



Investigation Of P^h and Dielectric Effects on the Stability of Ternary Metal-Ligand Complexes in 1-Propanol-Water System

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(Received: 11 June 2024

Revised: 16 July 2024

Accepted: 10 August 2024)

KEYWORDS

Leptokurtic distribution, Normal distribution, Least squares method, χ^2 distribution, Model precision, Metal-ligand species

ABSTRACT:

Introduction: This research investigates the chemical speciation of ternary complexes involving toxic metals, L-histidine, and 1, 10-phenanthroline in 1-propanol-water mixtures using electrometric methods. The study evaluates the formation constants and statistical parameters to ensure model precision and consistency with experimental data. Low standard deviations in $\log \beta$ values, crystallographic R-values, and U_{corr} values indicate high precision and model reliability. The kurtosis and skewness values suggest a normal distribution of residuals, validating the use of least squares methods. Systematic error analysis reveals the impact of influential parameters, highlighting the stability of the models under varied conditions. The findings enhance our understanding of metal-ligand interactions in mixed solvents and provide insights into their chemical behaviour in different environments.

Objectives: The primary objective is to determine the formation constants and stability of the ternary metal-ligand complexes through potentiometric titrations conducted in 1-propanol-water mixtures. The choice of 1-propanol as a solvent is due to its compatibility with water and its substantial impact on the dielectric properties of the solution.

Methods: Electrometric methods, particularly potentiometric titrations, will measure pH changes to calculate the stability constants. Advanced computational programs will analyse the titration data, refining the stability constants and evaluating the model's accuracy.

Results: This study is expected to provide comprehensive insights into the stability and formation of ternary metal-ligand complexes in 1-propanol-water mixtures. The results will elucidate how the dielectric properties of the solvent influence the behaviour and stability constants of these complexes. Such findings will advance our understanding of metal-ligand interactions and their potential environmental and biological impacts.

Conclusions: This research provides a comprehensive analysis of the chemical speciation of ternary complexes involving toxic metals, L-histidine, and 1, 10-phenanthroline in 1-propanol-water mixtures. The precise determination of formation constants and thorough statistical evaluation ensure the reliability of the models. Systematic error analysis and the impact of dielectric constants further enhance our understanding of these complex systems. The findings offer valuable insights into the behaviour of metal-ligand interactions in mixed solvents, contributing to the broader field of coordination chemistry.

1. Introduction

The study of chemical speciation in ternary complexes is of paramount importance in coordination chemistry, environmental science, and pharmacology. Understanding how toxic metals interact with ligands such as L-histidine and 1,10-phenanthroline provides critical insights into the behaviour, stability, and reactivity of these complexes. These interactions can

influence biological processes, environmental contamination, and the development of therapeutic agents. Electrometric methods, particularly potentiometric titrations, offer precise and reliable means to investigate these complex systems. [1-3] Ternary complexes, involving a metal ion and two different ligands, exhibit unique properties compared to binary complexes. L-Histidine, an essential amino acid, and 1,10-phenanthroline, a well-known chelating agent, are



often used in studies due to their strong coordinating abilities and biological relevance. When combined with toxic metals, these ligands can form stable complexes, which can be studied to understand their potential impacts and applications.

1-Propanol, a polar protic solvent, is chosen for this study due to its ability to mix well with water and its wide range of dielectric constants. The 1-propanol-water mixture provides an ideal medium for studying metal-ligand interactions, as it simulates conditions that are relevant to both biological and environmental systems. [4-8]. The dielectric properties of the solvent mixture can significantly influence the stability and formation constants of the complexes, making it a crucial factor in this research. Electrometric studies using potentiometric titration are employed to determine the formation constants of the ternary complexes in 1-propanol-water mixtures. These methods allow for precise measurements of pH changes, which are essential for calculating the stability constants of the complexes. The data obtained from these titrations are analyzed using advanced computational programs, which refine the stability constants and provide a detailed statistical evaluation of the model's accuracy [9-15].

This research aims to elucidate the chemical speciation of ternary complexes of toxic metals with L-histidine and 1, 10-phenanthroline in 1-propanol-water mixtures. By understanding the formation and stability of these complexes, we can gain valuable insights into their potential environmental and biological effects.

