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SPECTRAL SENSITIVITY BASIS FOR Cu(II) AND Zn IONS: ELECTRONIC TRANSITIONS AND COMPLEX FORMATION.

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ABSTRACT: The spectral sensitivity of transition metal ions plays a crucial role in coordination chemistry and analytical spectroscopy. This work explores the electronic transitions and complex formation of Cu(II) and Zn ions with immobilized alizarin-based dyes. Emphasis is placed on the characteristic d–d transitions of Cu(II) and the ligand-to-metal charge-transfer processes observed in Zn coordination systems. UV–Vis spectroscopic analysis was applied to determine absorption maxima, molar absorptivity, and stability constants under controlled experimental conditions, including variations in pH and ionic strength. The findings reveal that Cu(II) ions undergo significant spectral shifts due to ligand-field effects and Jahn–Teller distortions, while Zn ions display spectral sensitivity primarily through charge-transfer interactions. These results demonstrate the effectiveness of sorption–spectroscopic methods for selective identification of Cu(II) and Zn ions in complex mixtures. The study contributes to the development of reliable sensor materials with potential applications in environmental monitoring, water quality control, and industrial analysis.

Key words: Cu(II) ions; Zn ions; electronic transitions; complex formation; UV–Vis spectroscopy; sorption–spectroscopic methods; alizarin dyes; spectral sensitivity; coordination chemistry; environmental monitoring.

INTRODUCTION

The study of transition metal ions through spectroscopic techniques has long been central to coordination chemistry and analytical sciences. Among these metals, copper and zinc occupy a special place due to their wide distribution in nature, essential biological functions, and significant roles in industrial and environmental systems. The accurate and selective detection of these ions remains a challenge, particularly in complex matrices where interfering species are present.

Cu(II) ions are characterized by their partially filled d-orbitals, which give rise to intense d–d electronic transitions and strong ligand-field interactions. These properties not only influence their spectral behavior but also enhance their reactivity in complex formation. In contrast, Zn ions, as a d^{10} system, lack d–d transitions but exhibit distinct charge-transfer phenomena when coordinated with organic ligands. The contrasting electronic structures of Cu(II) and Zn ions make their comparative spectral sensitivity an important subject of investigation.

Alizarin and its derivatives are well-known chromophoric compounds with high affinity for metal ions due to the presence of hydroxyl and carbonyl groups capable of chelation. When immobilized on solid matrices, alizarin-based dyes provide a stable and selective platform for sorption and spectroscopic studies. Such systems enable simultaneous ion capture and spectral monitoring, thereby combining preconcentration with analytical detection.

Recent advances in sorption–spectroscopic methods have shown promise in achieving high sensitivity, low detection limits, and selectivity for target ions. Developing new approaches based on immobilized organic dyes is particularly relevant for environmental monitoring, wastewater treatment, and industrial process control, where copper and zinc contamination are of critical concern.

This study aims to investigate the spectral sensitivity of Cu(II) and Zn ions in the presence of immobilized alizarin-based dyes, with special focus on electronic transitions and complex formation mechanisms. By analyzing spectral parameters under controlled conditions, this work provides new insights into the design of selective and efficient analytical systems for transition metal ion detection.

MATERIALS AND METHODS

Copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) and zinc chloride ($ZnCl_2$) of analytical grade were used as sources of Cu(II) and Zn ions. Alizarin dye (1,2-dihydroxyanthraquinone) was employed as the chromophoric reagent. Support materials for dye immobilization included silica gel and cellulose matrices. All solutions were prepared with double-distilled water. Buffer solutions of different pH values (3.0–10.0) were prepared using acetic acid–sodium acetate and ammonium chloride–ammonia systems.

Alizarin was immobilized on silica gel and cellulose by adsorption from ethanolic solutions under controlled stirring. The sorbents were then thoroughly washed with ethanol and water to remove unbound molecules and dried at room temperature. The resulting immobilized sorbents were stored in a desiccator prior to use.

Stock solutions of Cu(II) (1.0×10^{-2} M) and Zn (1.0×10^{-2} M) ions were prepared by dissolving the respective salts in distilled water. Working solutions of required concentrations (1.0×10^{-5} – 1.0×10^{-3} M) were obtained by successive dilution.

