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pH-Metric Studies on Formation Constants of the Complexes of Substituted Pyrazoles with Some Lanthanide Metal Ions and the Influence of Ionic Strengths on Complex Equilibria in a 70% Dioxane–Water Mixture[1]

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Abstract—The pK_a values of N-heterocyclic compounds (substituted pyrazoles) in a 70% (v/v) dioxane–water mixture have been determined using pH-metric measurements. The stability constants of the complexes of Dy(III), Nd(III), Sm(III), and Tb(III) with 3-(2-hydroxyphenyl)-5-methylpyrazole, l-phenyl-3-(2-hydimyphenyl)-5-methylpyrazole 3-(2-hydroxy-4-methylphenyl)-5-methylpyrazole, and l-phenyl-3-(2-hydroxy-4-methylphenyl)-5-methylpyrazole have been determined by the pH-metric method at (300 ± 0.1) K. The effect of ionic strengths on the complexes of Sm^{3+} and Pr^{3+} ions with pyrazole has been investigated in the internal from 0.02 to 0.1 mol dm^{-3} (sodium perchlorate) in the pH range 2–3.

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INTRODUCTION

Metal complexes containing pyrazole-based ligands have been the subject of much interest owing, on the one hand, to 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]. They also show considerable numerous biological, medicinal, and agrochemical activity mainly acting as blood sugar controlling agent [3], antibacterial [4], antifungal [5], antihelmenthetic [6], antiviral remedies [7], as herbicides and fungicides [8].

The pyrazoles and their derivatives have long been known for their strong complex forming ability [9–12]. The nitrogen-containing ligand and metal complexes are used as catalysts for olefin polymerization [13], which were modified to give different microstructures and high molecular weights. The zinc pyrazole complexes work as luminescent compounds [14] that exhibit blue emission at room temperature. The hydroxy pyrazole should be a convenient entry into complex formation. This ligand readily forms complexes with various transition metals [15]. These compounds can react with metal ions by the loss of a proton from the hydroxyl group on the heterocyclic ring. The stability of the metal complexes with heterocyclic compounds was studied [16, 17]. The hydroxyl group plays an important role in complex formation [18].

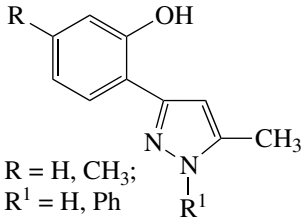
Many of the organic compounds that can affect the biological and ecological behavior of the lanthanide and actinide ions have carboxylate binding sites. The studies on complex formation by tripositive rare-earth ions with biologically important ligands are in progress because of their role in biological processes [19]. To the best of our knowledge, no examples of the interaction of substituted pyrazoles with rare-earth metal ions are known to date.

Swami [20] has discussed the stabilities of palladium chelates of substituted hydrazine and the effect of substituting groups CH_3, OCH_3, and Cl. An attempt has been made to correlate the pK_a values of ligand with the first step and overall stability constants. Agrawal [21] has reported the metal-ligand stability constants of 3-[3-(2-hydroxy-5-methylaryl]pyrazol-5-yl]-5-thiazolo[2,3-C]-S-triazol-5-(6H)one with transition metals in 70% ethanol-water mixtures. They showed the formation of 1 : 1 and 1 : 2 complexes in the pH range from 2.5 to 5.5. Jamode et al. [22, 23] have been reported the physicochemical properties and the stability constant of substituted pyrazoles with Cu(II), Co(II), and Ni(II). Some of the ligands acquired stepwise complex formation and other are simultaneously due to nitro and bromo electron-withdrawing groups, respectively. The binary complexes of various metal ions with substituted pyrazoles have been studied by many workers [24–26].

[1] The article is published in the original.

[†] Deceased.

The present paper reports pH-metric studies on the interaction of 3-(2-hydroxyphenyl)-5-methylpyrazole (**L[1]**), l-phenyl-3-(2-hydroxyphenyl)-5-methyl pyrazole (**L[2]**), 3-(2-hydroxy-4-methylphenyl)-5-methylpyrazole (**L[3]**), and 1-phenyl-3-(2-hydroxy-4-methylphenyl)-5-methylpyrazole (**L[4]**) with rare-earth metal ions (Dy^{3+}, Nd^{3+}, Sm^{3+}, and Tb^{3+}) in the 1 : 1 ratio at 300 ± 0.1 K. The present work also deals with the study at various ionic strengths. The ligands are insoluble in water and, hence, a 70% dioxane-aqueous mixture was used as solvent. Moreover, it acts as non-interfering and nonpolar solvent. The formation 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 equilibrium data.