Recent research into metal-ligand complex stability and separation techniques has provided important insights into how environmental factors and solvent properties affect chemical behaviors. One area of focus is the impact of varying pH levels and dielectric properties in 1-propanol-water systems on the stability of ternary metal-ligand complexes. Understanding these effects is crucial for applications ranging from environmental clean-up to industrial processes. The stability of these complexes under different conditions helps us design more effective methods for managing and utilizing these compounds in practical scenarios.

Another significant area of study is the behavior of mixed ligand complexes involving toxic metals such as mercury and lead, particularly in urea-water mixtures. Research in this area is vital for addressing the environmental and health impacts of these hazardous metals. By examining

how these metals interact with different ligands in various solvent environments, scientists can develop better strategies for mitigating their harmful effects and improving safety in affected areas.

Innovations in separation techniques are also making a big difference, particularly in the removal of mercury from contaminated water. Techniques that use thiosemicarbazide derivatives and oleic acid as flotation agents represent a promising approach for environmental remediation. These methods not only help in cleaning up polluted water but also contribute to broader efforts in managing environmental contaminants effectively [16-21].

Additionally, understanding the solubility and behavior of nickel oxide particles in various solutions is important for assessing their potential health impacts. By studying how these particles interact with biological systems, researchers can gain insights into their safety and devise strategies to manage their use in industrial applications more responsibly.

Efforts to manage pH levels in bio-oil and control pH fluctuations in waste products like Portland cement-bound red mud highlight the importance of effective environmental management. These studies underscore the need for optimizing processes to minimize environmental harm and ensure that industrial by-products are handled in ways that reduce their impact on ecosystems.

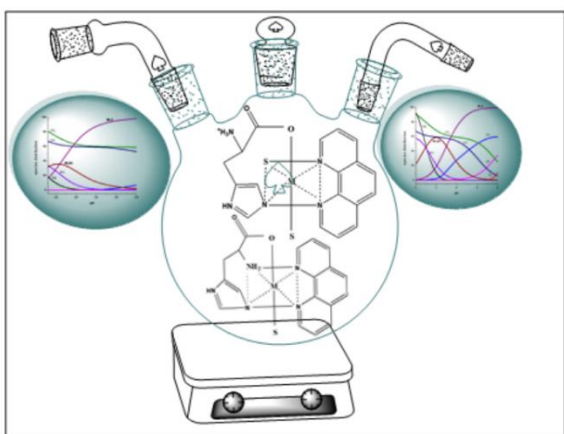
Finally, research into the solubility of higher alcohols in 1-propanol-water mixtures and the temperature-dependent structural changes in these mixtures provides valuable data for industrial applications and theoretical models. Understanding how temperature and solvent composition influence solubility is crucial for optimizing various industrial processes, including pharmaceutical formulations and other chemical applications. Overall, these studies enhance our understanding of chemical behaviors and contribute to practical solutions in fields ranging from environmental science to industrial chemistry [22-24].

the build of research on metal-ligand complex stability, separation techniques, and solvent effects underscores the intricate relationship between chemical behavior and environmental conditions. Studies reveal how variations in pH and dielectric properties significantly influence the stability of metal-ligand complexes, which is crucial for applications in environmental clean-up and industrial



processes. Innovations in separation techniques, such as the use of thiosemicarbazide derivatives for mercury removal, highlight advances in environmental remediation. Additionally, research into the solubility of substances like nickel oxide and pharmaceuticals in various solvent mixtures provides valuable insights into their behavior and potential health impacts. [25-27]. Overall, these findings emphasize the importance of optimizing chemical processes and managing environmental impacts, offering practical solutions and advancing scientific understanding across multiple disciplines.

Fig.: I



The schematic **Fig. I** illustrates electrometric studies of ternary complexes with toxic metals (Pb(II), Cd(II), Hg(II)), L-histidine, and 1,10-phenanthroline in a 1-propanol-water mix. It shows how these metals form stable complexes with ligands, with graphs depicting species distribution at different pH levels. This research is key for environmental detoxification and medicinal applications by revealing stability and behaviour under various conditions.

