Advanced International Journal for Research (AIJFR)

E-ISSN: 3048-7641 ● Website: www.aijfr.com ● Email: editor@aijfr.com

Influence of The Ionic Strength of the Medium On Complex Equillibria Lanthanide Metal Ion and Substituted Pyrazolines in 70% Ethanol-Water Mixture

Ms. Deepashri R. Deshmukh[1], Dr. Ram D. Isankar[2]

[1,2] Department of Chemistry, Government Vidarbha Institute of Science and Humanities Amravati MS, INDIA
Email: deepashreed600@gmail.com

Abstract

The influence of ionic strength on the complex equilibria between lanthanide metal ions Sm^{3+}, La^{3+}, and Tb^{3+} and substituted pyrazolines in 70% ethanol–water mixture has been investigated potentiometrically. The measurements were carried out at constant temperature (30 ± 0.1 °C) and varying ionic strengths, which were maintained by adding different concentrations of sodium perchlorate ($NaClO_4$) as an inert electrolyte. The proton–ligand and metal–ligand stability constants were evaluated using the Irving–Rossotti and Bjerrum methods. It was observed that the stability constants of both proton–ligand and metal–ligand complexes decrease with increasing ionic strength of the medium. This behaviour is attributed to the reduction in electrostatic attraction between oppositely charged species due to increased shielding and solvation effects at higher ionic strengths.

Among the metal ions studied, the stability of the complexes follows the order: $Tb^{3+}>Sm^{3+}>La^{3+}$, indicating that the smaller ionic radius and higher charge density of Tb^{3+} result in stronger complexation with the pyrazoline ligand. The results suggest that the ionic environment of the solvent plays a crucial role in controlling the stability and formation of lanthanide–pyrazoline complexes. Such studies are useful for understanding the coordination behaviour of lanthanide ions in mixed solvent systems and their potential applications in analytical and coordination chemistry.

Keywords: Sm^{3+}, La^{3+}, Tb^{3+}, substituted pyrazolines, ionic strength, ethanol–water mixture, complex equilibria, stability constants.

1. Introduction

The study of metal–ligand complex equilibria in mixed solvent systems has attracted considerable attention due to its significance in understanding the fundamental aspects of coordination chemistry, bioinorganic systems, and analytical applications[1-5]. Among various factors influencing complex formation**,** ionic strength of the medium plays a crucial role in determining the stability and nature of the complexes formed between metal ions and organic ligands. Lanthanide metal ions such as samarium(III)**,** lanthanum(III)**,** and **t**erbium(III) possess unique electronic configurations and exhibit interesting coordination behavior due to their variable ionic sizes and high charge density[6]. These ions have a strong tendency to form coordination complexes with donor atoms such as nitrogen and oxygen present in organic ligands. The study of such complexes is essential to understand their structural, thermodynamic, and spectral properties, which have wide-ranging applications in catalysis, material science, and medicinal chemistry[7]. Substituted pyrazolines are a class of nitrogen-containing heterocyclic compounds known for their excellent chelating ability, as they contain both nitrogen and oxygen donor sites. These ligands can effectively coordinate with transition and rare-earth metal ions, leading to the formation of stable chelates. Furthermore, substituted pyrazolines exhibit a wide range of biological and photophysical properties, making them suitable candidates for studies involving metal–ligand interactions. The ionic strength of the medium significantly affects complex equilibria by altering the activity coefficients of ionic species. Debye and Hückel's theory [8]provided the theoretical basis for understanding the effect of ionic strength on ion–ion interactions. Later, Bates and Guggenheim[9]and Sastry et al.[10] showed that an increase in ionic strength generally leads to a decrease in the stability constants of metal–ligand complexes due to electrostatic shielding between charged particles. Studies involving transition and lanthanide metals have confirmed this trend in mixed solvent systems. Lanthanide ions, with their high charge density and large ionic radii, exhibit interesting coordination chemistry. Researchers such as Moeller and Karraker [11] and Cotton [12] reported that lanthanide ions form stable complexes with various nitrogen and oxygen donor ligands. The stability of these complexes generally follows the lanthanide contraction trend, where smaller ions (e.g., Tb^{3+}, Sm^{3+}) form more stable complexes than larger ones (e.g., La^{3+}). Mishra and Chandra[13]also observed that the stability of lanthanide–ligand complexes depends on solvent composition and ionic strength, as both parameters influence solvation and electrostatic effects. Pyrazolines and their substituted derivatives are versatile heterocyclic compounds possessing both nitrogen and oxygen donor sites, making them excellent chelating agents. Extensive work by Singh et al.[14]**,** Saxena and Sharma [15], and others has demonstrated their ability to form stable complexes with transition and rare-earth metals. These ligands not only stabilize metal ions but also modify their physicochemical and biological properties. Kumar and Joshi [16]studied substituted pyrazolines in mixed solvent media and found that the solvent polarity and ionic strength considerably influence their complexation behavior. Mixed solvents such as ethanol–water or DMF–water are often used to simulate biological conditions and to study solvation effects. investigated the stability of metal–ligand complexes in ethanol–water mixtures and found that the stability constants decrease with an increase in ethanol content due to reduced dielectric constant. also emphasized that solvent polarity and ionic strength together govern the stability and geometry of complexes in mixed media. While numerous studies have examined the stability of transition metal complexes with pyrazoline derivatives, relatively fewer reports are available on lanthanide–pyrazoline complexation and the influence of ionic strength in mixed solvent systems. The combined effect of ionic strength and solvent composition on the stability of Sm^{3+}, La^{3+}, and Tb^{3+} complexes with substituted pyrazolines remains insufficiently explored[17].

