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Studies of stability constants of the complexes of chlorosubstituted pyrazoles and pyrazoline with Cu(II),Ni(II),Co(II) and Nd(III) metal ions in 70% dioxane-water mixture at 0.1 m ionic strength

Avinash Ramteke*[a] and Marutil Narwade[b]

[a]Department of Chemistry, Government Vidarbha Institute of Science and Humanities, Amravati(M.S.), India
[b]Department of Chemistry, Vidyabharati Mahavidyalaya, Amravati(M.S.), India

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ABSTRACT

The stability constants of the complexes of chlorosubstituted pyrazoles and pyrazoline in 70 % (v/v) dioxane-water mixture have been determined by P^H-Meter. The proton-ligand and metal-ligand stability constants of Cu(II),Ni(II),Co(II) and Nd(III) metal ions with 3-(2-hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(4'-methoxyphenyl)-1-phenylpyrazole(L_1),3-(2-hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(4'-methoxyphenyl)-1-phenylpyrazoline (L_2) and 4-(2-chlorophenyl)-3-(3-furanoyl-5-(2-hydroxyphenyl) pyrazole(L_3) have been performed pH metric method at 0.1 M ionic strength at 27± 0.1^0C. The value of Log K_1 and Log K_2 were used to determined the stepwise and simultaneous complex formation and to verify the validity of Log K= a. pK + b relation.

Keyword: stability constant, chlorosubstituted pyrazoles, pyrazoline, complex formation.

INTRODUCTION

The pyrazoles and their derivatives have been known for their strong complex forming ability [1, 2].The determination of the metal – ligand stability constant requires the knowledge of reliable and accurate values of proton-ligand stability constants. Thus, proton-ligand and metal-ligand stability constants are correlated with each other. Pyrazoline derivatives are found to be bactericidal [3], fungicidal [4] and also used in the dye industry [5]. The chlorosubstituted pyrazolines effectively used as antitumor [6] antidiabatic [7] and analgesic [8].Several type of drugs [9] such as antileprotic, high ceiling diuretics, antibacterial etc and their metal complexes have special importance in biochemical system. Some metal ion present in biological fluids e.g. cobalt, nickel and copper are energy sources of life. The protonation study of pyrazoles [10] in aqueous medium is already done by several peoples. Little information is known about the stability constant of substituted pyrazoles and metal complexes in 70% (v/v) dioxane-water medium with respect to their protonation and stability constant or salvation properties [11-13]. The hydroxy pyrazole is significant compound for formation of complex with various transition metals [14]. The electrochemical behavior of some sulphamoyl azonitro pyrazole has been studied over a wide range of p^H. The different substituted aryl pyrazole is used for the protection of plants against fungal diseases [15]. Some of the arylpyrozoles were reported to have nucleoside –HIV-1 reverse transcriptase inhibitor activity [16]. Paulmony et al [17] have studied antibacterial activity of the metal complexes of some Pyrazole and metal ions as Cu (II), Ni (II) and CO (II). Pyrimidino pyrazoles are being studied in the fight against Cancer [18]. 3-(4-pyridyl)-2-H-Naphtho -1,2-C-pyrazoles is an ant fertility agent for female mammals [19].The binary complexes of various metal ions with substituted pyrazoles have been studied by many workers [20,21]. Narwade et al [22] have investigated the metal-ligand stability constants of UO_2 (II) and Cu (II) complexes with some substituted sulphonic acids. The formation constants of the complexes of substituted pyrazoles with some lanthanides metal ions have been studied by Naik and Narwade [23]. Narwade [24] and Ramteke also reported the acoustical properties of chlorosubstituted pyrazoles at different concentration and percentage range.

The present work describes the interaction between Cu (II), Ni (II), Co (II) and Nd (III) with 3-(2-hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(4'-methoxy phenyl)-1-phenyl pyrazole(**L_1**), 3-(2-hydroxy-3,5-dichlorophenyl)-4-anisoyl- 5-(4'-methoxyphenyl)-1-phenyl pyrazoline(**L_2**) and 4-(2- chlorophenyl)-3-(3-furanoyl-5-(2-hydroxyphenyl) pyrazole(**L_3**) as ligands in 70% (v/v) dioxane-water mixture. The ligands are insoluble in water hence, 70% dioxane-aqueous medium was used as solvent. The stability constants were calculated using the MATLAB program, which is a computer program using the matrix-based environment for the second order global analysis of pH metric data.

