pH-METRIC STUDIES ON STABILITY CONSTANTS OF THE COMPLEXES OF SUBSTITUTED PYRAZOLES AND PYRAZOLINES WITH Cu(II), Ni(II) AND Cd(II) METAL IONS IN 70% DIOXANE-WATER MIXTURE

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Abstract : The interactions of Cu(II), Ni(II) and Cd(III) metal ions with 3-(4-chloro-1-hydroxynapthalene-2-yl)-5-(5-substituted furan-2-yl), 4-5 dihydro pyrazole-1-carbothioamide and 3-(4-chloro-1-hydroxynapthalen-2-yl)-5-(5-substituted furan-2-yl) pyrazole-1-carbothioamide have been studied at 0.1 M ionic strength in 70 % Dioxane-water mixture by Bjerrum method. The values of proton-ligand stability constant (pK) and metal-ligand stability constants (log k) were calculated and compared by using the data obtained. The effects of substituent were studied from estimated data. The pK & log k values were also used to study the effect of substituents.

Keywords: pyrazole, Bjerrum method, proton-ligand stability constant, metal-ligand stability constant.

INTRODUCTION

Metal complexes containing pyrazole-based ligands have been the subject of much interest because of their rich coordination chemistry and a number of established and potential application areas [1]. On the other hand, substituted pyrazole have been acclaimed for their medicinal value [2]. Knorr and Bank [3] studied the physical characters of substituted pyrazoles which act as antibiotic drugs and good chelating agents. This has led to the considerable commercial interest in pyrazole and pyrazoline as optical brightening agents for textile paper and fabrics [4]. Pyrazoles and pyrazolines find their applications in medicines for their anti aggregation [5], antidepressant [6], antiarthritic [7], antidiabetics [8] and antibacterial [9] activities. Beam [10] synthesized some new pyrazoles derivatives and revealed their antifungicidal activities.

The pyrazoles and their derivatives have long been studied for their strong complex forming ability [11–14]. Rossotti and Rossotti [15] Martell and Calvin [16] and Bjerrum [17] played an important role in the rapid progress for understanding of metal-complexes in aqueous as well as mixed solutions. Pratibha Agrawal [18] and Dinesh Pund [19] have determined metal-ligand stability constants of some carbamide complexes in solution at 0.1M ionic strength. Solanki and Narwade [20] have synthesized some substituted pyrazoles and studied their physical characters in 70% dioxane-water mixture. Swami [21] has explained the stabilities of palladium chelates of substituted hydrazine and the effect of substituting groups CH$_3$, OCH$_3$, and Cl. Fukuda et al [22] have studied formation constants and showed the effect of increasing size of the metal cations on constants. Jamode et al. [23, 24] have revealed the physicochemical properties and the stability constants of substituted pyrazoles with Cu(II), Co(II), and Ni(II). The binary complexes of various metal ions with substituted pyrazoles have been studied by many workers [25–27].

The present paper reports pH-metric studies on the interaction of 3-(4-chloro-1-hydroxynapthalen-2-yl)-5-(furan-2-yl) pyrazole-1-carbothioamide (L$_1$), 3-(4-chloro-1-hydroxynapthalen-2-yl)-5-(5-methylfuran-2-yl)pyrazole-1-carbothioamide (L$_2$), 3-(4-chloro-1-hydroxynapthalen-2-yl)-5-(5-(hydroxymethyl) furan-2-yl) pyrazole-1 carbothioamide (L$_3$) with Cu (II), Co (II), and Ni (II). The present work also deals with the study at various ionic strengths. Due to the insolubility of ligands in water, hence, a 70% dioxane-water mixture was used as solvent. The dioxane-water mixture acts as non-interfering and non polar solvent.

