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Metal-Dependent UV-Vis Response of Resorcinol in Alkaline Media: Comparative Study of Mg^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Fe^{2+}

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Abstract

The time-dependent UV-Vis response of resorcinol in alkaline solution (NH_4OH) was investigated in the presence of divalent metal ions Mg^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Fe^{2+} in order to elucidate the origin of metal-specific optical behavior and assess intrinsic selectivity. Distinct spectral responses were observed depending on the electronic structure of the metal ion. Mg^{2+} produced a pronounced, time-dependent visible absorption band accompanied by a bathochromic shift, indicative of ligand-centered chromophore formation. Ni^{2+} exhibited characteristic metal-centered d-d transitions with a small red shift attributed to gradual ligand-field modulation. In contrast, Cu^{2+} and Zn^{2+}showed no measurable red shift, displaying only intensity changes consistent with Jahn-Teller-dominated (Cu^{2+}) or spectroscopically silent (Zn^{2+}, d^{10}) behavior. Fe^{2+} showed no discernible absorption features beyond the blank, indicating the absence of either ligand-centered chromophore formation or stable metal-centered transitions under the experimental conditions. These results demonstrate that metal selectivity in the resorcinol-NH_4OH system is governed primarily by electronic structure rather than coordination alone, enabling clear differentiation among metal ions based on their spectral signatures.

Keywords

Resorcinol, UV-Vis Spectroscopy, Metal Selectivity, Ligand-Field Effects, Jahn-Teller Distortion

1. Introduction

Colorimetric and spectrophotometric methods based on organic ligands remain attractive for metal-ion sensing due to their simplicity, low cost, and potential selectivity [1] [2]. Phenolic compounds such as resorcinol are particularly sensitive to alkaline conditions, where deprotonation enables metal coordination and electronic delocalization. However, the optical response of such systems is highly metal-dependent and strongly influenced by the electronic configuration of the metal ion [3].

Resorcinol (1,3-dihydroxybenzene) acts as a bidentate ligand, forming chelate complexes through its hydroxyl groups. The complexation behavior is highly sensitive to the electronic configuration of the metal ion, making it a suitable probe for studying metal-ligand interactions and their time-dependent stability [4] [5]. Previous studies have primarily focused on single-metal systems; however, a comparative understanding of different metal ions under identical conditions can reveal valuable insights into coordination tendencies and kinetic profiles.

Resorcinol and its derivatives have been widely employed in analytical chemistry for applications such as spectrophotometric determination of metal ions [4], dye synthesis [6], pharmaceutical analysis [7], and sensing of phenolic or redox-active species [1]. In metal ion detection, resorcinol-based systems have been explored for their ability to form colored complexes without the need for sophisticated instrumentation. In contrast, many conventional metal ion detection methods rely on complexing agents such as dithizone, EDTA, 1,10-phenanthroline, Schiff bases, azo dyes, or fluorescent probes, which often require multistep synthesis, stringent pH control, masking agents, or advanced techniques such as atomic absorption spectroscopy (AAS), inductively coupled plasma-mass spectrometry (ICP-MS), or high-performance liquid chromatography (HPLC) [8]-[10]. While these methods offer high sensitivity and selectivity, they are typically time-consuming, expensive, and less suitable for rapid or field-based analysis. Therefore, a simple resorcinol-based colorimetric approach, combined with time-resolved UV-Visible monitoring, provides an attractive alternative for understanding metal ion selectivity and complexation kinetics, highlighting the practical importance of this method for low-cost analytical and sensing applications.

While spectroscopically inactive ions such as Mg^{2+} can induce ligand-centered chromophores, transition metal ions may exhibit metal-centered d-d transitions or, in some cases, no visible absorption at all. Understanding these differences is essential for rational interpretation of spectral data and for the development of selective analytical methods. In this work, we present a systematic comparison of the UV-Vis behavior of resorcinol in NH_4OH in the presence of Mg^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Fe^{2+}, emphasizing the mechanistic origins of their distinct spectral responses.

2. Experimental Section

2.1. Materials and Reagents

Resorcinol (≥99%), copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), $ZnSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, $MgSO_4$ and $FeSO_4 \cdot 7H_2O$ ammonium hydroxide (NH_4OH), and distilled water were used without further purification. All glassware, including flat-bottom volumetric flasks, pipettes, cuvettes, and test tubes, was thoroughly cleaned and rinsed with distilled water prior to use to avoid contamination.