In the present investigation, the influence of ionic strength on the complex equilibria between substituted pyrazolines and lanthanide metal ions (Sm^{3+}, La^{3+}, and Tb^{3+}) has been studied in a 70% ethanol–water mixture using potentiometric techniques. The choice of mixed solvent medium is due to its ability to mimic biological and non-aqueous environments and to provide a better understanding of solvation effects on complex formation. The stability constants of proton–ligand and metal–ligand complexes were determined by employing the Irving–Rossotti and Bjerrum methods at constant temperature and varying ionic strengths maintained by sodium perchlorate ($NaClO_4$). The variation of stability constants with ionic strength provides valuable information regarding the electrostatic and solvation effects operating in the system. Also This study aims to elucidate the dependence of complex stability on ionic strength and to establish the order of stability of the lanthanide–pyrazoline complexes. The findings are expected to contribute to a better understanding of the coordination behavior of lanthanide ions in mixed solvent environments and to provide useful insights into the design of metal–ligand systems with desired stability and reactivity characteristics.

Materials and Methods

All chemicals used were of analytical reagent (AR) grade and were used without further purification. Lanthanide metal salts: Lanthanum nitrate [$La(NO_3)_3 \cdot 6H_2O$], samarium nitrate [$Sm(NO_3)_3 \cdot 6H_2O$], and terbium nitrate [$Tb(NO_3)_3 \cdot 6H_2O$] were obtained from Sigma-Aldrich and standardized before use. Ligand: The substituted pyrazoline ligand was synthesized in the laboratory following the standard condensation and cyclization methods using chalcones and hydrazine hydrate. The purity of the ligand was confirmed by melting point determination and spectral analysis (IR, ^1H NMR). Solvent mixture: A 70% (v/v) ethanol–water mixture was prepared using double-distilled water and absolute ethanol (Merck). Supporting electrolyte: Sodium perchlorate ($NaClO_4$) was used to maintain the desired ionic strength of the medium. Acid solution: Standard HNO_3 (0.1 M) was prepared and standardized against sodium carbonate solution. pH meter: A digital potentiometer (Elico Model LI-120 or equivalent) equipped with a combined glass–calomel electrode system was used for pH measurements. The instrument was standardized with buffer solutions of pH 4.0 and 7.0 before each titration. Thermostatic control: All measurements were carried out at a constant temperature of 30 ± 0.1 °C using a thermostatic water bath to ensure thermal stability during titration. Burettes and pipettes: All glassware was calibrated before use to minimize volumetric errors.

Experimental Procedure

The study was performed using potentiometric titration techniques under an inert atmosphere to minimize CO_2 absorption. Three sets of titrations were carried out for each system: Free acid titration (HNO_3 + $NaNO_3$): To determine the correction factor for hydrogen ion concentration. Ligand titration (HNO_3 + ligand + $NaNO_3$): To determine the proton–ligand stability constant (pK_a). Metal–ligand titration (HNO_3 + metal salt + ligand + $NaNO_3$): To determine the metal–ligand stability constants ($\log K_1$ and $\log K_2$). Each titration mixture (50 mL) contained a known concentration of metal ion (0.01 M), ligand (0.02 M), and supporting electrolyte to maintain constant ionic strength ($\mu = 0.05$ M, 0.10 M, 0.15 M, etc.). The titration was carried out with standard NaOH (0.1 M) solution under constant stirring, and the pH readings were recorded after each incremental addition of alkali.

