

Studies in stability constants of Nd (III) and Sm (III) metal ion complexes with substituted pyrazoline, pH-metrically

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Abstract

In this work, we investigated the proton-ligand and metal-ligand stability constants of ligand 3-(2-hydroxy-5-methylphenyl)- 5,5-diphenyl-1-phenyl- Δ^2 -pyrazoline (L1) with inner transition metal ions such as Nd (III) and Sm (III), determined pH-metrically at 0.1 M ionic strength. (30 $\pm$ 10°C) in a 70% dioxane-water mixture by the Bjerrum method as adopted by Calvin Wilson. 1:1 and 1:2 complexes were formed between 3-(2-hydroxy-5-methylphenyl)- 5,5-diphenyl-1-phenyl- Δ^2 -pyrazoline (L1) and Nd (III) and Sm (III). We evaluated and compared the pK and log k values with the resulting data.

Keywords: Substituted Pyrazoline, Dioxane – water mixture, stability constant.

1. Introduction

The stability constant, also referred to as the formation constant or association constant, is an important quantitative parameter used to describe the strength and stability of a metal–ligand complex in solution. It represents the equilibrium tendency of a metal ion and ligand to associate and form a coordination complex. Stability constants are generally expressed as equilibrium constants and are denoted by K. A higher value of the stability constant indicates a greater tendency for the formation of the corresponding complex and, consequently, greater stability under the specified experimental conditions.

Stability constants can be determined using various experimental techniques, including spectrophotometric, potentiometric, polarographic, and calorimetric methods. These constants are of considerable significance in coordination chemistry, analytical chemistry, environmental chemistry, and biochemistry, as they provide useful information regarding the formation, stability, and behaviour of metal–ligand complexes in solution. They are also useful for understanding the interactions between metal ions and ligands and for predicting the extent of complex formation under different experimental conditions.

The magnitude of a stability constant is influenced by several factors, including the nature and electronic configuration of the metal ion, the structural and chemical properties of the ligand, pH, temperature, ionic strength, solvent, and the coordination environment. Therefore, stability constants provide valuable information concerning the thermodynamic and equilibrium aspects of complex formation. Their determination is particularly important for evaluating metal–ligand interactions and understanding the behaviour of coordination compounds in various chemical and biological systems.

A significant contribution to the systematic study of the stability constants of organic ligands and their metal complexes was made by Bjerrum¹ and Calvin². Their pioneering investigations established important theoretical and experimental approaches for the determination of formation constants of metal–ligand systems and provided a foundation for subsequent developments in the field of coordination chemistry.

Jaiswal et al.³ investigated the interaction of Pr(III), Nd (III), and Sm(III) metal ions with three ligands, namely 3-(2-hydroxy-5-methylphenyl)-5-(4-methoxyphenyl) isooxazoline, (L1), 3-(2-hydroxy-3-chloro-5-methylphenyl)-5-(4-methoxyphenyl) isoxazoline, (L2) and 3-(2-hydroxy-3-bromo-5-methylphenyl)-5-(4-methoxyphenyl) isooxazoline. (L3). The studies were carried out pH-metrically at 0.1 M ionic strength in a 70% ethanol–water medium using the Bjerrum method as modified by Calvin and Wilson. The experimental data were used to determine and compare the proton–ligand stability constants (pK) and metal–ligand stability constants (log K) by the half-integral and point-wise calculation methods. The results indicated the formation of a 1:1 complex between the metal ions and all three ligands.

Naik et al.⁴ determined the pK_a values of several N-heterocyclic compounds, particularly substituted pyrazoles, in a 70% (v/v) dioxane–water medium using pH-metric measurements. The stability constants of the complexes formed by Dy (III), Nd (III), Sm(III), and Tb (III) with 3-(2-hydroxyphenyl)-5-methylpyrazole, 1-phenyl-3-(2-hydroxyphenyl)-5-methylpyrazole, 3-(2-hydroxy-4-methylphenyl)-5-methylpyrazole, and 1-phenyl-3-(2-hydroxy-4-methylphenyl)-5-methylpyrazole were determined by the pH-metric method at 300 ± 0.1 K. The effect of ionic strength on the complexes of Sm(III) and Pr(III) with pyrazole was also investigated over the range of 0.02–0.10 mol dm⁻³ sodium perchlorate at pH 2–3.

