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Effect of ionic strength on complex equillieria between lanthanide metal ions and substituted pyrazole in dioxane -water mixture

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ABSTRACT

The proton ligand stability constants of 3 (4'-chlorophenyl) - 4- benzoyl -5 (2-hydroxy phenyl) pyrazole (L) and metal ligand stability constants of Pr (III), Nd (III) and Sm (III) complexes have been investigated at 0.02, 0.04, 0.06, 0.08 and 0.1 M ionic strength in dioxane-water mixture, pH metrically. From the values of pK and logK, the values of thermodynamic constants at zero ionic strength can be calculated. The value of pK and logK are found to be decreased with increasing ionic strengths of 1M KNO_3 solution

Key words: Stability constants, ionic strength, lanthanide metal ions, pyrazole.

INTRODUCTION

Substituted azoles have played an important role in many biological systems and used as a antibiotic, anticancer drugs[1-5]. Substituted pyrazoles play an important role in chelation and stability of complexes. Pyrazoles differ strongly from pyrazoline in its remarkable stability and more basic character. The important physical property of pyrazoles is the existence of tautomerism. Stability constants of transition metal ions complex with substituted pyrazoles was studied[6-7]. The influence of ionic strength on stability constant of Co (II), Sr (III), and Pr (III) complexes with substituted pyrazoles was reported[8]. The complexes of Pr (III) with substituted pyrazoles were studied by Davies *et al* [9]. Determination of stability constants of transition metal ions with substituted pyrazoles and oxazoles reported pH-metrically[10]. Stability constants for the lanthanide metal complexes in aqueous Solution at 25°C and 0.5 M ionic strength has also reported[11]. Gupta *et al* [12] have determined the stability constants of transition metal ion complexes with disalicylamide at different ionic strength. Palaskar[13] have studied the effect of ionic strength and dielectric constant of Cu (II) 3-nitrophthalic acid, potentiometrically at different ionic strengths in aqueous medium. Ultrasonic promotated synthesis of substituted pyrazoles & studies on proton ligand stability constants of some substituted pyrazoles has reported resently[14-15]. Hence an attempt has been made to study the determination of proton - ligand stability constants and metal - ligand stability constants of Pr(III) & Nd(III) complexes with 3 (2'-chlorophenyl) - p4-pyridoyl -5 (2-hydroxy phenyl) pyrazole (L) at various ionic strength (i.e. 0.02, 0.04, 0.06, 0.08, 0.1M) at 28 ± 0.1^{0}C in 70% dioxane - water mixture.

EXPERIMENTAL

The work has been studied by Calvin - Bjerrum pH - metric titration technique. All pH measurements were carried out with ELICO- LI 10 pH meter (accuracy ± 0.05 units) using combined electrode assembly at 28 ± 0.1^{0}C. Pr (III), Nd (III) and Sm(III) was used in the from of its nitrate and concentration was estimated by EDTA. Ethanol, sodium hydroxide, and KNO_3, were used are of A.R. Grade. The substituted pyrazoles is prepared by standard method[16-17]. It is insoluble in water and hence 70% dioxane- water (v/v) was used as a solvent.

Calvin Bjerrum Titration Technique

The titrations were carried out in an inert atmosphere of nitrogen. The ionic strength of solution was maintained constant by adding an appropriate amount of 1M KNO_3 solution. The values were recorded by pH meter. These values converted to $[H^+]$ values by applying the correction proposed by Van Uitert & Hass[18].

RESULTS & DISCUSSION

Substituted pyrazoles may be considered as a monobasic acid having one replaceable H^+ ion

Table : Proton- ligand stability constants & metal- ligand stability constants at various ionic strength

Table 1a: For system: Pr(III) – L

Ionic Strength(μ)	$\sqrt{\mu}$			pK	$LogK_1$	$logK_2$
0.02	0.1414	0.1238	0.1453	10.40	8.64	2.79
0.04	0.2000	0.1666	0.1355	9.62	7.60	2.00
0.08	0.2449	0.1967	0.1235	9.00	7.00	1.00
0.08	0.2828	0.2204	0.1066	8.72	6.55	0.89
0.10	0.3163	0.2402	0.0813	8.23	5.97	0.53

Table 1b: For system: Nd(III) – L

Ionic Strength(μ)				pK	$LogK_1$	$logK_2$
0.02	0.1414	0.1238	0.1453	10.40	8.80	3.00
0.04	0.2000	0.1666	0.1355	9.62	8.00	2.29
0.08	0.2449	0.1967	0.1235	9.00	7.75	1.90
0.08	0.2828	0.2204	0.1066	8.72	6.14	1.00
0.10	0.3163	0.2402	0.0813	8.23	5.55	0.63

Table 1c: For Sm (III) – L

Ionic Strength(μ)				pK	$LogK_1$	$logK_2$
0.02	0.1414	0.1238	0.1453	10.40	9.00	3.10
0.04	0.2000	0.1666	0.1355	9.62	8.24	3.98
0.08	0.2449	0.1967	0.1235	9.00	7.99	2.30
0.08	0.2828	0.2204	0.1066	8.72	7.20	2.15
0.10	0.3163	0.2402	0.0813	8.23	6.25	1.80

from phenolic OH^- group and can therefore be represented as

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

The titration data were used to construct the curve between volume of NaOH *vs* pH. They are called as acid titration curve, ligand titration curve and metal titration curve. The pKvalues of ligand and logK values of Pr(III), Nd(III) and Sm(III) complexes at various ionic strength were calculated by Irving and Rossotti's method [19]**.** It is shown in table no. (1), (2) and (3) has given bellow. It could be seen from table (1), (2) and (3) that the pK and logK values are found to be decreases with increasing ionic strength.

