Studies in Influence of Dielectric Constants on Complex Equilibria Between Substituted Pyrazolines and Lanthanide Metal Ions Ph Metrically

[1]Anil B. Naik and [2]Maroti Narwade

[1]Department of Chemical Technology, SGB Amravati University, Amravati-444602 (M.S.) India
[2]Vidya Bharati Mahavidyalaya, Amravati-444602 (M.S.) India

Abstract: The solution studies of binary (1:1) complexes of Sm (III) and Tb (III) with 3-(2-hydroxy-5-methylphenyl)-1,5-diphenyl-Δ^2 pyrazoline (HMPPPPz) and 3-(2-hydroxy-5-methylphenyl)-5-diphenyl-Δ^2 pyrazoline (HMPPPz) in 70% dioxane-aqueous medium at (27 ± 0.1) °C have been performed. The ionic strength $\mu = 0.1$ mol.dm^{-3} was maintained constant. The stability constants of the binary (1:1) systems decrease in order of Tb (III) > Sm (III). The studies of dielectric constants of ligand 3-(2-hydroxy-5-methylphenyl)-1, 5-diphenyl-Δ^2 pyrazoline (HMPPPPz) with Sm (III) and Tb (III) have been also studied.

Key words: Pyrazolines · Complex formation · Sodium perchlorate · Dielectric constant

INTRODUCTION

Pyrazoline derivatives are found to be bactericidal [1], fungicidal [2] and biodegradable agrochemical [3] also, used as intermediate in the dye industry [4]. The substituted pyrazolines effectively utilized as antitumer [5], antidiabatic [6], anaesthetic [7] and analgesic [8]. While the pyrazoline structure has shown a special ability to interact with UV and VIS radiation in linear and nonlinear optical sense; some of them used as drugs for prevention and diagnosis of many diseases [9]. Also, pyrazoline derivatives with different substitution show the electroluminescence and photoluminescence in OLED [10].

The lanthanide compounds have a remarkable importance in every day life [11,12]. More explicitly, in the previous decades their use in various organic technical processes led to a rapid growth especially in the field of complexes. In recent years the luminescence properties of rare earth metal complexes with different â-diketones have been widely studied due to their use in fabrication of polymer light emitting diodes to enable low cost, full color, flat panel displays. The effect of dielectric constants on pK and log K values is reported by many workers [13-15].

The present paper describes the complexation of Dy (III), Nd (III), Sm (III) and Tb (III) with 3-(2-hydroxy-5-methylphenyl)-1,5-diphenyl-Δ^2pyrazoline (HMPPPPz) and 3-(2-hydroxy-5-methylphenyl)-5-diphenyl-Δ^2 pyrazoline (HMPPPz) in 0.1 M ionic strength sodium perchlorate pH metrically. The present work also deals with the study at various ionic strengths. The ligands are insoluble in water and hence 70% dioxane-aqueous mixture solvent used. Moreover, it acts non-interfering and nonpolar solvent. The formation constants were calculated using the MATLAB program, a computer program using matrix-based, environment for second-order global analysis of pH metric equilibrium data. It also, deals with the study of the effect dielectric constant on proton-ligand and metal-ligand stability constants of Sm (III) and Tb (III) with [HMPPPz].

MATERIAL AND METHOD

The ligands [HMPPPPz] and [HMPPPz] are synthesized in the laboratory by known literature method [16]. Stock solutions of ligands were prepared by dissolving an accurate amount in dioxane solvent. Metal ion solutions were prepared by dissolving metal nitrate (Sigma-Aldrich) and standardized by EDTA [17]. A Carbonate free sodium hydroxide solution was prepared by dissolving the Analar pellets in deionsed water and the solution was standardized [18]. The stock solution of perchloric acid was prepared and used after standardization [19].
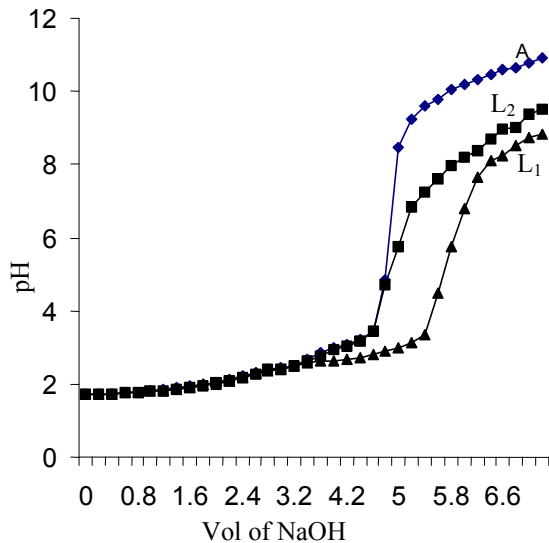

Corresponding Author: Anil B. Naik, Department of Chemical Technology, SGB Amravati University,
Amravati-444602 (M.S.) India