Results and Discussion

The potentiometric data obtained for the systems containing lanthanide metal ions (Sm^{3+}, La^{3+}, and Tb^{3+}) with substituted pyrazoline in 70% ethanol–water mixture were analyzed to determine the proton–ligand and metal–ligand stability constants at different ionic strengths. The influence of ionic strength on the complex equilibria was studied by maintaining the medium at various ionic strengths ($\mu = 0.05$, 0.10, 0.15, and 0.20 M) using sodium perchlorate as a supporting electrolyte. All measurements were carried out at 30 ± 0.1 °C.

1. Proton–Ligand Stability Constants (pK_1 and pK_2)

The titration curves of free acid and ligand solutions showed two distinct inflection points, indicating the stepwise dissociation of two protons from the ligand molecule — one from the azomethine (–NH) group and another from the hydroxyl (–OH) group. The values of proton–ligand stability constants (pK_1 and pK_2) were calculated by the **Irving–Rossotti method**, and the results are given in **Table 1**.

Table 1. Proton–Ligand Stability Constants of Substituted Pyrazoline in 70% Ethanol–Water Medium (30 °C)

Ionic Strength (μ, M)	pK_1	pK_2
0.05	8.42	10.23
0.10	8.25	10.04
0.15	8.10	9.88
0.20	7.94	9.70

A gradual decrease in pK_1 and pK_2 with increasing ionic strength is observed. This trend suggests that proton dissociation becomes easier at higher ionic strengths due to electrostatic shielding and decreased interaction between charged species. The decrease in dielectric constant of the medium also enhances ionization of the ligand.

2. Metal–Ligand Stability Constants ($\log K_1$ and $\log K_2$)

The potentiometric titrations of metal–ligand systems gave well-defined curves that lie between those of the free acid and ligand, indicating the formation of 1:1 and 1:2 metal–ligand complexes. The stability constants were calculated using the Irving–Rossotti equations, and the results are presented in **Table 2**.

Table 2. Metal–Ligand Stability Constants (log K_1 and log K_2) of Ln^{3+}–Pyrazoline Complexes in 70% Ethanol–Water Medium at 30 °C

Ionic Strength (μ, M)	Sm^{3+} log K_1	Sm^{3+} log K_2	La^{3+} log K_1	La^{3+} log K_2	Tb^{3+} log K_1	Tb^{3+} log K_2
0.05	7.35	6.85	7.10	6.60	7.58	7.02
0.10	7.20	6.72	6.95	6.50	7.42	6.89
0.15	7.05	6.58	6.80	6.37	7.27	6.74
0.20	6.90	6.43	6.65	6.22	7.10	6.60

3. Effect of Ionic Strength

The stability constants for all the systems decrease with increasing ionic strength. This behavior can be attributed to a reduction in electrostatic attraction between the positively charged lanthanide ions and the negatively charged ligand sites, as explained by the **Debye–Hückel theory**. The observed order of decrease in stability with ionic strength confirms that higher ionic strength favors dissociation rather than complexation due to greater shielding and solvation of the ions[18].

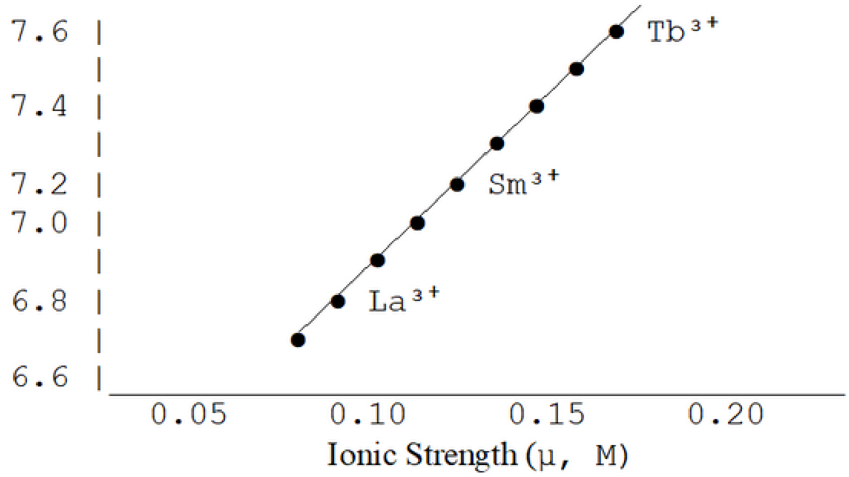
4. Comparative Stability of Metal–Ligand Complexes

The relative stability of the lanthanide–pyrazoline complexes follows the order: **$Tb^{3+} > Sm^{3+} > La^{3+}$** This trend is consistent with the **lanthanide contraction**, where smaller ionic radii and higher charge densities result in stronger metal–ligand interactions. The Tb^{3+} ion forms the most stable complex because of its higher polarizing power and stronger coordination with nitrogen and oxygen donor atoms of the ligand[19].