R= H, CH$_3$, CH$_2$OH
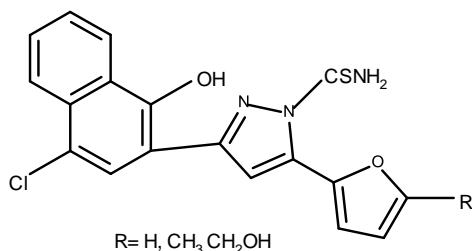
EXPERIMENTAL

- **Ligands:**
1) 3-(4-chloro-1-hydroxynapthalen-2-yl)-5-(furan-2-yl) pyrazole-1-carbothioamide (L_1),
2) 3-(4-chloro-1-hydroxynapthalen-2-yl)-5-(5-methylfuran-2-yl) pyrazole-1-carbothioamide (L_2),
3) 3-(4-chloro-1-hydroxynapthalen-2-yl)-5-(5-(hydroxymethyl) furan-2-yl) pyrazole-1 carbothioamide (L_3)

- **Metal ions:** Cu (II), Co (II), and Ni (II)
- 1 M KNO$_3$ solution, 0.1 M HNO$_3$ solution, 0.1 M NaOH and 0.01M metal ions solution are prepared in double distilled water.
- 0.01 M Pyrazole solution in 70% dioxane –water mixture.
- **Calvin –Bjerrum titration method:**

Titrations are carried out pH-metrically (pHmeter with model E614 accuracy ±0.05 unit) at 27±0.10c in 70% dioxane-water mixture and at an inert atmosphere by bubbling nitrogen gas.
Ionic strength is maintained constant by adding an appropriate amount of 1M KNO$_3$ solution.

General procedure:

Types of Titrations:

1. Acid titration: 2.5ml HNO$_3$ (0.1M) + 2. 5ml KNO$_3$ (1M) + 20ml 70% dioxane – water solution (A) (V_0 =25ml)

2. Ligand titration: 2.5ml HNO$_3$ (0.1M) +2.5ml KNO$_3$ (1M) + 5 ml ligand (in dioxane) + 15ml, 70% dioxane – water solution (A+L) (V_0=25ml)

3. Metal Titration: 2.5ml HNO$_3$ (0.1M)+ 2.5ml KNO$_3$(1M) +5ml ligand (in dioxane) +1ml metal ion sol^n +14 ml, 70% dioxane – water solution. (A+L+M) (V_0 = 25ml)

Detection Method:

Titration curves are used to determine the values of $\bar{n}_A$ (proton -ligand formation numbers) which are presented in Table (1) to (3). Formation curve are constructed between $\bar{n}_A$ values and pH. The pH values at 0.5 $\bar{n}_A$ corresponds the pK values (proton-ligand dissociation constants) of respective ligand. Proton ligand dissociation constants (pK values) are evaluated and presented in Table (4), they are calculated by Half Integral and Point wise calculations method.

Results and Discussion

The (acid + ligand) curves deviated from acid curves at pH 4.0 and continued up to pH 12.0. It clearly indicates the dissociation of – OH.

$$HL \longleftrightarrow H^+ + L$$

Metal ligand stability constants:

Metal ion hydrolysis: The pH at which metal ion starts hydrolyzing should be known to ascertain the complex formation with the ligand. The formation of hydroxide M(OH) is given by equation

$$M + H_2O \longleftrightarrow M(OH)^- + H^+$$
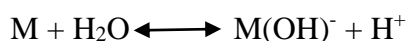
It causes deviation of metal titration curve even in absence of the reagent. The departure of metal complex titration curve is observed always at lowest pH values than the pH of hydrolysis. This indicated the complex formation before hydrolysis of metal ion.

Formation curves: The departure of metal titration curve from ligand curve (acid + ligand) is found from pH 2.95 and increased up to pH 11.0. This showed the commencement of complex formation.

The values of $\bar{n}$ (Metal-ligand formation number) are evaluated by applying Irving-Rossotti's expression presented in Table (5, 6 and 7) for respective systems. Metal-ligand stability constants of complex are determined by applying Irving-Rossotti's expression as shown in the Table (8).

