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pH –METRIC STUDY ON DETERMINATION OF METAL-LIGAND STABILITY CONSTANTS OF Co(II), Cu(II), Ni(II) and Zn(II) COMPLEXES WITH SUBSTITUTED PYRAZOLINES

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ABSTRACT

The interaction of Co(II), Cu(II) Ni(II) AND Zn(II) with 1-H-3(2"-Hydroxy-3"nitro-5"methylphenyl)-5-(3'-nitrophenyl)- Δ_2-pyrazoline (Ligand-1) and 1-H-3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-(3'4'-methylene dioxyphenyl)- Δ_2-Pyrazoline (Ligand-2) have been investigated by Bjerrum method as adopted by Calvin and Wilson. The stability constant of 1:1 and 1:2 complexes of Co(II), Cu(II) Ni(II) and Zn(II) have been studied at constant temperature (27±0.1°C) and 0.1 M ionic strength (NaOH) in 70% Dioxane-water mixture. It is observed that formation of 1:1 and 1:2 complexes is occurring simultaneously.
Key Words:SubstitutedPyrazolines, Stability Constants, Complex Formation, pH-metric study, metal-ligand, stability constant, Co(II), Cu(II) Ni(II) and Zn(II).

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INTRODUCTION

Pyrazolines are good chelating agents due to presence of electron donor nitrogen. Since the last four decades considerable research work has been done on the study of complexes in solution[1,2]. Bjerrum's dissertation[3] has taken the initative to develop the field. Some of the important characteristics added to the drugs play an important role in biological activities. Metal chelates of 3-(o-hydroxyphenyl)-5-phenyl isoxazole with Be(II), Mn(II), Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and UO_2(VI) have been investigated by Khadilkar etal[4]. The spectral properties of 3-(o-hydroxyphenyl-5-phenyl isoxazole were reported Murthyetal[5]. Metal ligand stability constant of lanthanides with somesustitutedpyrazolines and diketones studied by Sawalakhe and Narwade[6]. Mandakmareet al[7] have studied the metal-ligand stability constant of Cu(II) with some substituted coumarins pH-metrically in 70% dioxane water mixture. Sondawale et al[8] have determined metal-ligand stability constants of and adiabatic compressibility of Cu(II)-peptide complex recently. Gudadhe et al[9] have performed the study of stability constants of Th(IV) complex with substituted pyrazolines.

In view of analytical applications of pyrazolines, it is of interest to study the physico-chemical properties such as stability constants of Co(II), Cu(II) Ni(II) and Zn(II) complexes 1-H-3(2"-Hydroxy-3"nitro-5"methylphenyl)-5-(3'-nitrophenyl)-Δ_2-pyrazoline and 1-H-3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-(3'4'-methylene dioxyphenyl)- Δ_2-Pyrazoline have been investigated by Bjerrum

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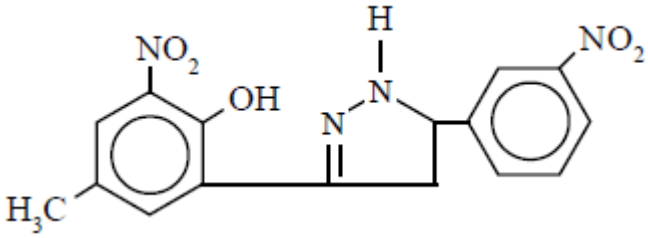
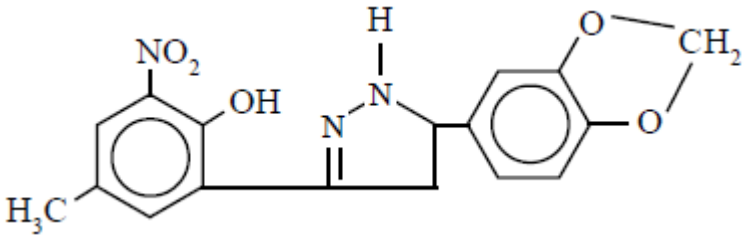
method. In the present investigation 70% dioxane-water mixture is used as solvent for preparation of solution.



Ligand-1



Ligand-2

EXPERIMENTAL

All chemicals such as sodium hydroxide, nitric acid, potassium nitrate and metal salts of A. R. grade were used in the present investigation. 1-H-3(2"-Hydroxy-3"nitro-5"methylphenyl)-5-phenyl-Δ_2-pyrazoline (Ligand-1) and 1-H-3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-(4'-methoxyphenyl)- Δ_2-Pyrazoline (Ligand-2) were prepared by following literature method. Both ligands are crystalized and their purity was checked by TLC before use. The solutions of purified ligands were prepared in DMF and standardized by potentiometric techniques.

ELICO pH_meter model LI-10 (accuracy ±0.05 unit) with a glass electrode and saturated calomel electrode was used for the measurement of pH. It was calibrated by buffer of pH 4.0, 7.0 and 9.2 at 27°C before proceeding for titrations.