EXPERIMENTAL

Materials and solutions. The ligands and their derivatives were synthesized by a known literature method [27]. Purity of these compounds exceeds 99.5% and was verified by TLC, and the structures were confirmed by NMR, IR, and melting points. The stock solutions of the ligands (4.0×10^{-2} mol dm^{-3}) were prepared by dissolving the required amount of the ligands in a minimum volume of dioxane subsequently diluted to the final volume. Nitrates of rare-earth metal ions (from Sigma and Aldrich) were used to prepare metal solutions (1.0×10^{-2} mol dm^{-3}) and standardized by the EDTA titration method as discussed in literature [28]. The stock solution of perchloric acid was prepared and used after standardization [29]. The ionic strength (0.1 mol dm^{-3}) was maintained constant by using 1 M sodium perchlorate solutions. The carbonate-free sodium hydroxide solution (0.1071 mol dm^{-3}) was prepared by Vogel's method [30].

Apparatus and procedure. The pH of solutions was measured with a EQUIP-TRONICS instrument (Model EQ-614) equipped with a combined electrode and a magnetic stirrer pH-meter model (accuracy ±0.005 units) with a combined glass electrode assembly. The instrument could read pH in the range from 0.00 to 14.00 in steps of 0.005. This pH-meter has been built in an internal electronic voltage supply with a temperature compensator covering the range from 0 to 100°C. The pH-meter was switched on half an hour before starting the titration for initial warming up of the instrument. The instrument was calibrated before each titration with an aqueous standard buffer solution of pH 4.20 (phthalate buffer), 7.00, and 9.10 (borate buffer) prepared from the Qualigens buffer tablets.

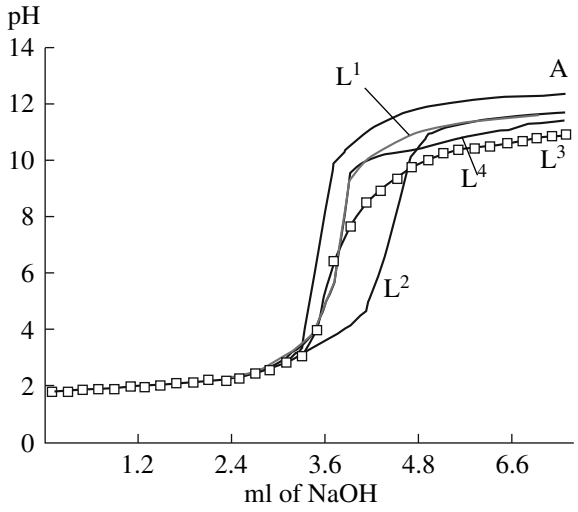


Fig. 1. pH against volume of 0.1071 mol dm^{-3} NaOH at I = 0.1 mol dm^{-3} at 300 K; A = perchloric acid, L^1, L^2, L^3, and L^4 are ligands.

The following solutions were prepared (total volume 25 cm^3): (a) perchloric acid (2.0×10^{-2} mol dm^{-3}, 2.5 ml) + sodium perchlorate (2.0×10^{-2} mol dm^{-3}, 2.5 ml), (b) solution a + ligand (1.0×10^{-2} mol dm^{-3}, 5 ml), (c) solution b + metal ion (1.0×10^{-2} mol dm^{-3}, 1 ml).

The ligands were acidified with $HClO_4$ in a 70% dioxane-water medium, and the ionic strength was kept constant by means of $NaClO_4$. The ligands were titrated against standard carbonate-free sodium hydroxide (0.1071 mol dm^{-3}) using Calvin-Bjerrum and Calvin-Wilson pH titration techniques. The curves of pH versus ml of base were plotted [31–33] (Fig. 1). The proton-ligand constants were calculated from the pH values obtained from the titration using the Irving-Rossotti method [31–33] and the MATLAB computer program (Table 1).