Table 1) Determination of ($\bar{n}_A$) values   Ligand 1

pH	V_1	V_2	$\Delta V = V_1 - V_2$	$\bar{n}_A$
6.4	2.46	2.63	0.17	0.6595
6.6	2.47	2.65	0.18	0.6396
6.8	2.48	2.66	0.18	0.6397
7.0	2.49	2.68	0.19	0.6199
7.2	2.50	2.70	0.20	0.6000
7.4	2.51	2.72	0.21	0.5802
7.6	2.52	2.73	0.21	0.5803
7.8	2.53	2.76	0.23	0.5405
8.0	2.54	2.78	0.24	0.5207
8.2	2.56	2.80	0.24	0.5210

Table 2) Determination of ($\bar{n}_A$) values   Ligand 2

pH	V_1	V_2	$\Delta V = V_1 - V_2$	$\bar{n}_A$
6.4	2.46	2.63	0.17	0.6595
6.6	2.47	2.65	0.18	0.6396
6.8	2.48	2.67	0.19	0.6197
7.0	2.49	2.69	0.20	0.5999
7.2	2.50	2.71	0.21	0.5800
7.4	2.51	2.73	0.22	0.5602
7.6	2.52	2.75	0.23	0.5403
7.8	2.53	2.79	0.26	0.4806
8.0	2.54	2.80	0.26	0.4808
8.2	2.56	2.82	0.26	0.4811
8.4	2.58	2.85	0.27	0.4616

Table 3) Determination of ($\bar{n}_A$) values   Ligand 3

pH	V_1	V_2	$\Delta V = V_1 - V_2$	$\bar{n}_A$
5.4	2.43	2.57	0.14	0.7193
5.6	2.43	2.59	0.16	0.6792
5.8	2.44	2.61	0.17	0.6593
6.0	2.44	2.63	0.19	0.6192
6.2	2.45	2.65	0.20	0.5993
6.4	2.46	2.67	0.21	0.5794
6.6	2.46	2.69	0.23	0.5393
6.8	2.47	2.72	0.25	0.4995
7.0	2.48	2.75	0.27	0.4596
7.2	2.48	2.76	0.28	0.4396
7.4	2.50	2.77	0.27	0.4600

Table 4) Proton –Ligand stability Constants (pk values)

Ligand	pk values Half integral method	pk values pointwise calculation
L1	8.68	8.62 ± 0.05
L2	7.92	$8.7.88 \pm 0.03$
L3	6.74	6.74 ± 0.06

Table 5) Determination of $(\bar{n})$ values   System: Cu (II) Ligand 1 complex

pH	V_2	V_3	$\Delta V = V_2 - V_3$	$\bar{n}$
3.4	2.39	2.49	0.10	1.0004
3.6	2.41	2.53	0.12	1.1987
3.8	2.43	2.56	0.13	1.2972
4.0	2.45	2.59	0.14	1.3954
4.2	2.46	2.61	0.15	1.4940
4.4	2.48	2.63	0.15	1.4929
4.6	2.49	2.65	0.16	1.5913
4.8	2.51	2.67	0.16	1.5902
5.0	2.53	2.69	0.16	1.5890
5.2	2.54	2.71	0.17	1.6871
5.4	2.56	2.73	0.17	1.6859

Table 6) Determination of $(\bar{n})$ values   System: Co (II) Ligand 1 complex

pH	V_2	V_3	$\Delta V = V_2 - V_3$	$\bar{n}$
3.6	2.41	2.50	0.09	0.9000
3.8	2.43	2.54	0.11	1.0984
4.0	2.45	2.57	0.12	1.1970
4.2	2.46	2.59	0.13	1.2958
4.4	2.48	2.62	0.14	1.3939
4.6	2.49	2.64	0.15	1.4924
4.8	2.51	2.67	0.16	1.5902
5.0	2.53	2.69	0.16	1.5890
5.2	2.54	2.71	0.17	1.6871

Table 7) Determination of $(\bar{n})$ values   System: Ni (II) Ligand 1 complex

pH	V_2	V_3	$\Delta V = V_2 - V_3$	$\bar{n}$
3.4	2.39	2.46	0.07	0.7010
3.6	2.41	2.50	0.09	0.9000
3.8	2.43	2.54	0.11	1.0984
4.0	2.45	2.57	0.12	1.1970
4.2	2.46	2.60	0.14	1.3949
4.4	2.48	2.62	0.14	1.3939
4.6	2.49	2.65	0.16	1.5913
4.8	2.51	2.68	0.17	1.6889
5.0	2.53	2.71	0.18	1.7864
5.2	2.54	2.73	0.19	1.8842
5.4	2.56	2.76	0.20	1.9813