2.2. Preparation of Metal Ion Solutions

A stock solution of $CuSO_4·5H_2O$ (0.01 M) was prepared by dissolving 0.2497 g of $CuSO_4·5H_2O$ (molar mass = 249.685 $g·mol^{-1}$) in distilled water and diluting to a final volume of 100 mL in a volumetric flask. The solution was agitated until complete dissolution was achieved.

A 0.001 M $CuSO_4·5H_2O$ solution was prepared by transferring 10 mL of the 0.01 M stock solution into a 100 mL volumetric flask and diluting to volume with distilled water. Similarly, a 0.0001 M solution was obtained by diluting 10 mL of the 0.001 M solution to 100 mL using distilled water. All solutions were stored in airtight containers and used for subsequent analysis. The same dilution protocol was applied for the preparation of other metal ion solutions when required.

The same solution preparation and serial dilution procedures were followed for other metal ions (Mg^{2+}, Ni^{2+}, Zn^{2+}, and Fe^{2+}), with all metal ion solutions prepared from their respective sulfate salts using distilled water.

2.3. Preparation of Resorcinol-Metal Ion Complexes

Colorimetric measurements were performed using a UV-Visible spectrophotometer equipped with matched quartz cuvettes. Distilled water was used as the blank. A resorcinol solution (0.5 M) was prepared separately and used throughout the experiments.

For complex formation, 5 mL of 0.5 M resorcinol solution was transferred into a clean Pyrex test tube, followed by the addition of 1 mL of ammonium hydroxide to establish alkaline conditions. Subsequently, 1 mL of the prepared metal ion solution was added to the mixture. Immediately after addition of the metal ion solution, the reaction mixture was agitated to ensure homogeneous mixing, and the reaction time was recorded using a stopwatch.

An aliquot of the resulting mixture was transferred into a cuvette, sealed with a lid, and used for spectroscopic analysis.

2.4. UV-Visible Spectrophotometric Measurements

Thermo Scientific-Evolution One UV-Vis spectrophotometer was used for data collection. UV-Visible absorbance measurements were recorded at 10-minute intervals over a period of 70 minutes using distilled water as the blank. The absorbance spectra were collected in the visible region to monitor the formation and time-dependent evolution of the resorcinol-metal ion complexes. The blank cuvette was re-measured as necessary to maintain baseline accuracy. All measurements were performed under identical instrumental conditions to ensure comparability of results. Spectra were collected in the range 400 - 800 nm at regular time intervals after mixing resorcinol with the respective metal ion in NH_4OH. Control experiments were performed using resorcinol in NH_4OH without added metal ions.

3. Results and Discussion

3.1. Blank and Control Experiments

Resorcinol in NH_4OH without metal ions exhibits no distinct absorption peak in the visible region. The spectra are shown in Figure 1(a). The spectra show only a weak, featureless absorbance tail that decreases monotonically with increasing wavelength and remains essentially unchanged with time. This confirms that alkaline conditions alone do not generate visible chromophores and establishes a reliable baseline for assessing metal-induced spectral changes.

Fe^{2+} displays a spectral response indistinguishable from the blank with no observable absorption maxima or time-dependent evolution in the visible region. However, the absorption intensity is higher for the Fe^{2+} solution. Figure 1(b) shows the UV-Vis spectrum of the solution containing Fe^{2+} ions. This indicates that Fe^{2+} does not promote ligand-centered chromophore formation under these conditions, nor does it produce stable, detectable metal-centered transitions in the examined wavelength range.

