونسب تكوينها و تـدرج ثبـات نظم الـتراكب المختلفة على ضـوء طبيعة الكاشف الـداخل فى التفاعل ومقارنة ثبات هذه النظم التركيبية المختلفة فى المعـايرات عند تغـير درجة تركيز أيون الهيدروجين بـالمحلول و ذلك لمعرفة الظـروف المثلى لتكـوين المتراكبـات موضع الدراسة و كـذلك اسـتخدمت فى هـذه الدراسـات قيـاس أطيـاف الامتصـاص المـرئى و الفـوق بنفسـجية خلال معايرات تتبع تغير درجة تركـيز أيـون الهيـدروجين بـالمحلول عند ظـروف تجريبية محـددة. وتم حسـاب ثـوابت التـأين لليجند و ثوابت تكوين المتراكبات . و أوضحت النتائج دراسة سلوك منحنيات الليجند الحر و متراكباته و أن نسبة تكوين المتراكبـات ومن النتـائج أمكن ترتيب ثباتية المتراكبات طبقا لقيم ثوابت الاستقرار.