The pK and logK values were employed to calculate the thermodynamic constants with the help of Bronster equation[20].

$$\log K = \log K^0 + A\ \Delta Z^2 \text{-} \sqrt{\mu} \qquad \text{...(1)}$$

and

Table 4: Thermodynamic dissociation constants pK^0 at zero ionic strength

System	Plot	pK^0 and $\log K^0$
L	pK *vs*	12.55
	pK *vs* / (1+)	12.30
	pK *vs* [- 0.3] / (1+)	11.76
L- Pr (III)	$\log K_1$ *vs*	12.00
	$\log K_1$ *vs* / (1+ $\sqrt{\mu}$)	11.94
	$\log K_1$ *vs* [- 0.3] / (1+)	11.00
	$\log K_2$ *vs*	5.92
	$\log K_2$ *vs* / (1+)	5.21
	$\log K_2$ *vs* [- 0.3] / (1+)	4.53
L-Nd (III)	$\log K_1$ *vs*	10.59
	$\log K_1$ *vs* / (1+)	11.02
	$\log K_1$ *vs* [- 0.3] / (1+)	11.16
	$\log K_2$ *vs*	4.57
	$\log K_2$ *vs* / (1+)	5.03
	$\log K_2$ *vs* [- 0.3] / (1+)	5.57
L-Sm(III)	$\log K_1$ *vs*	10.49
	$\log K_1$ *vs* / (1+)	10.80
	$\log K_1$ *vs* [- 0.3] / (1+)	10.96
	$\log K_2$ *vs*	4.49
	$\log K_2$ *vs* / (1+μ)	4.98
	$\log K_2$ *vs* [- 0.3 μ] / (1+μ)	5.01

Table 5 : Slopes and "Z ^{2} values from the plots of pK and logK *Vs*

System	pK *vs*		$\log K_1$ *vs*		$\log K_2$ *vs*	
	Slope	z^2	Slope	z^2	Slope	z^2
L	0.59	0.37	-	-	-	-
L – Pr (III)	-	-	0.466	0.189	0.267	0.140
L – Nd (III)	-	-	0.219	0.064	0.125	0.072
L-Sm(III)	-	-	0.118	0.057	0.120	0.059

Table 6: Values of "Z^2

System	Constants	Reaction equlilibra	Value of "Z^2	
			Expected	Observed
L	pK	$HL^- \leftrightarrow H^+ + L^-$	0.279	0.879
Pr(III) - L	$\log K_1$	$Pr^{3+} + L^- \leftrightarrow H^+ + (Pr\ L)^+$	- 2.000	-7.00
	$\log K_2$	$(Pr\ L)^+ + L^- \leftrightarrow Pr\ L_2$	- 0.117	- 0.288
Nd(III)-L	$\log K_1$	$Nd^{3+} + L^- \leftrightarrow H^+ + (Nd\ L)^{2+}$	- 0.175	- 0.600
	$\log K_2$	$(Nd\ L)^{2+} + L^- \leftrightarrow (Nd\ L_2)^+$	- 0.139	-0.500
Sm(III)-L	$\log K_1$	$Sm^{3+} + L^- \leftrightarrow H^+ + (Sm\ L)^{2+}$	- 0.173	- 0.588
	$\log K_2$	$(Sm\ L)^{2+} + L^- \leftrightarrow (SmL_2)^+$	- 0.132	- 0.432

$$pK = pK^0 - A\ \Delta Z^2 - \sqrt{\mu} \qquad ...(2)$$

Where, A – Debye-Huckel constant, ΔZ^2-Difference in the square of the charges of product and reactant ions, K^0 – Is the formation constant at zero ionic strength, μ - ionic strength

The values of pK, $\log K_1$, and $\log K_2$ were plotted against the values of . The plot of logK *vs* and pK,*vs* gave straight lines The magnitude of ΔZ^2 and slope were calculated from graphs. The data obtained of pK and logK values could be utilized to know the mechanism of complex equilibria. The expected and observed values for ΔZ^2 values for the corresponding dissociation and association equilibria are given bellow.

It is observed from the table-05, that the slope values of pK and are more than expected values, while the logK values are less than expected values. Those values do not give conclusive evidence regarding the magnitude of the charges of reacting species. The discrepancy may be due to the limited applicability of Bronsted equation.

The plots of pK, logK *Vs* , / (1+) and

[- 0.3] / (1+)

are also plotted and slops values were determined. It shows that modified Debye -Huckel equation also not show much more improvement in the slope values. The discrepanay been observed and excepted slope value was thought to be due to the concentration and did not activity terms used in the equation of stability constants.

Thermodynamic stability constants

The thermodynamic stability constants observed from various plots at zero ionic strength are presented in table - 04.

It can be seen that there is good an agreement among thermodynamic constants obtained from various plots.

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