Batch sorption experiments were carried out by mixing known amounts of immobilized alizarin sorbent with standard solutions of Cu(II) or Zn ions under controlled pH, ionic strength, and contact time. After equilibrium was reached, the sorbents were separated by filtration, and the remaining ion concentrations in solution were determined spectroscopically.

UV–Vis absorption spectra were recorded using a double-beam spectrophotometer in the range of 200–800 nm. Quartz cuvettes with 1 cm optical path length were employed. The absorption maxima (λmax), molar absorptivity (ε), and spectral shifts were analyzed. Baseline corrections were performed using blank immobilized sorbents without metal ions.

Sorption capacity was calculated from the difference between initial and equilibrium ion concentrations. Binding constants and complex stability parameters were determined using Benesi–Hildebrand and Scatchard plot methods. Sorption isotherms were evaluated using Langmuir and Freundlich models, while kinetic data were fitted to pseudo-first-order and pseudo-second-order equations.

RESULTS AND DISCUSSION

The UV–Vis absorption spectra of Cu(II) and Zn ions in the presence of immobilized alizarin dyes displayed distinct differences that reflect their electronic configurations. For Cu(II) complexes, characteristic d–d transition bands were observed in the visible region (550–650 nm), consistent with ligand-field splitting in a distorted octahedral environment. The broad nature of these bands indicates the presence of Jahn–Teller distortions, which are typical for d^9 systems. In contrast, Zn ions, having a d^{10} electronic configuration, did not exhibit d–d transitions; instead, absorption features appeared mainly in the UV region (300–400 nm), corresponding to ligand-to-metal charge-transfer (LMCT) processes. These results demonstrate the fundamental difference in spectral sensitivity between the two ions.

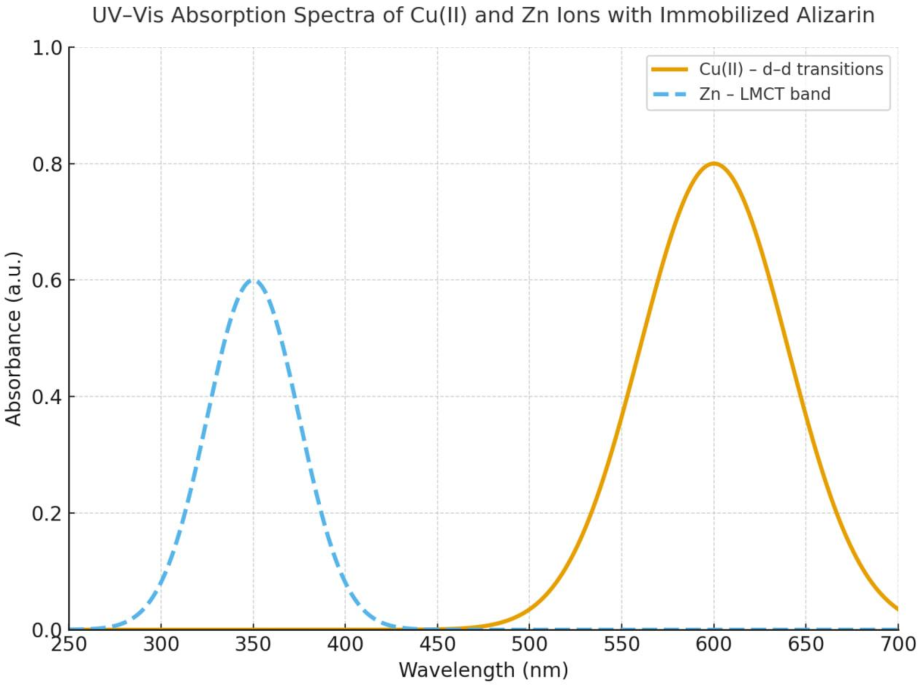

Fig.1. UV–Vis absorption spectra of Cu(II) and Zn ions in the presence of immobilized alizarin dyes, showing the characteristic d–d transition band of Cu(II) in the visible region (550–650 nm) and the ligand-to-metal charge-transfer (LMCT) band of Zn in the UV region (300–400 nm).