RESULTS AND DISCUSSION

The extent of deviation may be the dissociation of OH group completely. The proton-ligand formation number $\tilde{n}_A$ 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 pointwise calculation and also estimated from formation curves $\bar{n}_A$ vs pH (half-integral method) by noting pH at which $\bar{n}_A = 0.5$ (Bjerrum, 1957). The accurate values of pK were determined by pointwise

Table 1. Proton-ligand dissociation constants at 300 ± 0.1 K and at the ionic strength I = 0.1 mol dm^{-3} $NaClO_4$ in a 70% dioxane–water medium

Ligand	pH	V_1	V_2	$(V_2 - V_1)$	$\bar{n}_A$
L^1	6.2	3.20	3.38	0.18	0.6259
	6.4	3.20	3.39	0.19	0.6051
	6.6	3.20	3.42	0.22	0.5483
	6.8	3.20	3.44	0.24	0.5012
	7.0	3.20	3.45	0.25	0.4804
L^2	3.4	2.98	3.16	0.18	0.6227
	3.6	3.00	3.20	0.20	0.5814
	3.8	3.04	3.26	0.22	0.5402
	4.0	3.06	3.34	0.28	0.4152
L^3	4.8	3.10	3.30	0.20	0.5832
	5.0	3.12	3.33	0.21	0.5623
	5.2	3.14	3.36	0.22	0.5418
	5.4	3.16	3.40	0.24	0.5005
	5.6	3.16	3.41	0.25	0.4797
L^4	4.50	3.05	3.26	0.21	0.5612
	4.70	3.06	3.28	0.23	0.5405
	4.90	3.10	3.34	0.24	0.4995
	5.10	3.11	3.36	0.25	0.4788

Table 2. pK Values of ligands L^1–L^4

Ligand	pK (half-integral method)	pK (pointwise calculation method)
L^1	6.80	6.7205 ± 0.03
L^2	3.90	3.7851 ± 0.05
L^3	5.40	5.1790 ± 0.04
L^4	4.90	4.6834 ± 0.02

calculation. The $\bar{n}_A$ (exptal) values were calculated from the following equation (Table 1):

$$\bar{n}_A = \gamma - \left[\frac{(E^0 + N)(V_2 - V_1)}{(V^0 + V_1)T_I^0}\right], \quad (1)$$

where γ denotes the number of dissociable protons, N is the concentration of sodium hydroxide (0.1071 mol dm^{-3}), $(V_2 - V_1)$ is the measure of the displacement of the ligand curve relative to the acid curve, where V_2 and V_1 are the volume of alkali added to reach the same pH reading to get accurate values of $(V_2 - V_1)$; the titration curves were drawn on an enlarged scale; E^0 and T_I^0 are the resultant concentration of sodium perchlorate and the concentration of the ligand, respectively; V^0 is the initial volume of the reaction mixture (25 cm^3). The practical protonation constants were then confirmed by the graphical method.

The evaluated proton-ligand dissociation constants for various ligands in the present study are in good concordance with reported values. The pH-metric titration curve shows only one inflection point indicated that there is only one acidic group, and the proton dissociation constants for HL have been calculated by using the following equations:

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

$$K' = \frac{[H^+][L^-]}{[HL]}.$$

The curves obtained for pH vs volume of alkali added to the mixture (perchloric acid + ligand) at 300 K were utilized for the evaluation of the volume of NaOH at different pH.

The values of pK calculated by the pointwise calculation method is in good concordance with those obtained by the half-integral method (Table 2).

Similarly, the metal-ligand stability constants were determined by the half-integral method by plotting $\bar{n}_{(cal)}$ vs pL. The experimental $\bar{n}$ values are determined using the expression

$$\bar{n} = \left[\frac{(E^0 + N)(V_3 - V_2)}{(V^0 + V_2)T_m^0}\right], \quad (2)$$

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_m^0 (0.001 mol dm^{-3}) is the concentration of the metal ion in the reaction mixture. The stability constants for various binary complexes have been calculated and are tabulated in Table 3 as log$K$. This may be explained on the basis of the difference in charge and coordination number of metal ions. The smaller size (higher charge) and higher coordination number of rare-earths permit their closer interaction with the ligands, and at the same time, allow a minimum repulsion to occur because of the expanded coordination number resulting in the formation of more stable complexes compared to those with trivalent metal ions.