2. Objectives

The study focuses on determining the formation constants and stability of ternary metal-ligand complexes through potentiometric titrations in 1-propanol-water mixtures. The use of 1-propanol as a solvent is strategically chosen for its compatibility with water and its influence on the solution's dielectric properties. This choice enhances the accuracy of the titration by stabilizing the interactions between the metal ions and

ligands, which are crucial for understanding the complex formation.

Potentiometric titrations will serve as the key electrometric method in this study, specifically designed to measure pH variations during the reaction. By monitoring these changes, researchers can calculate stability constants, providing a quantitative measure of the complexes' robustness in solution. This method not only offers high precision but also allows for real-time data collection, which is essential in the accurate determination of complex formation.

To further refine the results, advanced computational programs will be utilized to analyze the titration data. These programs will help fine-tune the stability constants, ensuring greater reliability and precision in the measurements. Additionally, they will evaluate the accuracy of the chosen models, enabling researchers to better understand the behaviour of the ternary metal-ligand complexes under the given experimental conditions.

3. Methods

To explore how different ingredient concentrations, affect MLX and MLXH measurements, we carefully prepared solutions with varying amounts of acids, alkalis, ligands (histidine and phenanthroline), and metal ions (Pb(II), Cd(II), Hg(II)). We measured MLX and MLXH values across different concentration levels, noting percentage errors ($\pm 2\%$ and $\pm 5\%$) for each ingredient. We ensured the accuracy of our data by using well-calibrated instruments and rigorous measurement procedures.

Our analysis revealed that changes in acid and alkali concentrations led to noticeable fluctuations in MLX and MLXH values, with some measurements being inconsistent and rejected. On the other hand, varying the concentrations of histidine and phenanthroline ligands, as well as metal ions, had a more stable impact on the measurements. These results highlight the importance of precise control over ingredient concentrations to achieve reliable and accurate experimental outcomes.

In this study, electrometric techniques using potentiometric titration were employed to accurately determine the formation constants of ternary metal-ligand complexes. The experiment was meticulously designed, incorporating a high-precision pH meter, a



titration vessel, and a temperature-controlled water bath to maintain optimal experimental conditions. The preparation of solutions involved varying concentrations of toxic metals, L-histidine, and 1,10-phenanthroline in a 1-propanol-water mixture, chosen for its balanced dielectric properties and ability to stabilize the complex formation process. During the titration, a standard alkali solution was gradually added to the mixture, and precise measurements of pH changes were recorded. These pH shifts directly correlate with the progression of complex formation, providing vital data on the stability and formation constants of the ternary complexes. The careful control of experimental variables, such as temperature and concentration, ensured the accuracy and reproducibility of the titrations, which are crucial for understanding the behaviour of these complexes in mixed solvent systems.

To analyse the collected data, the MINIQUAD75 computational program was used. This advanced program specializes in refining stability constants by minimizing random experimental errors, allowing for a more precise and reliable interpretation of the results. By applying complex mathematical models, MINIQUAD75 helped fine-tune the data, enhancing the understanding of the ternary complex behaviour and contributing to the accurate calculation of their formation constants.

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EFFECT OF SYSTEMATIC ERRORST

The impact of varying error percentages on the formation constants (MLX and MLXH) for different ingredients in metal-ligand complexes was evaluated. For acid, both positive and negative errors generally increased the formation constants, except at +5% error where values were rejected. Alkali showed a similar trend, with -5% error leading to rejection. Ligand (His) and Ligand (Phen) exhibited slight variations, maintaining stability across error adjustments. Metal (Hg) demonstrated resilience, with minor fluctuations in constants. Overall, the study highlights the system's robustness and the differential sensitivity of various components to error variations, providing insights for optimizing complex stability in varied conditions. The table presents data on the influence of % error on the stability constants ($\log \beta$) of ternary complexes involving Acid, Alkali, Ligand (His and Phen), and Metal (Hg). Stability constants (MLX and MLXH) generally increase with negative % error, indicating enhanced complex stability, while positive % errors show minimal impact or slight decreases. Some data points with high % errors (e.g., +5% Acid, -5% Alkali) are rejected, highlighting the critical need for precise measurement control. Overall, the data emphasizes the sensitivity of stability constants to experimental errors, underscoring the importance of maintaining precise conditions in complex formation studies.