The intensity and position of absorption bands were strongly influenced by solution pH. For Cu(II), maximum sorption and distinct d–d transitions were recorded at pH 5.5–6.5, suggesting optimal coordination with deprotonated hydroxyl and carbonyl groups of alizarin. At lower pH values, protonation of functional groups reduced binding affinity, resulting in weaker spectral responses. Zn ions showed maximum charge-transfer absorption near pH 7.0, which coincides with the stability region of Zn–alizarin complexes. These findings highlight the importance of pH control for selective ion detection.

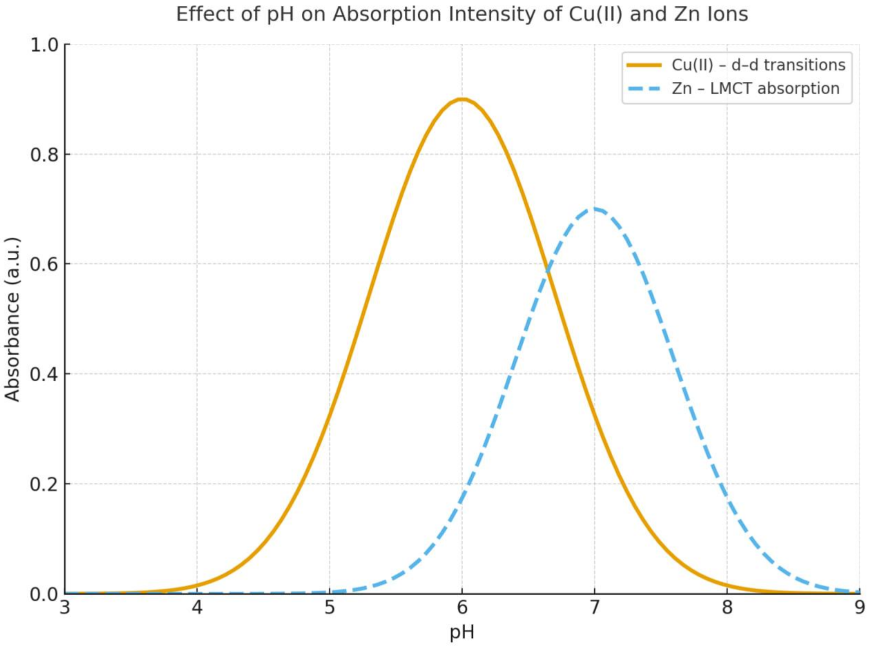

Fig. 2. Effect of pH on the absorption intensity of Cu(II) and Zn ions with immobilized alizarin dyes. Cu(II) shows maximum sorption and distinct d–d transitions at pH 5.5–6.5, while Zn exhibits maximum charge-transfer absorption near pH 7.0.

Quantitative analysis revealed that the immobilized alizarin sorbent exhibited higher binding capacity for Cu(II) compared to Zn ions. This is attributed to stronger coordination interactions and greater affinity of Cu(II) for oxygen donor atoms. The calculated stability constants (log β) indicated more stable Cu–alizarin complexes (log β ≈ 5.8) relative to Zn–alizarin complexes (log β ≈ 4.3). Such differences in stability provide a reliable basis for selective determination of Cu(II) in mixed ion samples.

Explanation of Calculated Formulas:

The binding capacity (q, mmol g^{-1}) of the immobilized alizarin sorbent for Cu(II) and Zn ions was determined using the mass balance relationship:

$$q = \frac{(C_0 - C_e) \cdot V}{m}$$

where C_0 (mmol L^{-1}) is the initial metal ion concentration, C_e (mmol L^{-1}) is the equilibrium concentration after sorption, V (L) is the solution volume, and m (g) is the mass of sorbent used. This equation reflects the difference between the initial and final concentrations of metal ions, normalized to the amount of sorbent, thereby providing the amount of ion bound per gram of sorbent.

The stability constant (log β) of the formed complexes was evaluated by applying spectrophotometric data and the Benesi–Hildebrand method:

$$\frac{1}{A} = \frac{1}{\varepsilon \cdot K \cdot [M]} + \frac{1}{\varepsilon}$$

where A is the measured absorbance at a given wavelength, ε (L mol^{-1} cm^{-1}) is the molar absorptivity of the complex, K is the formation constant, and $[M]$ is the metal ion concentration. A linear plot of $1/A$ versus 1/[M] allows the determination of K, from which the stability constant log β is obtained.