MATERIALS AND METHODS

2.*1 Materials and Solutions*

The ligands were synthesized by known literature methods [25, 26]. The purity of these compounds was verified by TLC, and structures were confirmed by NMR, IR and melting points. All chemicals used were Anala R grade KNO_3, HNO_3 and NaOH .The stock solutions of the ligands (0.01 M) were prepared by dissolving the requisite quantity of the ligands in a minimum volume of dioxane subsequently diluted to the final volume. Nitrates of transition and lanthanide metal ions were used to prepare metal solutions (0.01 M) and standardized by the EDTA titration method as discussed in literature [27]. The ionic strength (0.1 mol dm^{-3}) was maintained constant by using 1 M potassium nitrate solution. The carbonate free sodium hydroxide solution (0.1057 mol dm^{-3}) was prepared.

2.2Apparatus and procedure

All pH-metric titration were carried out at 27 ^{0}C in an inert atmosphere by bubbling oxygen free nitrogen gas through an assembly containing the electrodes in order to prevent atmospheric oxidation using carbonate free NaOH. The pH of the solution measured using with EQUIP-TRONICS digital p^H meter (model EQ – 610) equipped with combined glass electrode and magnetic stirrer (accuracy ± 0.005 units). The instrument could read p^H in the range 0.00 – 14.00 in the steps of 0.005. This p^H meter has built in internal electronic voltage supply with temperature compensator covering the range 0 to 100^0C. The p^H meter was switched on half an hour before starting the titration for the initial warm up of the instruments. Before taking any reading, the electrodes were washed with distilled water and dried with filter paper. The readings were recorded only when the instrument registered a steady value for at least one minutes. The p^H meter was standardized before each titration with a buffer solution of p^H 4.00, 7.00 and 9.20, prepared from a Qualigens buffer tablets.

The following three solutions were titrated separately against standard carbonate free NaOH (total volume 25 ml). a) Free HNO_3 (2.5 ml) + KNO_3 (2.5 ml). b) Solution a + ligand solution (5 ml). c) Solution b + metal solution (1 ml). The ligands were acidified with HNO_3 in a 70% dioxane-water medium and the ionic strength was kept constant by added the KNO_3. The ligands were titrated against standard NaOH (carbonate free) using Calvin-Bjerrum and Calvin-Wilson pH titration methods [28, 29]. The pH meter reading were taken after fixed interval until stable reading was obtained and then curves of pH verses ml of alkali were plotted (Fig.1). The proton-ligand constant were calculated from the pH values obtained from the titration using the Irving-Rossotti method [30].

RESULTS AND DISCUSSION

The proton-ligand stability constant and metal-ligand stability constants(Log K) of L_1,L_2,L_3 and their complexes with Cu(II),Ni(II),Co(II) and Nd(III) metal ions determined in 70% dioxane-water mixture at ±27 ^{o}C. The extent of deviation may be the dissociation of OH group completely. The proton-ligand formation number n_A was calculated by the Irving-Rossotti expression. The pK values of the ligands and formation constants of the complexes were calculated by the algebraic method point wise calculation and also estimated from formation curves $n_{A\ VS}$ pH (half integral method) by noted the pH at which $n_{A\ =}$ 0.5 (Bjerrum 1957). The accurate values of pK were determined by point wise calculations which are represented in Table 1. The n_A values were calculated by using the equation.

$$\bar{n}_A = \gamma \ - \left(\frac{(E^0 + N) \text{ x } (V_2 - V_1)}{(V_0 + V_1) \text{ x } T^0{}_L} \right) \qquad (1)$$

Where γ denote the replaceable H^+ ion, $T_L{}^0$ is concentration of ligands, E^0 is concentration of acid, N is normality of alkali, and V^0 is the total volume of the mixture. The data of n_A obtained at various p^H values along with horizontal difference (V_2-V_1) for representative systems. The acid + ligand titration curves (A+L) deviated from acid titration curves (A) in case of ligand (L_1) at p^H 3.10, ligand (L_2) at p^H 4.40 and Ligand (L_3) at p^H 9.30 and deviation increased continuously up to p^H 13.00, p^H 12.10 and p^H 12.80 respectively, which shows the dissociation of -OH group of ligands. The increase in deviation is due to the dissociation of –OH group of the ligands. The ligands used in present investigation may be considered as monobasic acid containing only one dissociable H^+ ion from phenol –OH group and it can be therefore, represented as HL. The dissociating equilibrium can be shown as