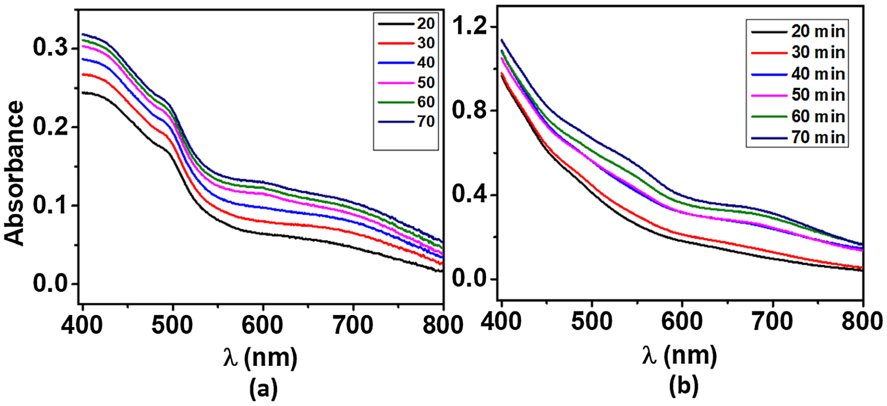

Figure 1. UV-Vis spectra recorded at 10-minute intervals after mixing resorcinol (in NH_4OH) without (a) metal ion and (b) Fe^{2+} ion. No absorption peaks are observed in both cases.

3.2. Magnesium (II): Ligand-Centered Chromophore Formation

In the presence of Mg^{2+}, a broad visible absorption band develops and intensifies with time. Figure 2(a) shows the UV-Vis spectra of the solution containing Mg^{2+} ions. Notably, the absorption envelope undergoes a pronounced bathochromic shift, with the apparent maximum moving progressively toward longer wavelengths. Because Mg^{2+} is a d^0 ion and lacks intrinsic visible electronic transitions, the observed absorption must be ligand-centered. The spectral evolution is therefore attributed to deprotonation of resorcinol followed by coordination to Mg^{2+} and gradual reorganization of Mg-resorcinolate species, leading to increased electronic delocalization. The absence of an isosbestic point suggests the coexistence of multiple Mg-resorcinolate species rather than a simple two-state interconversion.

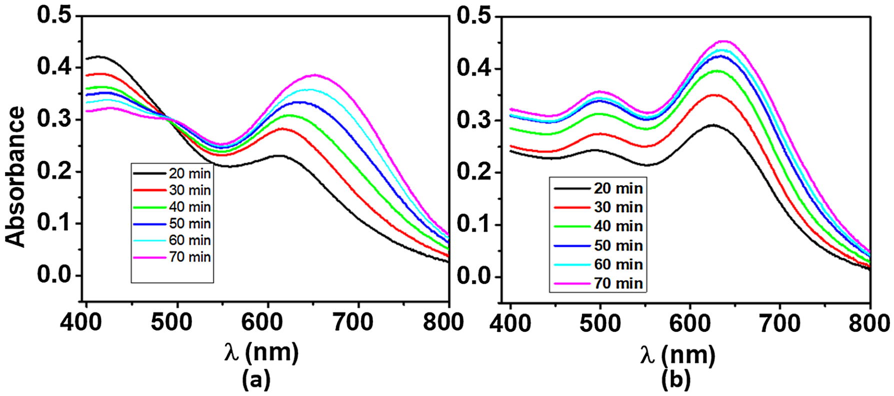

Figure 2. UV-Vis spectra recorded at 10-minute intervals after mixing resorcinol (in NH_4OH) with (a) $Mg^{2+}$and (b)Ni^{2+}. The absorption peaks shift from lower to higher wavelengths with the time passage and the peak intensity increases monotonically from 20 to 70 min while the shapes remain constant.

3.3. Nickel (II): Ligand-Field Modulation

Figure 2(b) shows the UV-Vis spectra of the solution containing Ni^{2+} ions. Ni^{2+} exhibits two broad absorption features in the visible region, centered near ~500 nm and ~600 - 630 nm, characteristic of spin-allowed d-d transitions in octahedrally coordinated d^8 systems. The absorbance of these bands increases with time, accompanied by a small but systematic red shift. This behavior reflects gradual changes in ligand-field strength as resorcinol coordinates to Ni^{2+}. Unlike Mg^{2+}, the transitions remain metal-centered, limiting the magnitude of the wavelength shift.

3.4. Copper (II): Jahn-Teller-Dominated Behavior

Figure 3(a) shows the UV-Vis spectra of the solution containing Cu^{2+} ions. Cu^{2+} displays a broad visible absorption band whose intensity increases with time but whose λmax remains essentially constant. This behavior is consistent with the strong Jahn-Teller distortion inherent to d^9 Cu^{2+} complexes, which dominates the electronic structure and renders d-d transition energies relatively insensitive to incremental ligand substitution. As a result, no measurable red shift is observed despite coordination with resorcinol. Although Cu^{2+} was examined at a tenfold lower concentration to remain within the linear absorbance range, its lack of bathochromic shift is concentration-independent and reflects the Jahn-Teller-dominated electronic structure of d^9 Cu^{2+} complexes.