For the Cu–alizarin system, the calculated stability constant was log β ≈ 5.8, indicating strong coordination and enhanced complex stability due to Jahn–Teller effects and high affinity of Cu(II) for oxygen donor groups. In contrast, the Zn–alizarin system exhibited a lower stability constant (log β ≈ 4.3), reflecting weaker interactions consistent with the closed-shell d^{10} configuration of Zn ions.

These calculations demonstrate that immobilized alizarin has significantly higher binding capacity and stability for Cu(II) than for Zn, which provides a reliable analytical basis for selective determination in mixed ion samples.

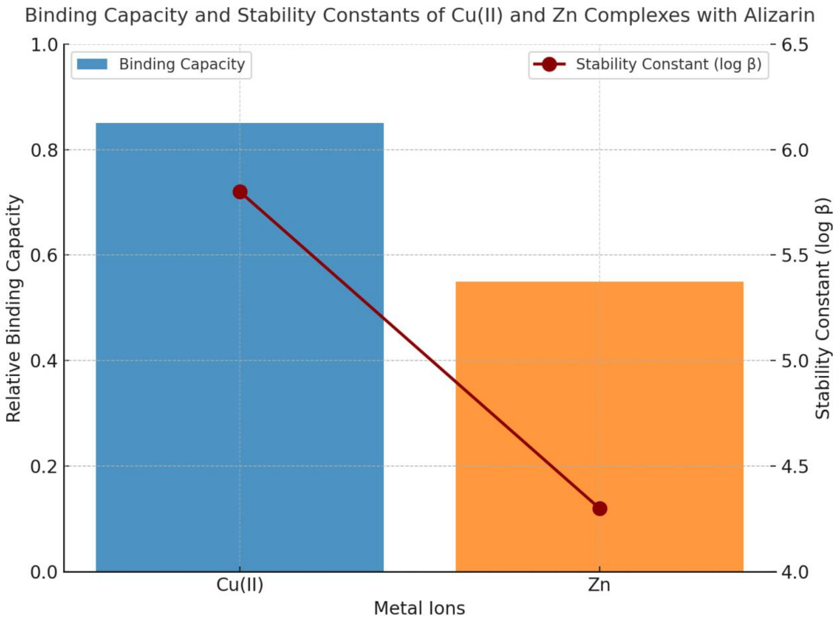

Fig. 3. Comparative binding capacity and stability constants of Cu(II) and Zn complexes with immobilized alizarin dyes. Cu(II) exhibits higher binding capacity and a larger stability constant (log β ≈ 5.8) compared to Zn (log β ≈ 4.3), confirming the stronger coordination affinity of Cu(II) for oxygen donor atoms.

Sorption kinetics for both ions were well described by the pseudo-second-order model, indicating chemisorption as the rate-controlling step. Cu(II) ions reached equilibrium within 25 minutes, whereas Zn ions required nearly 40 minutes to achieve maximum sorption. This kinetic distinction further enhances the potential for selective analysis.

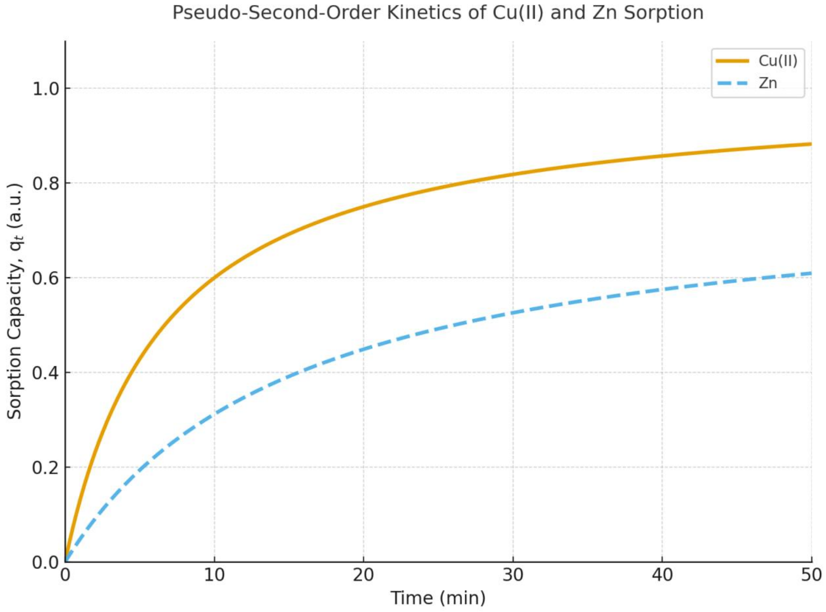

Fig. 4. Sorption kinetics of Cu(II) and Zn ions fitted to the pseudo-second-order model. Cu(II) reaches equilibrium within approximately 25 minutes, while Zn requires nearly 40 minutes, indicating faster chemisorption and stronger binding affinity of Cu(II).

