SHORT COMMUNICATIONS

Proton/Metal-Ligand Stability Constants of Complexes of Sr(II), Cr(II), and Al(III) with N-Phthaloyl Aminoacid and Benzimidazole Derivatives in Dioxane-Water Mixture¹

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Abstract—Formation of complexes Sr(II), Cr(II), and Al(III) with ligands (1,3-dioxo-1,3-dihydro-2H-iso-indol-2-yl)acetic acid (L1), 2-(1-(2-(4-nitrophenyl)-1H-benzo[d]imidazol-1-yl)-1-oxobutan-2-yl)-2,3-dihydroinden-1-one(L2) and 2-(2-(2-(4-chlorophenyl)-1H-benzo [d] imidazol-1-yl)-2-oxoethyl)isoindo-line-1,3-dione (L3) investigated using pH metric technique in 70% dioxane-water mixture. Proton ligand formation number and metal-ligand formation number determined. Proton-ligand stability constants pK values and metal – ligand stability constants log k values evaluated using half integral method. It indicates that Sr(II), Cr(II), and Al(III) metal ions formed 1 : 1 and 1 : 2 complexes with the ligands L1, L2, and L3. These can be of interest for specialists in the field of coordination chemistry.

Keyword: proton–ligand and metal–ligand stability constants, pH-metric study, benzimidazole derivative, Irving–Rossetti expression

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INTRODUCTION

Naik et al. [1], El-Gammal et al. [2], Anan et al. [3], Fukada et al. [4], and O'Sullivan et al. [5] reported pH-metric studies of metal complexes. Szpak et al. [6] explained Coordination abilities of *N*-methyl alkyl-aminomethane-1, 1-diphosphonic acids towards zinc(II), magnesium(II), and calcium(II) metal ions. El-Bindary et al. [7] reported thermodynamic studies of azo dye ligand and its metal complexes potentio-metricaly.

In our ongoing endeavor, we studied Proton/metal-ligand stability constants of complexes of Ni(II), Cu(II), and Co(II) [8, 9]. In continuation to our earlier work, here in this paper we have reported the study of Proton/Metal Ligand Stability Constants of Complexes of Sr(II), Cr(II), and Al(III) with *N*-phthaloyl and benzimidazol derivatives pH metrically.

EXPERIMENTAL PROCEDURE

pH-Measurements carried out with digital pHmeter model Equiptronics EQ-610. The experimental procedure involves pH titration of following 3 sets of mixtures (keeping total volume constant) against a carbonate free standard alkali.

1. Free acid (0.01 M) titration.

2. Free acid (0.01 M) and ligand (20×10^{-4}) titration.

3. Free acid (0.01 M), ligand (20×10^{-4}) and metal ion (4×10^{-4}), against standard NaOH solution.

The ionic strength of all the solutions maintained constant (0.1 M) by addition of appropriate quantity of 1 M NaClO_4 solution.

a. Proton-ligand formation numbers $\overline{\eta}A$:

$$\overline{\eta}A = \gamma \frac{(E^0 + N)\Delta V}{(V^0 + V_1)T_L^0},$$

where V^0 is initial volume of solution (50 mL), *N* is normality of sodium hydroxide, T_L^0 is concentration of ligand in 50 mL solution, E^0 is initial concentration of free acid (HClO₄), γ is number of dissociable protons from ligand, $\overline{\eta}A$ is proton-ligand formation number, $(V_2 - V_1) = \Delta V$ are volumes of alkali consumed by acid and ligand at the same pH.

b. Proton-ligand formation curves ($\overline{\eta}A$). Formation curves are plotted between $\overline{\eta}A$ and pH The half

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integral method employed for the determination of proton-ligand stability constants.

c. Half integral method. The proton-ligand stability constant (pK values) are calculated from formation curve.

d. Metal-ligand formation number $(\overline{\eta})$:

$$\overline{\eta} = \gamma \frac{(E^0 + N)\Delta V}{(V^0 + V_2)T_M^0},$$

where V^0 is initial volume of solution (50 mL), *N* is normality of sodium hydroxide, T_M^0 is concentration of metal ions, $\bar{\eta}$ is metal–ligand formation number, E^0 is initial concentration of free acid (HClO₄), γ is number of dissociable protons from ligand, $(V_3 - V_2) =$ ΔV are volumes of alkali consumed by acid and ligand at the same pH.

e. Metal-ligand formation curves. Formation curves are plotted between $\overline{\eta}$ and pH. The metal-ligand stability constants determined by half integral method.