The stability constants of chlorosubstituted pyrazoles and pyrazolines in a 70% (v/v) dioxane–water medium were also determined by pH-metric measurements. The proton–ligand and metal–ligand stability constants of Cu (II), Ni (II), Co (II), and Nd (III) with three ligands 3-(2-hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(4'-methoxyphenyl)-1-phenylpyrazole, (L1) 3-(2-hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(4'-methoxyphenyl)-1-phenylpyrazoline, (L2) and 4-(2-chlorophenyl)-3-(3-furanoyl)-5-(2-hydroxyphenyl) pyrazole (L3) were investigated by the pH-metric method at 0.1 M ionic strength and 27 ± 0.1 °C. The values of log K₁ and log K₂ were used to evaluate the stepwise and simultaneous complex formation equilibria and to examine the validity of the linear relationship between log K and pK.⁵

Jagtap et al.⁶ investigated the stability constants of Ni (II) complexes with substituted pyrazole carboxylic acid derivatives at 298 K in a 70% DMF–water medium. Thakur et al.⁷ studied the complex formation of lanthanum (III) with Schiff-base ligands using pH-metric titration based on the Calvin–Bjerrum method. The study also included the determination of thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS). Thorat et al.⁸ investigated the complex formation of Pr(III) and Sm(III) metal ions with substituted isoxazoline ligands, including 3-(2-

hydroxy-3-nitro-5-methylphenyl)-5-(3-nitrophenyl) isoxazoline, 4-chlorophenyl isoxazoline, and 2-furyl isoxazoline.

Tambatkar⁹ have studied the complexation behaviour of Ce (III), Pr(III), Nd (III), Sm(III), Gd (III), Dy (III), Yb (III), and Lu (III) metal ions with two substituted chalcone ligands, namely 2'-hydroxy-(3,4-dioxymethylene)-5'-methylchalcone (Ligand-I) and 2'-hydroxy-5'-methyl-4-methoxychalcone (Ligand-II), using the pH-metric technique. The studies were carried out at an ionic strength of 0.1 M and a temperature of 27 ± 0.1 °C in a 70% dioxane–water medium. The experimental data were analysed to determine the proton–ligand stability constants (pK) and metal–ligand stability constants (log K). The results indicate that all the investigated lanthanide (III) ions—Ce (III), Pr(III), Nd (III), Sm(III), Gd (III), Dy (III), Yb (III), and Lu (III)—form stable 1:1 and 1:2 metal-to-ligand complexes with both substituted chalcone ligands under the experimental conditions. The stability constants provide useful information regarding the complexation behaviour and relative binding affinities of these lanthanide (III) ions toward the selected chalcone ligands.

Pagaria et al.¹⁰ has investigated Formation of complexes of Cu(II) and Fe(III) transition metal ions with ligands 3-(5'-chloro-2'-hydroxy-4'-methylphenyl)-5-(4'-nitrophenyl)-1-phenyl pyrazole (L1), 3-(5'-chloro-2'-hydroxy-4'-methylphenyl)-5-(4'-bromophenyl)-1-phenyl pyrazole (L2), 3-(5'-chloro-2'-hydroxy-4'-methylphenyl)-5-(4'-nitrophenyl) isoxazole (L3) and 3-(5'-chloro-2'-hydroxy-4'-methylphenyl)-5-(4'-bromophenyl) isoxazole (L4) have been studied at 0.1M ionic strength at 27 ± 0.1 °C in 70% dioxane-water mixture pH-metrically by Bjerrum method as adopted by Calvin and Wilson. It was observed that Cu (II) and Fe (III) metal ions formed 1:1 and 1:2 complexes with ligands L1-L4. The values of proton-ligand stability constants (pK) and metal-ligand stability constants (logK) were calculated using the half-integral method and compared from the resulting data. The stability constants of complexes indicate that the ratio $\log K_1/\log K_2$ is positive in all cases, implying little or no steric hindrance to the addition of a secondary ligand molecule. This can be of interest for specialists in the field of coordination chemistry and plays a supporting role toward the development of new drugs.