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

The formation curves are constructed by plotting the values of n_A against $\bar{p}^H$ of the solution. The dissociation constant p^K of ligands are calculated from formation curves. The values of p^K obtained are given in Table 2. The accurate p^K values of the ligands are calculated by the point wise calculation method is in good concordance with those obtained by the half integral method (Table 2). The metal-ligand stability constants were calculated by the half integral method by plotting n vs pL. The n values are determined by using the equation

$$\bar{n} = \left(\frac{(E^0 + N) \text{ x } (V_3 - V_2)}{(V^0 + V_2) \text{ x } T^0{}_m} \right) \qquad (2)$$

Where N, E^0, V^0 and V_2 have the same significance as in Eq. (1) V_3 is the volume of alkali added in the metal titration to attain the given pH reading, and $T^0{}_m$ is the concentration of the metal ion in the reaction mixture. The stability constants of complexes have been calculated and are represented in the Table. 3.

It is observed that from the Table 2, the p^K value for ligand (L_3) is found to be greater as compared to other and showed the p^K values order is $p^K{}_1 < p^K{}_2 < p^K{}_3$. The p^K values of L_1 and L_2 are smaller than p^K values of L_3. This may be due to the fact of the presence of chloro as electron withdrawing group nearer to OH group. The p^K values of ligand L_3 is greater than ligand L_1 and L_2, this is because the absence of chloro group. The accurate values of proton-ligand stability constants are used for the determination of metal-ligand stability constants. The log K_1 and log K_2 values obtained are found to be in good concordance with half integral method and point wise calculation methods. Higher values of log K_1 and log K_2 showed that ligands are stronger chelating agents and vice versa. Metal.-ligand stability constants of the complexes (log K_1 and log K_2) from Table 3 showed that the log K_1 values are slightly greater than log K_2 values. It could be also, seen from same table that there is reduction of log K_1 and log K_2 values for Cu (II) – L_2 and Ni (II) – L_2 systems that may be due to their pyrazoline ring. It is also observed from (Table 3) metal-ligand stability constants of the complexes that the difference between log K_1 and log K_2 values for Co (II), Ni (II) and Nd (III) is greater. This shows the stepwise complex formation but in case of Cu (II), there is simultaneous formation of complex due to minimum difference between log K_1 and log K_2 values. The proton – ligand stability constant (p^K) and metal-ligand stability constants (log K) are used to verify the validity of log K = a. p^K + b relation. This relation was verified for vanadyl ion complexes of sulphonic acids [31] and uranyl complexes of chalcones [32] at 0.1 M ionic strength. This relationship has proved good to many workers [33, 34] for the use of a series of similar ligands. The validity of this relationship can be tested only for the metal complexes of similar substituted ligands. The linear relationship between log K and p^{KOH} was observed by Irving and Rossotti [35] for complexes of some metals with substituted oximes and substituted salicylaldehyde were attributed by Jones et al [36] to the fact that study was limited to two particular groups of ligands with variation of dissociation constants within a narrow range. For complexes of Fe (III) with oximes and substituted salicylic acids [37], the values of slopes are 0.90 and 0.75

respectively whereas Cu (II) and Ni (II) imidoacetates [38] and catechol complexes of Cu (II), Ni (II) and Zn (II) gave slopes greater than one. On other hand, for phthalic acid complexes of Cu (II) and Ni (II), the slopes less than unity have been reported.