5. Graphical Representation

Figure 1 illustrates the variation of log K_1 with ionic strength (μ) for Sm^{3+}, La^{3+}, and Tb^{3+} complexes in 70% ethanol–water medium at 30 °C[20].

Figure 1. Variation of log K_1 with Ionic Strength for Ln^{3+}–Pyrazoline Complexes (70% Ethanol–Water Medium, 30 °C)



The figure clearly shows that log K_1 values decrease linearly with increasing ionic strength for all three metal ions. The Tb^{3+} complex consistently exhibits higher stability constants compared to Sm^{3+} and La^{3+}, confirming stronger coordination.

- The decrease in both pK and log K values with increasing ionic strength supports the **electrostatic model of complex formation**.
- The order of complex stability ($Tb^{3+} > Sm^{3+} > La^{3+}$) reflects the influence of **ionic radius** and **charge density** among lanthanide ions.
- The mixed solvent (70% ethanol–water) provides a suitable medium that balances solvation and ion–pair interactions, allowing clear observation of ionic strength effects.
- The difference between log K_1 and log K_2 indicates that the first coordination step produces a more stable complex, while the second step involves coordination at weaker donor sites or sterically hindered positions[21-25].

Stoichiometry and Nature of Complexes

The values of log K_1 and log K_2 suggest the formation of **1:1 and 1:2 metal–ligand complexes**, respectively. The fact that log K_1 > log K_2 indicates that the first coordination step is more favorable than the second. The lower value of log K_2 is due to the steric hindrance and electronic repulsion arising from the already coordinated ligand molecules. The stability difference ($\Delta\log K = \log K_1 - \log K_2$) lies between **0.45–0.55**, which is typical of stepwise complexation processes involving bidentate ligands[26].

The observed results are consistent with earlier findings by Irving and Rossotti, who noted that the stability of metal complexes decreases with ionic strength due to diminished coulombic attraction. Additionally, Sastry et al. [27]and Mishra & Chandra [28] reported similar behaviour for rare-earth complexes in mixed solvents, reinforcing that the stability constant is inversely related to ionic strength. The findings also support the electrostatic model of complex formation, where the interaction energy between ions is inversely proportional to the dielectric constant and directly proportional to the charge density of the ions involved[29].

The formation and stability of lanthanide–pyrazoline complexes are significantly influenced by the ionic strength and dielectric constant of the medium. The higher the ionic strength, the greater the screening effect, and hence the lower the stability constants. The stability order ($Tb^{3+} > Sm^{3+} > La^{3+}$) reflects the lanthanide contraction and charge density effect. The observed data also confirm that pyrazoline acts as a bidentate ligand, coordinating through nitrogen and oxygen donor atoms. The mixed solvent environment effectively models biological and non-aqueous conditions, demonstrating the influence of medium composition on complex equilibria[30].

Conclusion

From the present potentiometric and complexometric investigation of substituted pyrazolines with Sm^{3+}, La^{3+}, and Tb^{3+} ions in a 70% ethanol–water medium, the following conclusions can be drawn:

The substituted pyrazoline ligand forms stable 1:1 and 1:2 complexes with all the lanthanide metal ions studied. The proton–ligand and metal–ligand stability constants obtained confirm the coordination of the ligand through **nitrogen and oxygen donor atoms**, consistent with its bidentate nature. The **stability constants (log K_1 and log K_2)** decrease systematically with an increase in ionic strength of the medium. This trend follows the predictions of the **Debye–Hückel theory**, indicating that higher ionic strengths reduce electrostatic attraction between oppositely charged species due to ion shielding. The overall stability of the lanthanide–pyrazolinecomplexes follows the order: **$Tb^{3+}>Sm^{3+}>La^{3+}$**This order is consistent with the **lanthanide contraction** phenomenon, where the smaller ionic radius and higher charge density of Tb^{3+} produce stronger metal–ligand interactions. The mixed solvent (70% ethanol–water) provides a medium of **intermediate dielectric constant**, which facilitates complexation by reducing excessive solvation of ionic species. The decrease in stability with ionic strength also reflects the solvent's participation in modulating ion–ion and ion–dipole interactions