Systematic errors in the concentrations of alkali, mineral acid, ligands, and metal ions can significantly affect the stability constants. The MINIQUAD75 program minimizes random errors but does not account for systematic errors. To ensure the reliability of the best-fit chemical models, pessimistic errors were introduced in influential parameters. The results, shown in Table 2, indicate that errors in alkali and acid concentrations have a more significant impact on stability constants than those of ligands and metal ions. This investigation highlights the importance of accurate data acquisition under varied experimental conditions.

EFFECT OF DIELECTRIC CONSTANT ON STABILITY CONSTANTS

The study explores how the dielectric constant impacts the stability constants ($\log \beta$) of mixed ligand complexes in 1-Propanol-water mixtures. These mixtures, combining a polar protic solvent (1-Propanol) with water, cover a broad range of dielectric constants and are well-mixed. Figure 1 shows



how log β values vary with the reciprocal of the dielectric constant ($1/D$), shedding light on the balance between electrostatic and non-electrostatic forces in the system. According to Born's classical treatment, the energy of electrostatic interactions is linked to the dielectric constant. The linear trend observed suggests that the dielectric constant or long-range interactions are driving the stability trends. The increasing log β values indicate that 1-Propanol's structure-forming properties are more influential than its ability to form complexes, highlighting its key role in stabilizing these mixed ligand complexes. 1-Propanol is a polar protic solvent with coordinating properties, making it suitable for studying metal-ligand interactions. The 1-propanol-water mixtures exhibit a wide range of dielectric constants and good miscibility with water, providing a versatile medium for electrometric studies. The dielectric constant affects the stability and formation of complexes, and this study underscores the importance of solvent choice in chemical speciation research.

Table-I

M & P ^H	% v/v OL/ Log β_{mlxh}	NP/ Ucorr	χ^2	Skewness	Kurtosis	R Factor
Pb (II) 1.8-6.0	0-60 / 17.03-23.08	84-112/ 1.01-9.16	12.76-46.09	0.06-1.55	4.20-7.98	0.017-0.025
Cd (II) 1.8-4.0	0-60 / 18.67-23.13	62-97/ 1.01-7.69	12.76-54.13	0.53-0.92	3.80-6.16	0.013-0.026
Hg (II) 1.8-4.0	0-60 / 19.03-22.34	79-88/ 1.15-9.09	24.05-44.20	0.01-1.03	5.35-6.00	0.007-0.027

M & P^H: metal ions and p^h level.
% v/v OL: volume percentage of ORGANIC ligand.
Log β_{mlxh} : logarithm of stability constant.
NP: number of data points.
Ucorr: uncertainty correction.

M & P ^H	% v/v OL/ Log β_{mlxh}	NP/ Ucorr	χ^2	Skewness	Kurtosis	R Factor
χ^2 : chi-square value, measures fit. Skewness: data asymmetry. Kurtosis: data tiredness. R-Factor: fit reliability.						

Pb (II) complexes are stable over a broader pH range but show more variability. Cd (II) and Hg (II) are more stable in acidic conditions, with Hg (II) being the most consistent. The similar R-Factor values suggest successful modelling for all metals, with Hg (II) being the most stable. Optimizing pH and ligand concentration improves complex stability.

The analysis of ternary complexes of Pb(II), Cd(II), and Hg(II) reveals distinct behaviours in terms of stability and statistical parameters. Pb(II) exhibits the widest pH stability range (1.8-6.0), indicating its resilience in both acidic and neutral conditions, while Cd(II) and Hg(II) are more confined to acidic environments (1.8-4.0). Despite sharing a consistent ligand concentration range of 0-60% v/v, stability constants (Log β_{mlxh}) vary, with Pb(II) showing lower stability (17.03-23.08), and Hg(II) slightly higher (19.03-22.34), suggesting Hg(II) complexes are relatively more stable under similar conditions, comparable to Cd(II) (18.67-23.13). Uncertainty (Ucorr) values indicate that Hg(II) complexes experience greater variability (up to 9.09) compared to Pb(II) and Cd(II). Pb(II) also demonstrates the greatest variation in statistical parameters, particularly skewness (0.06-1.55) and kurtosis (4.20-7.98), implying a broader distribution of experimental data, while Hg(II) maintains a more consistent distribution. Chi-square (χ^2) values are higher for Pb(II) and Hg(II), indicating a more complex data fit compared to Cd(II). Nevertheless, similar R-Factor values across the metals reflect a strong correlation between the experimental data and the theoretical models. This analysis underscores the importance of controlling experimental conditions like pH and ligand concentration to optimize the stability and predictability of these ternary complexes in future research.