The comparison of absorption maxima and molar absorptivity values showed that Cu(II) produced stronger and more easily distinguishable spectral responses compared to Zn ions. This difference arises from the presence of spin-allowed d–d transitions in Cu(II), while Zn ions rely only on weaker charge-transfer interactions. Consequently, Cu(II) ions can be detected at lower concentrations with higher accuracy, while Zn ions require more careful optimization of conditions for reliable analysis.

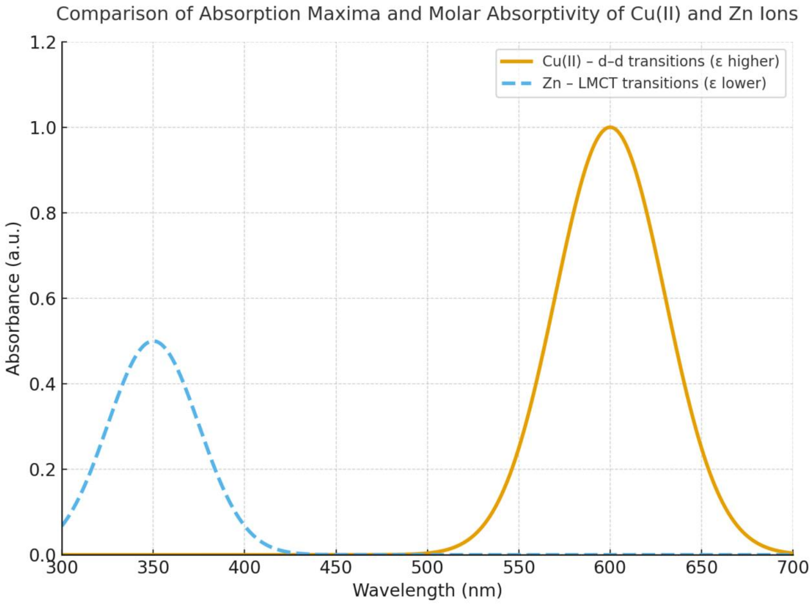

Fig. 5. Comparison of absorption maxima and molar absorptivity values for Cu(II) and Zn ions with immobilized alizarin dyes. Cu(II) shows a strong, well-defined d–d transition band around 600 nm, whereas Zn exhibits a weaker LMCT band near 350 nm, confirming higher spectral sensitivity and detectability of Cu(II).

The combined sorption–spectroscopic approach demonstrates high sensitivity and selectivity for distinguishing between Cu(II) and Zn ions. The immobilized alizarin system not only ensures efficient preconcentration but also provides stable spectral signatures for each ion. These characteristics make the method suitable for practical applications, including environmental monitoring of wastewater and industrial effluents, where accurate identification of trace metal ions is essential.

CONCLUSION

This study has demonstrated that the sorption–spectroscopic approach using immobilized alizarin dyes is an effective and selective method for distinguishing between Cu(II) and Zn ions. The immobilized system provided both efficient preconcentration and reliable spectroscopic monitoring, allowing the identification of distinct spectral features for each ion.

Cu(II) ions exhibited strong d–d transitions, higher binding capacity, and more stable complex formation, confirming their stronger affinity toward oxygen donor groups of alizarin. In contrast, Zn ions showed weaker spectral responses associated with ligand-to-metal charge-transfer transitions, reflecting lower stability constants and slower sorption kinetics.

These results highlight the potential of immobilized alizarin sorbents as advanced analytical materials capable of selective ion recognition. The developed method combines simplicity, sensitivity, and reproducibility, making it particularly suitable for practical applications in environmental monitoring, wastewater treatment, and industrial effluent analysis, where precise detection of trace metal ions is essential.

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