It is observed that at pH ~2.0 free metals are present in 99 to 100% amounts, and the percentage of free metal ion decreases gradually on increasing the pH of

the solution and attains an almost zero value at higher pH. This suggests that with increasing pH of the solution the metal ions are distributed in ML^{2+} species (for all metal-ligand complex systems in the pH ranges). This shows the reaction mechanism of complex equilibria:

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

$$M^{3+} + L^- \rightleftharpoons ML^{2+},$$

$$ML^{2+} + L^- \rightleftharpoons ML^+.$$

For the determination of metal-ligand stability constants the accurate values of proton-ligand stability constants are required. Metal-ligand stability constants of the complexes ($\log K_1$ and $\log K_2$) from Table 3 showed that there is no an appreciable difference between $\log K_1$ and $\log K_2$ values. This indicates the simultaneous formation of complexes. It could be also seen from the same table that there is a reduction for the $\log K_1$ and $\log K_2$ values of a Tb–L^4 system that may be due to the presence of the phenyl ring, which acts as an electron-withdrawing group. The series is Tb(III) < Dy(III) < Sm(III) < Nd(III).

The plot of $\sqrt{\mu}$ vs $\log K$ values showed a linear relationship, and slope values are found at unit (Fig. 2). This unity indicates compensation ion of binding energy between the ligand and complex. The $\log K_1$ and $\log K_2$ values obtained are found to be in good concordance with the half-integral method and pointwise calculation methods. Narwade et al. [34, 35] have reported the metal–ligand stability constants of Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+} transition metal ions with substituted chalcones, isoxazolines, pyrazolines, and phenylpyrazolines at 0.1 M ionic strength measured pH-metrically and spectrophotometrically. Mahajan [36] has also investigated the metal-ligand stability constants of transition metal ions with sulfonic acids. Higher values of $\log K_1$ and $\log K_2$ showed that the ligands are stronger chelating agents. Metal–ligand stability constants of complexes have played an important role in thermochemistry for determining the thermodynamic parameters (ΔH, ΔG, ΔS).

Effect of ionic strengths. The dissociation constants of L-2-amino-3-hydroxypropanic acid [37] have been determined at various ionic strengths. The stability constants on complexation of VO_2^+ with glycine discussed the effect of ionic strengths on protonation and complexation [38]. The effect of ionic strength on N-(trihydroxymethyl)glycine (Tricine) [39] with transition metal ion (Co^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}) complexes has been studied. It is found that values of pK_a and $\log K$ were found to decrease with increasing ionic strength. In the present work, the Sm^{3+} and Pr^{3+} metal ions complexes with ligand L^4 at various ionic strengths in a 70% dioxane-water mixture medium have been investigated by the Calvin-Bjerrum pH-metric technique at (300 ± 0.1) K. It is found that the pK values decrease with an increase

Table 3. The stability constants of complexes of Dy(III), Nd(III), Sm(III), and Tb(III) with various ligands (1 : 1 and 1 : 2 ratios) at 300 ± 0.1 K and the ionic strength I = 0.1 mol dm^{-3} $NaClO_4$ in a 70% dioxane–water medium

System	Constant	Method	
		half-integral	pointwise
Dy(III)–L^1	$\log K_1$	6.2448	6.1525 ± 0.050
	$\log K_2$	5.1540	5.2504 ± 0.040
Nd(III)–L^1	$\log K_1$	6.4449	6.5506 ± 0.055
	$\log K_2$	5.7537	5.8005 ± 0.030
Sm(III)–L^1	$\log K_1$	5.8449	5.7155 ± 0.035
	$\log K_2$	4.5541	4.4995 ± 0.025
Tb(III)–L^1	$\log K_1$	5.3550	6.5525 ± 0.055
	$\log K_2$	4.2506	5.4055 ± 0.030
Dy(III)–L^2	$\log K_1$	2.6450	2.7000 ± 0.040
	$\log K_2$	2.1540	2.0055 ± 0.055
Nd(III)–L^2	$\log K_1$	3.0440	3.1500 ± 0.035
	$\log K_2$	2.7541	2.0801 ± 0.040
Sm(III)–L^2	$\log K_1$	3.8437	3.7985 ± 0.035
	$\log K_2$	3.5541	3.5095 ± 0.025
Tb(III)–L^2	$\log K_1$	3.3477	3.3400 ± 0.020
	$\log K_2$	3.0569	3.1155 ± 0.035
Dy(III)–L^3	$\log K_1$	5.3435	5.3555 ± 0.025
	$\log K_2$	4.6537	4.5513 ± 0.045
Nd(III)–L^3	$\log K_1$	5.0446	5.1108 ± 0.050
	$\log K_2$	4.3507	4.3105 ± 0.020
Sm(III)–L^3	$\log K_1$	5.2445	5.1825 ± 0.015
	$\log K_2$	4.5538	4.4550 ± 0.035
Tb(III)–L^3	$\log K_1$	4.8447	4.7758 ± 0.050
	$\log K_2$	4.3535	4.5525 ± 0.030
Dy(III)–L^4	$\log K_1$	4.2446	4.4485 ± 0.045
	$\log K_2$	3.6537	3.7005 ± 0.030
Nd(III)–L^4	$\log K_1$	4.7447	4.6015 ± 0.010
	$\log K_2$	4.0541	4.0642 ± 0.025
Sm(III)–L^4	$\log K_1$	4.2450	4.0319 ± 0.045
	$\log K_2$	3.3540	3.2673 ± 0.035
Tb(III)–L^4	$\log K_1$	4.1449	4.2247 ± 0.050
	$\log K_2$	3.2540	3.1673 ± 0.040