In present investigation, linear relation between log K_1 / log K_2 and p^K is observed for Cu (II), Ni (II) and Co (II). The values of slopes of the straight lines are given in Table 4(Slope value are calculated from the straight line which obtained from plot of log K, Vs p^K). The slope values are nearly equal to unity. This indicated that the change in partial molar free energy of metal – ligand and proton – ligand complexes exactly compensated with each other, so, log K, Vs p^K plot should give a straight line with unit slope such a line was obtained for 1:1 and 1:2 complexes. Thakare [39] has also studied transition and lanthanide metal complexes with some pyrazoles. Meshram [40] has studied the transition metal complexes Cu (II), Ni (II) and Co (II) with pyrazolines. The transition metal complexes are reported to exhibit a major deviation from unit slope for ligands with substituent adjacent to the chelating atom [41]. In the present investigation lanthanide metal complex with some chlorosubstituted pyrazoles and pyrazolines obey linear relationship for 1:1 complexes the slope values are as given in Table 4. The slopes value of Co (II) complexes is not in good agreement with the values of Jones et al [36], the disagreement may be attributed to the fact that π - electrons donating and accepting properties of cation may not be the only factor which influences slope values of other factors, such as ionization potential of metal ion, nuclear repulsion between metal ion and donor atoms, tendency of metal ions to form π - bonds, ligand field stabilization may influence-slope values. The difference between log K_1 and log K_2 complexes was less than 2.5, indicating the simultaneous formation of 1:1 and 1:2 complexes. They showed the linear relationship between log K and p^K values of ligands suggesting identical binding sites in all ligands. Irving and Rossotti have observed that irrespective of the nature of ligand, stability of metal complexes always follow the following order (Mg < Zn < Ni < UO_2 < Cu) whether the sterric hindrance occurs or not.

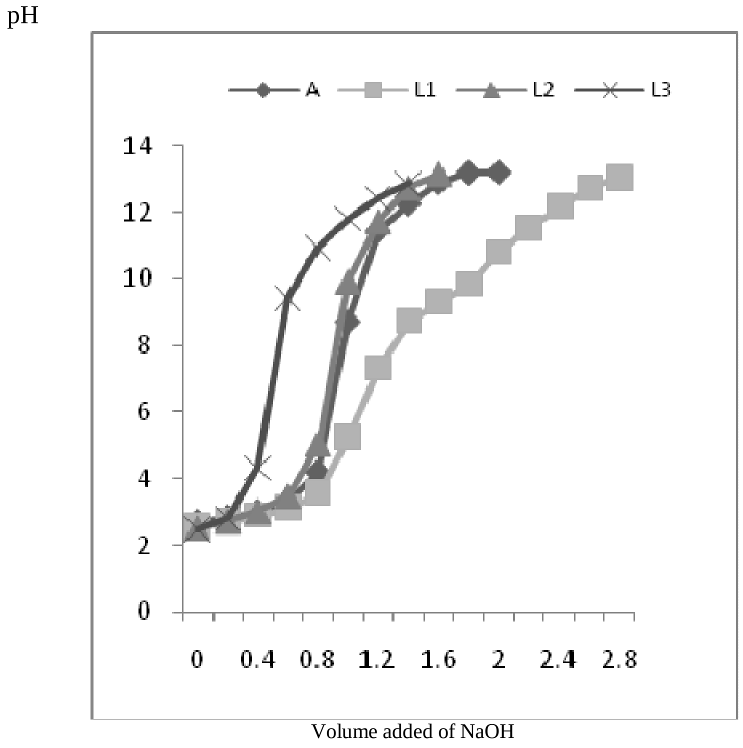

Figure 1: pH (on y-axis) against volume of NaOH (on x-axis) in ml at Constant ionic strength 0.1 mol dm^{-3} at ±27 ^{0}C.

The stability constants of metal complexes in the present investigation, the order of metal complexes of chlorosubstituted pyrazoles and pyrazolines are neither the Irving – Williams nor any of the empirical order reviewed by Irving – Williams. Most of the log K values of Nd (III) complexes are greater than transition complexes. Ingle [42] has observed similar discrepancy in the order for complexes of substituted acetophenone-oximes ligand, in which chelation occurs through nitrogen and oxygen donor atoms. But the difference between log K_1 and log K_2 values is smaller in all systems. It seems therefore that both 1:1 and 1:2 complexes are formed simultaneously and not in a stepwise process.

Table 1: Proton-ligand dissociation constants at 27 °C±0.1 K and at the ionic strength I= 0.1 mol.dm^{-3} KNO_3 in 70% dioxane-water medium.