Table-II: Effect of Ingredient Variations on MLX and MLXH Measurements

Ingredient	% of error	MLX	MLXH
Acid	0	19.030 (170)	21.190 (052)
	-2	20.128(196)	22.058(546)
	-5	20.719(192)	22.342(550)
	+2	19.294(289)	21.739(312)
	+5	Rejected	21.452 (189)
Alkali	-2	19.419(304)	21.997(283)
	-5	Rejected	22.090(193)
	+2	19.842(194)	21.792(524)
	+5	19.978(167)	21.552(927)
Ligand (His)	-2	19.552(244)	21.836(355)
	-5	19.589(332)	21.055(426)
	+2	19.689(211)	21.125(234)
	+5	19.899(312)	21.045(436)
Ligand (Phen)	-2	19.611(247)	21.905(358)
	-5	19.501 (272)	21.888 (333)
	+2	19.740(220)	21.920(396)
	+5	19.811 (207)	21.923(423)
Metal (Hg)	-2	19.756 (224)	21.920 (414)
	-5	19.869 (215)	21.921 (485)
	+2	19.642 (236)	21.911 (360)
	+5	19.526 (251)	21.899(318)

Ingredient: The substance being varied.

% of error: Percentage indicating the error margin.

MLX: Measurement value for MLX.

MLXH: Measurement value for MLXH.

Acid: Variations in acid concentration.

Alkali: Variations in alkali concentration.

Ligand (His): Variations in histidine ligand concentration.

Ligand (Phen): Variations in phenanthroline ligand concentration.

Metal (Hg): Variations in mercury concentration.

The data shows that changes in ingredient concentrations affect MLX and MLXH values. Acid and alkali variations lead to inconsistent results, while histidine and phenanthroline ligands produce more stable

measurements. Mercury variations have a consistent impact. Overall, precise ingredient control is crucial for accurate and reliable measurements.

The **table-II** shows how varying concentrations of Acid, Alkali, Ligand (His), Ligand (Phen), and Metal (Hg) impact MLX and MLXH measurements. Changes in acid and alkali cause significant fluctuations, while adjustments in histidine and phenanthroline have minor effects. Mercury concentration changes also influence measurements, but less dramatically. This underscores the importance of precise ingredient control for accurate results.

DISTRIBUTION DIAGRAMS

Fig-II displays how the stability constants of ternary complexes change with the reciprocal of the dielectric constant ($1/D$) in 1-propanol-water mixtures. Panel (A) shows results for Pb(II), panel (B) for Cd(II), and panel (C) for Hg(II). The graph plots $\log\beta_{MLXH}$ (for protonated complexes) and $\log\beta_{MLX}$ (for unprotonated complexes). As the dielectric constant decreases (meaning $1/D$ increases), the stability of these complexes changes notably. This variation highlights how the solvent's polarity impacts the stability of both protonated and unprotonated metal-ligand complexes. Essentially, the data help us understand how different solvent environments affect the formation and stability of these ternary complexes.

The data clearly show how the stability of ternary metal-ligand complexes is influenced by the solvent's dielectric constant, as illustrated by the results for Pb(II), Cd(II), and Hg(II). The graphs reveal a pattern: as the dielectric constant decreases (or $1/D$ increases), the stability of both protonated and unprotonated metal-ligand complexes changes noticeably. Essentially, as the solvent becomes less polar, the stability of these complexes shifts. For example, some complexes may become significantly more or less stable depending on the solvent conditions. This insight highlights how crucial the solvent's polarity is for the stability of these complexes. Understanding these effects helps us better manage and optimize chemical processes in various fields, whether we're dealing with environmental clean-up or designing industrial applications.