Table 8) Metal Ligand Stability Constant (Log K)

Ligands	Metal	Stability Constant		Difference in Stability Constants $(LogK_1 - LogK_2)$
		$Log(K_1)$	$Log(K_2)$	
L1	Cu	4.4833	1.5004	2.9829
	Co	4.1840	1.4003	2.7838
	Ni	4.2427	1.4199	2.8228
L2	Cu	3.9216	1.3130	2.6087
	Co	2.9866	0.9999	1.9867
	Ni	3.9210	1.3122	2.6088
L3	Cu	4.1250	1.3810	2.7439
	Co	3.5409	1.1850	2.3559
	Ni	4.2948	1.4373	2.8575

REFERENCES:

[1] Mukharjee R.; Coord. Chem. Rev., 2000, 203, 151.

[2] Trofimenko O.S.; Chem. Rev., 1972, 72, 500.

[3] L. Knorr, A. Bank; Ber, Dfson Chem. Ges, 1985 , 18, 316.

[4] H. Dorlars, J. Schooder ; Angew Chem. Ind. Ed.Eng., 1975 , 14, 664.

[5] K.Y. Lee, J.M. Kim; Tetradedron Lett., 2003 , 44, 6737.

[6] P.G.Baraldi, G. Pavani, B. Vitali; Biorg. Medicinal Chem., 2002 , 449, 1012.

[7] R. Store, J. Ashtan, H.M. Hann; J. Nucleosides , 1999 , 203, 1812 .

[8] P. Erhan, A. Mutlu, U. Tayfun, E. Dilck; J.Medicinal Chem., 2001 , 36, 539 .

[9] N.Paolella P.L., Anderson; J.A.U.S. US4 , 1982 ,359, 475.

[10] C. Beam; J.Chem. Abstr., 2006 , 102, 166656t.

[11] Poddar S.N. and Roychaudhary S.; J. Indian Chem.Soc., 1972,11,49,1175.

[12] Poddar S.N., Roychaudhary S. and Bhattacharya S.M., Indian J. Chem., 1974, 7,12, 754.

[13] Poddar S.N., Bhattacharya S.M., Roychaudhary S.,et al.;Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys.,Theor. Anal. Chem., 1979, 18, 252.

[14] Warburton B.A., Nichols D. and Bagley M.J.; J. Chem. Soc., A., 1970, 2694

[15] Rossotti F. J. C, and Rossotti H. S., "Determination of stability constants", McGraw Hill book Co. P-l, 1961.

[16] Martell A. E., and Calvin M., "Chemistry of metal chelate compounds", Prentice Hall INC, England, 1962.

[17] Bjerrum J., "Metal amine complex formation in aqueous solution", P. Haas and sons, Copenhagen, 1941.

[18] P. B.Agrawal, M.L. Narwade ; Asian J. Chem., 2006 ,18,4, 3141 .

[19] D.A Pund; Ph.D. Thesis in Chemistry, Amravati:Amravati Univ., 2009.

[20] P.R. Solanki ; M.L. Narwade; Ind. J. Chem Council, 2007 , 24,2, 43.

[21] Swami, V.K., Ultra Sci., 2006, 18, 1, 97.

[22] V. Fukuda R., Morishita ,K. Sone ; J.Chem.Soc.Jpn.,1984 ,49,4, 1017.

[23] Jamode V.S., Mohod, J.R. and Malkhede D.D.; J. Pradushan Nirmulan., 2005, 2, 2, 34.

[24] Jamode, V.S., Deshmukh, P.N. and Malkhede, D.D.; J. Pradushan Nirmulan., 2005, 2, 2, 27.

[25] Sawalakhe, P.D., Ph.D. Thesis in Chemistry, Amravati:Amravati Univ., 1992.

[26] Thakare, D.V. and Jamode V.S.; Asian J. Chem., 2003,15, 2,1552.

[27] Poddar S.N., Ghosh S., Bhattacharya S.M. and Roychaudhuri S.; J. Inorg. Nucl. Chem., 1997, 39, 739.