Ligand	p^H	V_1	V_2	$\Delta V = V_2-V_1$	$\bar{n}_A$
L_1	6.4	0.90	1.05	0.15	0.6815
	6.6	0.95	1.10	0.15	0.6821
	6.8	0.95	1.15	0.20	0.5745
	7.0	0.95	1.15	0.20	0.5745
	7.2	0.95	1.20	0.25	0.4681
L_2	9.0	0.79	0.97	0.18	0.6160
	9.2	0.79	0.98	0.19	0.5949
	9.4	0.79	0.99	0.20	0.5730
	9.6	0.79	1.00	0.21	0.5520
	9.8	0.79	1.10	0.31	0.3380
L_3	11.0	0.67	0.81	0.14	0.7001
	11.2	0.70	0.85	0.15	0.6790
	11.4	0.72	0.90	0.18	0.6151
	11.6	0.74	0.93	0.19	0.5941
	11.8	0.76	1.10	0.34	0.2741

Table 2: pK Value of ligands L_1, L_2 and L_3.

Ligand	p^K (Half Integral Method)	p^K (Point wise calculation Method)
L_1	7.12	7.1882 ± 0.02
L_2	9.64	9.3596 ± 0.05
L_3	11.70	11.3405 ± 0.01

Table 3: Metal-ligand stability constants by different methods

System	Constants	Method	
		Half Integral	Point wise
Cu (II) – L_1	log K_1	5.9440	5.9335 ± 0.01
	log K_2	3.8510	3.7188 ± 0.04
Ni (II) – L_1	log K_1	7.1430	7.1250 ± 0.01
	log K_2	4.6530	4.4994 ± 0.06
Co (II) – L_1	log K_1	7.1430	6.9641 ± 0.05
	log K_2	4.1072	3.9688 ± 0.06
Nd (III) – L_1	log K_1	7.5440	7.3285 ± 0.08
	log K_2	3.7566	3.6146 ± 0.05
Cu (II) – L_2	log K_1	3.4313	3.3738 ± 0.05
	log K_2	1.1553	1.1048 ± 0.05
Ni (II) – L_2	log K_1	3.8380	3.8004 ± 0.03
	log K_2	1.1554	1.1023 ± 0.05
Co (II) – L_2	log K_1	4.0413	3.9850 ± 0.05
	log K_2	2.7558	2.3820 ± 0.08
Nd (III) – L_2	log K_1	6.1430	6.0817 ± 0.06
	log K_2	3.1643	3.0881 ± 0.07
Cu (II) – L_3	log K_1	8.7403	8.6123 ± 0.08
	log K_2	4.2552	4.1999 ± 0.05
Ni (II) – L_3	log K_1	5.5440	5.4608 ± 0.08
	log K_2	3.8567	3.8027 ± 0.05
Co (II) – L_3	log K_1	7.9444	7.8582 ± 0.06
	log K_2	4.6757	4.6714 ± 0.01
Nd (III) – L_3	log K_1	7.0413	6.8587 ± 0.08
	log K_2	6.0530	5.9560 ± 0.07

Table 4: Slopes values for transition and lanthanide metal ions.

Metal ions	Slope values
Cu (II)	0.644
	0.299
Ni (II)	0.410
	0.200
Co (II)	0.113
	0.052
Nd (III)	0.246
	0.502

CONCLUSION

The stability constants of complexes of chlorosubstituted pyrazoles and pyrazolines with metals Cu (II),Co (II), Ni (II) and Nd (III) that concluded the difference between log K_1 and log K_2 values for Co (II), Ni (II) and Nd (III) is greater. This shows the stepwise complex formation but in case of Cu (II), there is simultaneous formation of complex due to minimum difference between log K_1 and log K_2 values. The observed values of the proton – ligand stability constant (p^K) and metal-ligand stability constants (log K) are used to verify the validity of log K = a. p^K + b relation, from their slope value. The linear relation between log K_1 / log K_2 and p^K is observed for Cu (II), Ni (II) Co (II) and Nd (III) metal complexes. The slopes values of the straight lines are given in Table 4. The difference between log K_1 and log K_2 complexes was less than 2.5, indicating the simultaneous formation of 1:1 and 1:2 complexes. They showed the linear relationship between log K and p^K values of ligands suggesting identical binding sites in all ligands.

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