2. Experimental methodology

2.1. Materials and Methods

All chemicals used are AR-grade. The ligand (L₁) was synthesised in the laboratory by the reported protocol¹¹. The stock solution of the ligand was prepared by dissolving the required amount of ligand in a 70% (dioxane and water) mixture.

2.2. General procedure

Types of Titrations

i) Free acid HNO₃ (0.01 M)

ii) Free acid HNO₃ (0.01 M) and ligand (20×10^{-4} M)

iii) Free acid HNO₃ (0.01 M) and ligand (20×10^{-4}) and metal ions (4×10^{-4} M) against a standard 0.1N NaOH solution. The ionic strength of all the solutions was maintained at 1 M by adding the appropriate amount of KNO₃ solution. All the titrations were carried out in a 70% (dioxane and water) mixture, and the readings were recorded for each 0.1 mL addition. The graph of the volume of alkali added (NaOH)

against pH was plotted. The ligand involved in the present work may be considered a monobasic acid having only one dissociable H⁺ ion from the phenolic OH group, and it can therefore be represented as HL. The dissociation equilibrium can be shown as.



By the law of mass action, we have,

$$K = [HL] / ([H^+] [L^-]) \quad (1)$$

Where the quantities in brackets denote the activities of the Species at equilibrium.

3. Result and Discussion

3.1 Calculation of Proton-Ligand Stability Constant (n_A)

The plots of the volume of NaOH and the pH of the solution were used to determine the proton-ligand stability constant (representing the replacement of H⁺ ions from the functional group of the ligand with respect to the pH value). The horizontal difference (V₂-V₁) was measured accurately between the titration curves of free acid and acid + ligand. It was used to calculate the formation number n at various pH values and a fixed ionic strength μ = 0.1 M using Irving and Rossotti's equation [1, 2].

$$n_A = \gamma \frac{(E_0 + N) (V_2 - V_1)}{(V_0 + V_1) T_L^0} \quad (2)$$

Where V⁰ is the initial volume of the solution. E⁰ and T_L⁰ are the initial concentrations of the mineral acid and ligand, respectively. V₁ and V₂ are the volumes of alkali of normality N during the acid and ligand titration at a given pH. γ is the replaceable proton in the ligand. The data on n_A obtained at various pH values, along with the horizontal difference for some representative systems, are represented in Table 1. The metal-ligand formation number (n) is estimated by Irving-Rossotti's equation.

$$n = \frac{(E_0 + N) (V_3 - V_2)}{(V_0 + V_2) T_m^0} \quad (3)$$

Where the notations have the same meaning as given in the earlier equation. The horizontal difference (V₃-V₂) between the metal complex (A+M+L) and reagent (A+L) curve is used to evaluate the value of n using Irving-Rossotti's equation.

Table 1 Proton ligand stability constant (pK)

Ligand	System	pK	
		Half integral method	Point wise method
L ₁	3-(2-hydroxy-5-methylphenyl)-5,5-diphenyl-1-phenyl-Δ ² pyrazoline (L ₁)	9.0052	6.8500

Table 2: Metal-ligand stability constant (log K)

System	LogK ₁	LogK ₂	Δ LogK
Nd (III)+L ₁	7.3723	5.5008	1.8715
Sm (III)+L ₁	6.1776	5.1032	1.0744

Conclusion

From the titration curves, it is observed that the departure between the acid-ligand (A+L) curve and the acid-ligand-metal (A+L+M) curve for all systems started at pH 3.6. This indicated the commencement of complex formation. Also, the change in colour from yellow to orange in the pH range from 3.8 to 8.9 during titration showed the complex formation between metal and ligand.

The difference between LogK₁ and LogK₂ is less than 2.5, indicating the simultaneous formation of 1:1 and 1:2 complexes. When the difference is greater than 2.5, a stepwise complex formation takes place.¹² From Table 2, it is observed that in all systems, Nd (III)-L₁ and Sm (III) + L₁, the difference between log K₁ and log K₂ is sufficiently small, which indicates that the simultaneous formation of complexes between metal ions and ligands takes place.

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