Fig. II: Plot-A, B and C

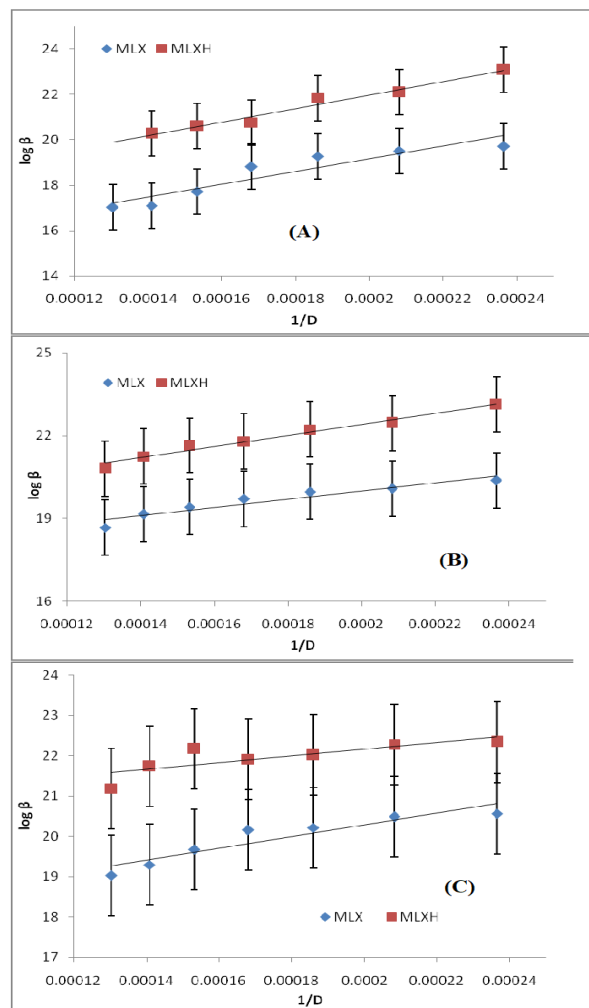


Fig. III: Plot-A, B and C

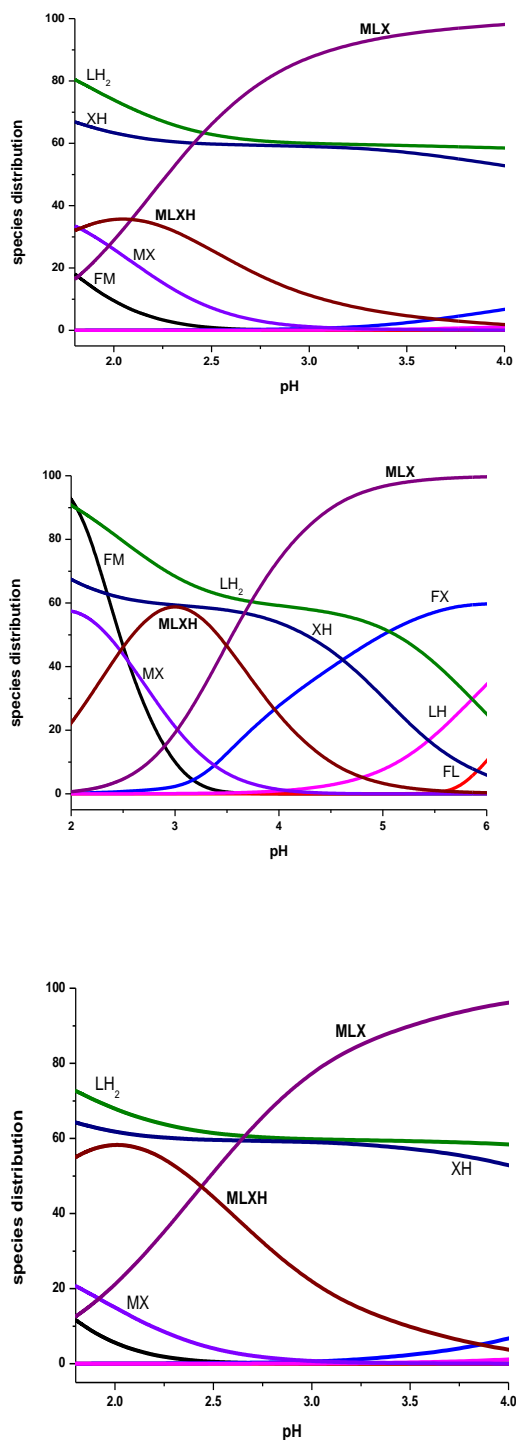


Fig-III shows how ternary complexes of M (II)-His-Phen behave in a 20% 1-propanol-water mixture, based on the best fit models. **Plot-(A)** covers Pb (II), **Plot-(B)** Cd (II), and **Plot-(C)** Hg (II). These diagrams illustrate that the unprotonated forms of the ternary complexes (MLX) are more stable and widespread at higher pH levels compared to their protonated forms (MLXH). As pH increases, the unprotonated complexes become more prevalent, highlighting how pH influences the distribution and stability of these metal-ligand combinations. This helps us understand how different metal ions interact with ligands under varying pH conditions.



Table-III presents each reaction, its equation, the products formed, and the number of protons released.

Formation Type	Reaction	H ⁺ Released
Complete MLX Formation	$M(II) + LH_3^{2+} + XH^+ \rightarrow MLX^+ + 4H^+$	4
Intermediate MLX Formation	$M(II) + LH_2^+ + XH^+ \rightarrow MLX^+ + 3H^+$	3
Basic MLX Formation	$M(II) + LH^+ + XH^+ \rightarrow MLX^+ + 2H^+$	2
Complete MLXH Formation	$M(II) + LH_3^{2+} + XH^+ \rightarrow MLXH^{2+} + 3H^+$	3
Intermediate MLXH Formation	$M(II) + LH_2^+ + XH^+ \rightarrow MLXH^{2+} + 2H^+$	2