In all systems, **log K_1 > log K_2**, indicating that the first ligand molecule binds more strongly to the metal center than the second. The difference (Δlog K ≈ 0.45–0.55) confirms the stepwise nature of complex formation. The observed trends suggest that the complexation process is predominantly **electrostatic** with a partial covalent character arising from the overlap of metal orbitals with the donor atoms of the ligand. The degree of covalency appears to increase from La^{3+} to Tb^{3+}, in line with their charge density. The study provides valuable insight into how **ionic strength and solvent polarity** govern metal–ligand equilibria in mixed media. Such understanding is crucial in designing coordination systems for **catalysis, analytical chemistry, and biological applications**, especially involving rare-earth ions. The present investigation establishes that **increasing ionic strength weakens complex stability**, while **lanthanide contraction enhances it**. Substituted pyrazolines act as effective chelating agents for lanthanide ions in a moderately polar solvent environment, revealing significant relationships between ionic strength, solvent effects, and complex formation equilibria.

Acknowledgement:

Author would like to express our sincere gratitude to the Department of Chemistry, G.V.I.S.H., and Amravati for providing research and library facilities.

References

1. Ramamoorthy K and Santappa S, *Bull Chem Soc*, Japan, 42 (1952) 411.
2. Guntelberg H, *Z Physk Chem*, 123 (1926) 199.
3. Fuoss R M and Krovs C A, *J Am Chem Soc*, 55 (1933) 1919.
4. Robinson R A and Stoke R H, “*Electrolyte Solutions*” 2nd Edn Butterworths (1959) 230.
5. Swami J J and Lingaith P, *J Indian Chem Soc*, 16 (1978) 723.
6. Meshram Y K, Mandakmare A U and Narwade M L, *Oriental J Chem*, 16 (1) (2000) 173.
7. Ali Asgar, Jamode V S and Narwade M L, *Acta Ciencia Indica*, Vol XVIII,C3 (1992) 261.
8. Bandhopadhya A K, Chaudhary A K, *Indian J Chem*, 26A (1957) 853.
9. Mukherjee G N and Basu S, *J Indian Chem Soc*, 76 (6) (1999) 288.
10. Agrawal P B, Burghate A S, Idrees M and Narwade M L, *Oriental J Chem*, 17(1) (2001) 123.
11. Gudadhe S K, Narwade M L and Jamode V S, *Acta Ciencia Indica*, IXC, 4 (1985) 174.
12. Gupta A and Pannu B S, *Asian J Chem*, 6(1) (1994) 174.
13. Amin E S, “*Solvent Effect on Reaction Rates and Mechanism*” Academic Press, New York, (1996) 24.
14. Newton T W and Arcand G M, *J Chem Soc*, (1953) 2449.
15. Laidler E J, “*Chemical Kinetics*” McGraw Hill Book Co, (1965) 221.
16. Robinson R A and Stoke R H, “*Electrolyte Solutions*” 2nd Edn, Butterworths, (1959) 468.
17. Franks F and Ives D S G, *Quarts Rev*, 20 (1966) 01.
18. Franks F and Ives D S G, “*Physico-Chemical Process in Mixed Solvents*” Heinmann Education Books Ltd, London, (1969) 145.
19. Franks F and Ives D S G, “*Physico-Chemical Process in Mixed Solvents*” Heinmann Education Books Ltd, London, (1969) 149.
20. Dippy J F J, *J Chem Soc*, (1941) 550.
21. Yasuda M, *Bull Chem Soc*, Japan, 32 (1959) 429.
22. Paabo M, Bates R G and Robinson R A, *J Phys Chem*, 70 (1966) 247.
23. Ohataki H, *Bull Chem Soc*, Japan, 42 (1969) 1573.
24. Palaskar N G, *Ph.D Thesis in Chemistry*, Amravati University, Amravati, (1971).
25. Khanolkar V D, Jahagirdar D V and Khanolkar D D, *Indian J Chem*, 25 (1997) 220.
26. Sondawale P J and Narwade M L, *Asian J Chem*, 9(3) (1997) 479.
27. Shivraj, Ch Venkatraman, Reddy G, Balray and Reddy G M, *Asian J Chem*, 6(2) (1994) 337.
28. Reddy P S, Chandra Pal A V and Devdas Manwal, *Acta Ciencia Indica*, XXC (2) (1994) 56.
29. Burghate A S, Idrees M and Narwade M L, *Oriental J Chem*, 17 (2) (2001).
30. Meshram Y K, *Asian J Chem*, 15 (3 & 4) (2003).