The value of $pL = \log K$ is calculated with the help of following expression.

$$pL = \log \left[\frac{[\mathrm{H}^+]/K_L}{T_L^0 - T_M^0 \overline{\eta}} \right].$$

f. Relation between log K and pK values. The proton-ligand stability constant (pK) and metal-ligand stability constants (log K) used to verify the validity of log K = apK + b relation. The validity of this relationship tested only for the metal complexes of similar substituted ligands.

Ligands used for this work are:

1. (1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl) acetic acid (*N*-phthaloyl glycine), i.e., L1



2. 2-(1-(2-(4-Nitrophenyl)-1H-benzo[d]imidazol-1-yl)-1-oxobutan-2-yl)-2,3-dihydroinden-1-one, i.e., L2



3. 2-(2-(2-(4-Chlorophenyl)-1H-benzo[d]imidazol-1-yl)-2-oxoethyl)isoindoline-1,3-dione i.e., L3



The values of slope and intercept in present work are not in good agreement. The disagreement may be attributed to the fact that pi electrons donating and accepting properties of cations may not be the only factor which influences slope values. Other factors, such as ionization potential of metal ion, nuclear repulsion between metal ion and donor atoms. Tendency of metal ions to form pi bonds. Ligand field stabilization may influence slope values.



Fig. 1. Acid curve (A), acid–ligand titration curve (A + L) and acid–ligand–metal (Sr(II), Cr(II), and Al(III)) (A + L + M) titration curves for L1, L2, and L3.

RUSSIAN JOURNAL OF PHYSICAL CHEMISTRY A Vol. 92 No. 12 2018

Table 1. Proton ligand stability constant for complexes of metal (Sr(II),Cr(II), and Al(III)) with ligands (L1, L2, and L3)

S.N.	System	Constant half p <i>K</i> integral method
1	L1	1.99×10^{-5}
2	L2	1.548×10^{-6}
3	L3	9.332×10^{-6}

RESULTS AND DISCUSSION

A. Free acid titration curve, acid + ligand titration curve, and acid + ligand + metal titration curve. As per Fig. 1, the deviation between free acid titration curve and ligand titration (acid + ligand) curve is conformation of the dissociation of proton/OH group (of -COOH) from ligand L1 and OH group (of enol form) L2 and L3. The deviation between (acid + ligand) curve and (acid + ligand + metal) curve shows the commencement formation of complex. The change of color in the range of pH 2.5 to 7.5, shows the formation of complex.

B. Proton ligand stability constant (p*K*). Table 1 shows the p*K* values (proton–ligand stability constants) calculated from the formation curves between pH vs. $\overline{\eta}A$ by half integral method, which increases in order: L1 > L3 > L2. The difference in p*K* values of two ligands is due to the relative position of the groups in the structure. p*K* value is less in case of L2 may be due to presence of electron withdrawing $-NO_2$ group. In case of L2 and L3, p*K* value is less than L1 which may be due to steric hindrance.

C. Metal ligand stability constant (log k_1 and log k_2). Tables 2, 3 show the p*L* values (metal-ligand stability constants) calculated from the formation curves between pH vs. $\overline{\eta}$ by half integral method. Ordinarily log k_1 values are greater than log k_2 values for all metal complexes except L2–Al(III) complex.