3.5. Zinc (II): Spectroscopically Silent Metal Ion

Figure 3(b) shows the UV-Vis spectra of the solution containing Zn^{2+} ions. Zn^{2+} (d^{10}) shows no discernible red shift and only modest intensity changes relative to the blank. Because Zn^{2+} lacks low-energy electronic transitions, any observed absorption is weak and ligand-based. The absence of a red shift indicates that Zn^{2+} does not induce significant electronic delocalization in resorcinol comparable to that observed for Mg^{2+}.

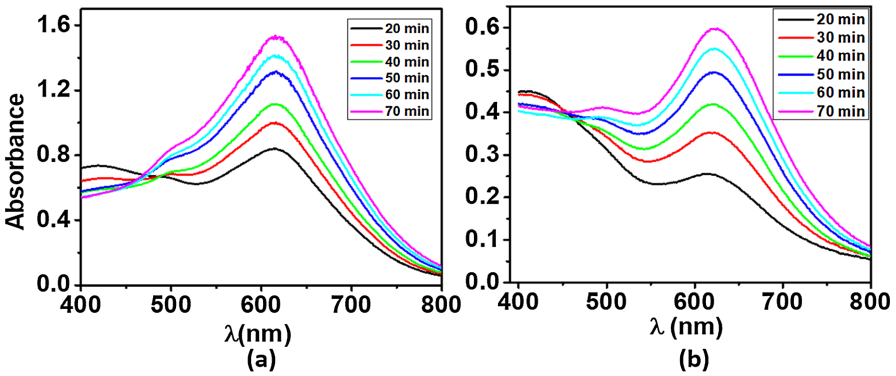

Figure 3. UV-Vis spectra recorded every 10 min after mixing resorcinol (in NH_4OH) with metal ion solutions. (a) Cu^{2+} (initially 0.0001 M) spectra showing much higher molar absorptivity and similar time-dependent intensity growth. (b) Zn^{2+} (0.001 M) spectra showing increasing intensity of the broad band centered at ~620 nm.

3.6. Comparative Analysis and Metal Selectivity

The contrasting spectral behaviors of the studied metal ions are summarized in Table 1.

Table 1. Comparative UV-Vis behavior of resorcinol in NH_4OH in the presence of divalent metal ions.

Metal ion	d-electron configuration	Visible absorption	Red shift	Dominant origin
Mg^{2+}	d^0	Strong	Yes	Ligand-centered chromophore
Ni^{2+}	d^8	Moderate	Small	Metal-centered (d-d)
Cu^{2+}	d^9	Very strong	No	Jahn-Teller-dominated d-d
Zn^{2+}	d^{10}	Weak	No	Ligand-based, weak
Fe^{2+}	d^6	None	No	No effective chromophore

All metal ion solutions were prepared at an initial concentration of 0.001 M, except for Cu^{2+}, which was studied at 0.0001 M to avoid detector saturation due to its high absorbance. Spectral trends (presence or absence of red shift, band shape, and mechanistic origin) are therefore compared qualitatively rather than on absolute absorbance intensity measured at 0.0001 M Cu^{2+}; higher concentrations exceeded the instrument's linear absorbance range.

These results demonstrate that metal selectivity in this system is governed primarily by electronic structure rather than coordination alone. Only Mg^{2+} produces a strong, red-shifting ligand-centered response, enabling clear discrimination from transition metals such as Ni^{2+} and Cu^{2+}, as well as spectroscopically silent ions such as Zn^{2+} and Fe^{2+}.

4. Conclusion

A systematic UV-Vis investigation of resorcinol in alkaline media reveals fundamentally different optical responses depending on the identity of the metal ion. Mg^{2+} uniquely induces a strong, time-dependent, red-shifting visible absorption band arising from ligand-centered chromophore formation. Ni^{2+} exhibits metal-centered d-d transitions with modest ligand-field modulation, while Cu^{2+} and Zn^{2+} show no red shift due to Jahn-Teller stabilization and d^{10} electronic configuration, respectively. Fe^{2+} produces no detectable spectral features beyond the blank. These findings establish a clear electronic-structure-based framework for understanding metal selectivity in resorcinol-based spectrophotometric systems and provide guidance for the rational design of selective metal-ion sensing methods.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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