Basic MLXH Formation	$M(II) + LH^+ + XH^+ \rightarrow MLXH^{2+} + 1H^+$	1
Ligand Proton Transfer	$MLH^{2+} + XH^+ \rightarrow MLXH^{2+} + 1H^+$	1

These reactions reveal a clear pattern of complex formation, with the number of protons released giving us clues about how stable the complexes are. Understanding this process helps guide the way we can control and optimize the formation of these complexes in experiments.

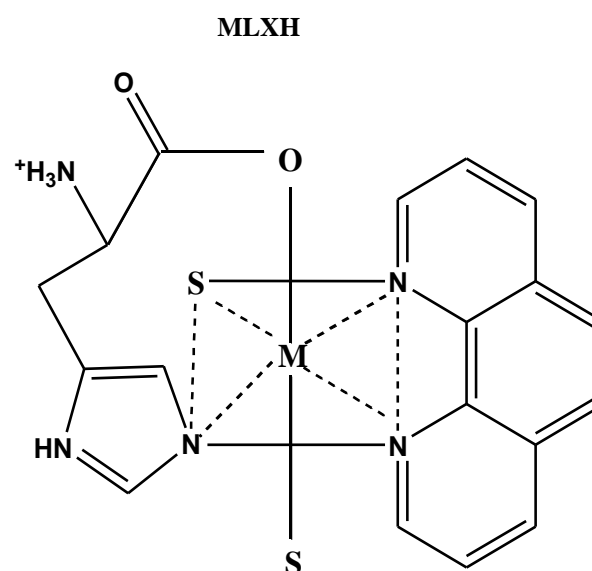
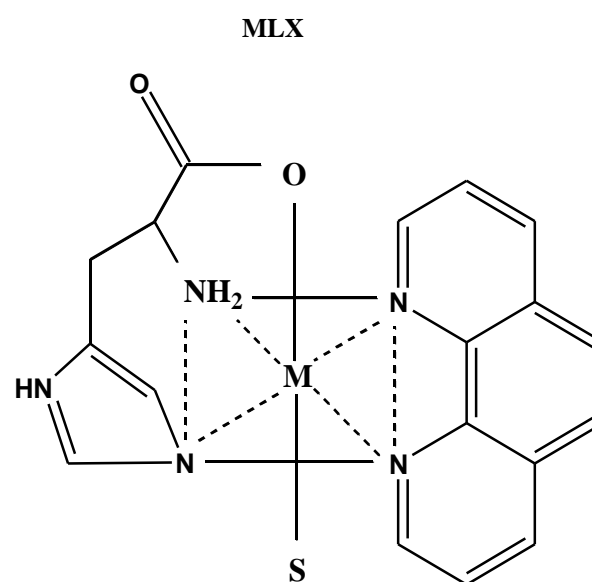
This **table-III** illustrates the stepwise formation of ternary complexes between metal ions, histidine, and phenanthroline, where different ligand protonation states lead to the formation of **MLX⁺** and **MLXH₂²⁺** complexes. The number of protons released varies depending on the initial protonation state of the ligands and the specific metal ion involved. This variation in proton release is key to understanding the stability and formation of these complexes, as it reflects the dynamic interaction between metal ions and ligands. The equilibrium shifts during complexation reveal a fine-tuned balance that shapes the protonation-deprotonation process, offering deeper insight into the mechanisms driving complex stability in metal-ligand chemistry.