Fig. 1: pH against volume of 0.1071 mol.dm-3 NaOH at
μ= 0.1 mol.dm-3 at 300 K
A = Perchloric acid, L1 and L2 are ligands

Measurements: All measurements were carried out at $(27\pm0.1)°C$. The ionic strength was maintained 0.1 mol.dm^{-3} by addition of an appropriate amount of 1M sodium perchlorate. An EQUIP-TRONIC pH meter with magnetic stirrer used for pH measurements. A pH meter had a sensitivity of 0.01 units. The instrument could read pH in the range 0.00 to 14.00 in steps of 0.005. This pH meter has a built in internal electronic voltage supply with temperature compensator covering the range 0 to 100 °C. The pH meter was switched on half an hour before starting the titration for initial warm 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 a "Qualigens" buffer tablets. The hydrogen ion concentration was measured with combined glass electrode.

Procedure: The following solutions were prepared for pH metric titrations (total volume 25 cm³),

- Perchloric acid (2.0 x 10^{-2} mol.dm^{-3}, 2.5ml) + sodium perchlorate (2.0 x10^{-2} mol.dm^{-3}, 2.5 ml)
- Solution a + ligand (1.0x10^{-2} mol.dm^{-3}, 5ml)
- Solution b + metal ion (1.0x10^{-2} mol.dm^{-3}, 1ml)

The solutions 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-base solution were plotted [20-25] (Figure 1). The proton-ligand constants were calculated from the pH values obtained from the titration using the Irving-Rossotti method [20-25] and MATLAB computer program (Table 1).

RESULTS AND DISCUSSION

The extent of deviation may be the dissociation of -OH group completely. The proton-ligand formation numbers $\bar{n}_A$ were calculated by Irving-Rossotti expression. The pK values of ligands and formation constants of complexes were calculated by algebraic method point wise 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 point wise calculation. The $\bar{n}_A$ values (experimental) were calculated from the following equation (Table 1).

$$\bar{n}_A = \gamma - \left[\frac{\left(E^0 + N \right).\left(V_2 - V_1 \right)}{\left(V^0 + V_1 \right) \times T_l^0} \right] \qquad (1)$$

Where 'γ' denotes the number of dissociable protons. 'N' is the concentration of sodium hydroxide (0.1071 mol.dm^{-3}). The (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. $E°$ and T_l^0 are the resultant concentrations of perchloric acid and concentration of ligand respectively. $V°$ is the initial volume of the reaction mixture (25 cm³). The practical protonation constants were then confirmed by (Schwarzenbach's 1947) graphical method.

The evaluated proton-ligand dissociation constants for various ligands in the present study are in good concordance with reported values.

The curve obtained between pH versus volume of alkali added to the mixture (perchloric acid + ligand) at 300 K was utilized for the evaluation of volume of NaOH at different pH. The deviation between acid and acid + ligand L$_1$ is more than acid and acid + ligand L$_2$. That might due to presence of biphenyl group stronger electron sink.

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

Table 1: Proton- ligand Dissociation constants at (27 ± 0.1) °C and at ionic strength μ = 0.1 mol.dm⁻³ NaClO₄ in 70 % dioxane-water medium

Ligand	pH	V_1	V_2	$(V_2 - V_1)$	$\bar{n}_A$
L_1	4.80	5.25	5.40	0.15	0.7095
	5.00	5.25	5.45	0.20	0.6126
	5.20	5.25	5.48	0.23	0.5545
	5.40	5.26	5.51	0.25	0.5151
	5.60	5.26	5.52	0.26	0.4965
	5.80	5.26	5.54	0.28	0.4578
	6.00	5.28	5.62	0.34	0.3421
L_2	5.00	4.70	4.85	0.15	0.7041
	5.20	4.72	4.90	0.18	0.6451
	5.40	4.74	4.95	0.21	0.5863
	5.60	4.75	4.98	0.23	0.5470
	5.80	4.75	4.99	0.24	0.5273
	6.00	4.75	5.00	0.25	0.5076
	6.20	4.80	5.10	0.30	0.4101

Table 2: pK Values of Various Ligands

Temp. = 27 ±1 °C   μ = 0.1M

Ligand	pK (Half Integral Method)	pK (Pointwise calculation Method)
L_1	5.60	5.4929±0.01
L_2	5.90	5.7658±0.04

Table 3: Metal-ligands (log K) of Dy (III), Nd (III), Sm (III) and Tb (III) with various ligands (1:1 and 1:2 ratio) at (27±0.1)°C and ionic strength μ= 0.1 mol.dm⁻³ NaClO₄ in 70% dioxane-water medium.