Therefore, L2–Al(III) complex occurred simultaneously, because there is no appreciable difference between $\log k_1$ and $\log k_2$ values. Rest of the complexes occurred stepwise due to sufficient difference between $\log k_1$ and $\log k_2$ values increases in the following order:

CONCLUSION

The proton-ligand and metal-ligand stability constant of complexes of Sr(II), Cr(II), and Al(III) with *N*-phthaloyl and benzimidazole derivatives pH metrically reported here in 70% dioxane-water mixture.

According to the titration curves, the deviation between acid + ligand (A + L) curve and acid + ligand + metal (A + L + M) curve for all systems started from pH 2.5 to 3. This indicated the commencement of complex formation.

pK value is less in case of L2 because of presence of electron withdrawing $-NO_2$ group. In case of L2 and L3, pK value is less than L1 because of steric hindrance. However there is a difference in $\log K_1$ and $\log K_2$ values which shows the stepwise formation of 1:1 and 1:2 complexes with all three ligands. The results shows that the ratio of $\log K_1 / \log K_2$ is positive in all cases, consequently it leads to the formation of stable complexes. L2-Al(III) complex formation occurred simultaneously, as there is no appreciable difference between $\log k_1$ and $\log k_2$ values. Rest of the complexes occurred stepwise due to sufficient difference between $\log k_1$ and $\log k_2$ values; $\log k_1$ and $\log k_2$ values of Sr(II) are maximum for L3 means Sr(II) forms most stable complex with L3. Conversely $\log k_1$ and $log k_2$ values of Cr(II) and Al(III) are maximum

S.N.	System	$\log k_1$ i.e., p L_1	$\log k_2$ i.e., p L_2	$\log k_1 - \log k_2$	$\log k_1 / \log k_2$
1	L1–Sr(II)	2.948	1.7803	1.1677	1.6778
2	L1–Al(III)	2.817	1.799	1.018	1.5658
3	L1–Cr(II)	2.977	1.87	1.107	1.591
4	L2–Sr(II)	3.056	2.729	0.327	1.1198
5	L2–Al(III)	4.146	4.219	0.073	0.9826
6	L2–Cr(II)	4.207	3.169	1.038	1.3275
7	L3–Sr(II)	3.476	2.739	0.737	1.2690
8	L3–Al(III)	3.636	3.139	0.497	1.1583
9	L3–Cr(II)	3.336	2.219	1.117	1.5033

Table 2. Metal-ligand stability constants for complexes of Metal (Sr(II), Cr(II), and Al(III)) with ligands (L1, L2, and L3)

S.N.	Details of data mentioned in tables	Intercept	Slope
1	Curve of pH vs. $\overline{\eta}A$ values for L1	0.471012	0.046012
2	Curve of pH vs. $\overline{\eta}$ values for L1 + Sr(II)	6.342667	-0.52133
3	Curve of pH vs. $\overline{\eta}$ values for L1 + Al(III)	5.338545	-0.32545
4	Curve of pH vs. $\overline{\eta}$ values for L1 + Cr(II)	1.508545	0.594545
5	Curve of pH vs. $\overline{\eta}A$ values for L2	0.157697	0.077697
6	Curve of pH vs. $\overline{\eta}$ values for L2 + Sr(II)	3.598364	0.036364
7	Curve of pH vs. $\overline{\eta}$ values for L2 + Al(III)	1.426364	0.636364
8	Curve of pH vs. $\overline{\eta}$ values for L2 + Cr(II)	4.34697	0.26897
9	Curve of pH vs. $\overline{\eta}A$ values for L3	0.278182	0.062182
10	Curve of pH vs. $\overline{\eta}$ values for L3 + Sr(II)	-16.3836	3.208364
11	Curve of pH vs. $\overline{\eta}$ values for L3 + Al(III)	-17.4685	3.995515
12	Curve of pH vs. $\overline{\eta}$ values for L3 + Cr(II)	2.653636	0.411636

Table 3. Values of slope and intercept for proton–ligand titration and metal–ligand titration

for L2 means Cr(II) and Al(III) forms most stable complex with L2.

Notwithstanding the proton-ligand stability constant (p*K*) and metal-ligand stability constants (log *K*) used to verify the validity of log $K = a \times pK + b$ relation.

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