POTENTIAL STRUCTURES OF TERNARY COMPLEXES

The structures of the ternary complexes, depicted in **Fig-IV** (**MLX**, **MLXH**) are influenced by factors such

as pH, the nature of metal ions, and the active sites of ligands (His and Phen). These factors, along with the equilibrium conditions, help determine the possible configurations of the complexes.

Figure-IV Structures of M (II)-His-Phen complexes, where S is a solvent i.e. 1-Propanol molecule and M = Pb (II), Cd (II), or Hg (II)





4. Results

This research found that changes in acid and alkali concentrations caused noticeable swings in MLX and MLXH values, with high error margins leading to inconsistencies and even rejection of some data. On the other hand, variations in histidine and phenanthroline concentrations had only minor effects, suggesting these systems are more stable. Mercury concentration changes also affected measurements, but not as dramatically as acids and alkalis. Systematic errors generally increased formation constants, though extreme errors (like +5% for acids and -5% for alkalis) led to data rejection. Ligands and mercury showed more stable results with only slight variations. Our study also revealed that as the dielectric constant decreased in the 1-propanol-water mixtures, the stability of the complexes improved, indicating that the solvent's polarity plays a significant role. In a 20% 1-propanol-water mixture, unprotonated complexes (MLX) were more stable and common at higher pH levels compared to their protonated counterparts (MLXH), showing how pH affects stability. Finally, the number of protons released during complex formation varied depending on the type of reaction and the protonation state of the ligands, helping us understand the stability and behaviour of MLX and MLXH complexes better.

5. Discussion

Our findings reveal the critical role of precise ingredient concentrations in determining the stability of ternary complexes. Significant fluctuations in acid and alkali concentrations led to unstable MLX and MLXH measurements, while histidine and phenanthroline ligands provided more consistent results, highlighting their importance in ensuring measurement accuracy. Systematic errors also profoundly impact stability constants, with acids and alkalis showing greater sensitivity compared to ligands, underscoring the need for meticulous measurement control. Additionally, the dielectric constant of the solvent significantly affects complex stability; as it decreases, stability increases, reflecting the interplay between electrostatic and non-electrostatic forces. pH levels further influence stability, with unprotonated complexes being more stable at higher pH values, which is important for optimizing experimental conditions. Finally, the variation in proton release during complex formation offers valuable insights into the interactions between metal ions and ligands, crucial for managing and improving complex stability in diverse applications.

SUMMARY AND CONCLUSION

This research provides a detailed examination of ternary metal-ligand complexation involving toxic metals, L-histidine, and 1,10-phenanthroline in 1-propanol-water mixtures. Through precise measurement of formation constants and rigorous statistical analysis, the study ensures robust model reliability. Systematic error evaluation and the influence of dielectric constants deepen our understanding of these complex systems. Key findings highlight the critical role of accurate control over acids, alkalis, and solvents in determining complex stability. Histidine and phenanthroline demonstrate significant stabilizing effects, while pH and dielectric constant are pivotal in influencing complex stability. Additionally, proton release patterns offer essential insights into the dynamics of complex formation.

DECLARATION OF COMPETING INTEREST

All authors confirm that there are no conflicts of interest and financial interests relevant to this research work.

ACKNOWLEDGMENT

We wish to convey our profound gratitude to the Department of Chemistry at *Raghu Engineering College*, Visakhapatnam, for their exceptional support and insightful scientific discussions, which have greatly enriched our research. We also extend our sincere thanks to *Andhra University* for their steadfast support, which has been pivotal in facilitating the successful completion of this work.

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