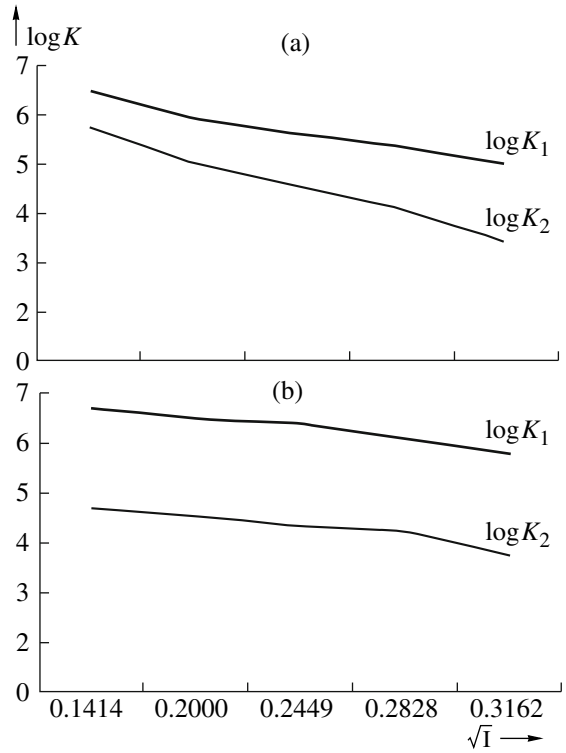


Fig. 2. Systems: Pr(III)–L^4 (a) and Sm(III)–L^4 (b).

in the ionic strength that is in accordance with the Debye–Hückel theory. The ionic strength data was used to study the correct mechanism of the complexation reaction.

The system has been studied at 0.02, 0.04, 0.06, 0.08, and 0.10 mol/l ionic strengths by varying the concentrations of sodium perchlorate. In addition to sodium perchlorate, the titrating system contained ions from perchloric acid, metal nitrate, and sodium hydroxide. The total ionic strength of the medium is calculated by following expression:

$$I = \frac{1}{2}\sum c_i Z_i^2, \quad (3)$$

where c_i and Z_i are the concentration and valence of metal ion, respectively.

The stability constants for the following systems were determined at 0.02, 0.04, 0.06, 0.08, and 0.10 mol/l ionic strengths. The log$K$ values for various systems at various ionic strengths are presented in Table 4. It may inferred from the experimental data that increases the ionic strength of the system and causes a decrease in log$K$ values. The thermodynamic dissociation constants are evaluated at $\sqrt{I} = 0$ from plots $\sqrt{I}$ vs log$K$ (Fig. 2).

Table 4. $\log K_1$ and $\log K_2$ values of complexes of Pr(III) and Sm(III) at different ionic strengths (I)

I	$\sqrt{(I)}$	Pr(III)–L^4		Sm(III)–L^4	
		$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
0.02	0.1414	6.65	4.60	6.32	4.50
0.04	0.2000	6.44	4.35	6.10	4.25
0.06	0.2449	5.85	4.06	5.75	3.90
0.08	0.2828	4.73	3.85	4.55	3.62
0.10	0.3162	4.50	3.60	4.24	3.37

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