The experimental procedure involves pH-metric titrations of (i)free acid (0.01 M), (ii)free acid (0.01M) and Ligand (20 X 10^{-4} M). (iii) Free acid(0.01 M)+ligand (20X10^{-4} M)+metal ion (4X10^{-4} M) against standardNaOH solution. The ionic strength of all the solutions was maintained constant (0.1 M) by adding appropriate quantity of 1 M potassium nitrate.

The titrations were carried out in 100 mL pyrex glass beaker kept in a water bath maintained at constant temperature (27±0.1°C). Nitrogen gas was slowly bubbled thorugh the solution to remove the oxygen and carbon dioxide. The pH meter readings were taken only after the gas bubbling was completely stopped. In aqueious organic mixture pH values were corrected by use of Van Utert and Hass equation.

RESULTS AND DISCUSSION

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Determination of proton-ligand formation constants(pK).

The ligand (1-2) in the present investigation are mono basic acid having only one dissociable proton from hydroxyl group of the ligand. In general ligands can be represented as HL and dissociated as

$HL \rightleftharpoons H^{+}+L^{-}$

It is found that, the deviation of acid-ligand curves from acid curves started at about pH=5.70 for both ligands and increased continuously upto pH=11.50. It shows that dissociation of –OH group occurs which is present in the ligand part of the complex structure. The values ofŋA were calculated by Irving –Rossotti expression. The pKavalue of both systems were calculated by half integral and pointwisecalculatios which are presented in Table-1. Most accurate values were calculated from pointwise calculations.

Table-1
Determination of proton-ligand stability constants(pK) of some substituted pyrazolines at 0.1 M ionic strength at (27±0.1°C) temperature.

Sr. No.	System	Constant pK Half Integral	Constant pKPoint wise Calculation
1	1-H-3(2"-Hydroxy-3"nitro-5"methylphenyl)-5-(3'-nitrophenyl)- Δ_2-pyrazoline(Ligand-1)	7.35	7.40±0.04
2	1-H-3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-(3'4'-methylene dioxyphenyl)- Δ_2-Pyrazoline(Ligand-2)	7.75	7.71±0.05

Determination of metal-ligand stability Constants (log K)

The values of ŋA were evaluated from Irving-Rossoti'sexpression which were used to calculate the metal-ligand stability constants. The metal ligand stability constants for all the systems were calculated by half integral and pointwise calculation methods. The values were presented in table-2. It can be seen from table-2.that there is no differences as such between log K values for both the complexes. It showed that there must be simultaneously complex formations and not stepwise formation. The order of stability of metal ligand complexes is Co(II)<Cu(II)<Ni(II)<Zn(II) for pyrazoline ligand-1 and Co(II)>Cu(II)>Ni(II)>Zn(II) for pyrazoline ligand-2. The lesser values of log K in case of pyrazoline ligand-1 maybe due to presence of nitro group as the electron withdrawing group at 3" position and also the presence of 3' position group.

Table-2:Determination of metal-ligand stability Constants (log K)

Sr. No.	System	Constants	Constants
		$\log K_1$	$\log K_2$

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		Half Integral	Pointwise Calculation	Half Integral	Pointwise Calculation
1	Co(II) 1-H-3(2"-Hydroxy-3"nitro-5"methylphenyl)-5-(3'-nitrophenyl)- Δ_2-pyrazoline	6.445	6.337±0.05	5.857	5.785±0.06
2	Cu(II) 1-H-3(2"-Hydroxy-3"nitro-5"methylphenyl)-5-(3'-nitrophenyl)- Δ_2-pyrazoline	6.559	6.395±0.04	5.995	5.887±0.03
3	Ni(II) 1-H-3(2"-Hydroxy-3"nitro-5"methylphenyl)-5-(3'-nitrophenyl)- Δ_2-pyrazoline	6.778	6.493±0.07	6.317	5.997±0.04
4	Zn(II) 1-H-3(2"-Hydroxy-3"nitro-5"methylphenyl)-5-(3'-nitrophenyl)- Δ_2-pyrazoline	6.977	6.570±0.05	6.715	6.310±0.04
5	Co(II) 1-H-3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-(3'4'-methylene dioxyphenyl)- Δ_2-Pyrazoline	9.047	9.117±0.02	8.159	8.059±0.04
6	Cu(II) 1-H-3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-(3'4'-methylene dioxyphenyl)- Δ_2-Pyrazoline	8.043	8.093±0.03	7.063	7.017±0.04
7	Ni(II) 1-H-3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-(3'4'-methylene dioxyphenyl)- Δ_2-Pyrazoline	8.025	8.087±0.03	6.993	6.907±0.05
8	Zn(II) 1-H-3-(2"-Hydroxy-3"-nitro-5"-methylphenyl)-5-(3'4'-methylene dioxyphenyl)- Δ_2-Pyrazoline	8.010	8.075±0.03	6.850	6.750±0.05

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