System	Constants	Method Half Integral	Method Pointwise
Dy (III) - L_1	log K_1	4.5446	4.4869±0.045
	log K_2	4.0539	4.1066±0.025
Nd (III) - L_1	log K_1	4.9948	5.0245±0.035
	log K_2	4.8039	4.8859±0.010
Sm (III) - L_1	log K_1	4.6232	4.7783±0.025
	log K_2	4.5040	4.6829±0.035
Tb (III) - L_1	log K_1	4.6437	4.7520±0.045
	log K_2	4.3538	4.4053±0.040
Dy (III) - L_2	log K_1	5.1444	5.0186±0.050
	log K_2	4.5537	4.6425±0.065
Nd (III) - L_2	log K_1	5.0953	5.1348±0.020
	log K_2	5.0530	5.0342±0.010
Sm (III) - L_2	log K_1	5.4440	5.5473±0.025
	log K_2	5.2337	5.3691±0.035
Tb (III) - L_2	log K_1	5.1445	5.2648 ±0.045
	log K_2	5.0525	5.1264±0.030

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,

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

N, $E°$, 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 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 minimum repulsion because of the expanded coordination number resulting in the formation of more stable complexes compared to those with trivalent metal ion.

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 attain almost zero value at higher pH. This suggests that with increasing pH of the solution the metal ions distributed in ML^{3+} species (for all metal-ligand systems in the pH ranges).

For the determination of metal-ligand stability constants requires the accurate values of proton-ligand stability constants. Metal-ligand stability constants of the complexes (log K_1 and log K_2) from the table 3 showed that there is no an appreciable difference between log K_1 and log K_2 values that indicates the formation of complexes simultaneously.

The plot between pK and log K values showed linear relationship and slope values are found at unit (one). This unity indicates compensation ion of binding energy between ligand and complex. The log K_1 and log K_2 values obtained are found to be in good concordance with half integral method and pointwise calculations method. Narwade *et al.* [26,27] have reported metal-ligand stability constants of Fe (III), Co (II), Ni (II) and Cu (II) transition metal ions with substituted chalcones, isoxazolines, pyrazolines and phenyl pyrazoline at 0.1M ionic strength pH metrically and spectro-photometrically. Mahajan [28] has also investigated metal-ligand stability constants of transition metal ions with sulphonic acids. Higher values of log K_1 and log K_2 showed that ligands are stronger chelating agents. Metal-ligand stability constants of complexes have played an important role in thermochemistry for determining thermodynamic parameters (ΔH, ΔG, ΔS).

Table 4: pK and log K values of Sm (III) - L_2 and Tb (III) - L_2 at different percentages of Dioxane-water mixture at 0.01M ionic strength

| | | | | | Sm (III)-L_2 | | |
| | | | | | --------------------- | | |
Dioxane	D	1/D	M	pK	log K_1	log K_2	log (K_1-K_2)
60 %	27.2	0.0367	0.260	10.20	6.03	5.10	0.93
65 %	24.0	0.0416	0.295	10.35	6.20	5.20	1.00
70 %	19.5	0.0512	0.329	10.55	6.40	5.25	1.15
75 %	16.0	0.0625	0.340	10.60	6.55	5.35	1.20
					Tb (III)-L_2		

Dioxane	D	1/D	M	pK	log K_1	log K_2	log (K_1-K_2)
60 %	27.2	0.0367	0.260	10.20	4.863	3.553	1.3100
65 %	24.0	0.0416	0.295	10.35	5.049	3.854	1.1950
70 %	19.5	0.0512	0.329	10.55	5.1445	4.052	1.0925
75 %	16.0	0.0625	0.340	10.60	5.630	4.450	1.1800

Where *D Dielectric constant, M Mole fraction*

Table 5: log K_1 and log K_2 values for Sm (III), Tb (III)-L_2 at different percentage of dioxane-water at 0.01M ionic strength

| | | Sm (III) | | Tb (III) | |
| | | ---------------------------- | | ---------------------------- | |
% dioxane	pK	log K_1	log K_2	log K_1	log K_2
60	10.20	6.03	5.10	4.863	3.553
65	10.35	6.20	5.20	5.049	3.854
70	10.55	6.40	5.25	5.144	4.052
75	10.60	6.55	5.35	5.630	4.450

Effect of Dielectric Constant: The proton-ligand and metal-ligand stability constants are strongly affected by the dielectric constant of the medium because of the fact that at least one of the constituents is charged and other is either charged or has a dipole moment. Jahagirdar and Khanolkar [29] have investigated the effect of dielectric constant on pK and log K values of Cu (II)-3, 5-dibromosalicyclic acid. Sondalwale *et al.* [30] have investigated the effect of methanol-water mixtures on stability constants of Cu (II) amino acid peptide complexes. Khobragade [31] has investigated the effect of dielectric constants of nonproteic solvent and proteic solvent (ethanol) on dissociation and association of Cu (II)-Glycyl-Glycyl-Glycine. Ikhe [32] has reported the effect of dielectric constant of Cd (II), Sr (III) and Sm (III) with Captopril of different dioxane-water mixtures. Gulwade [33] has also reported the effect of dielectric constant of Co (II) and Sm (III) with 2-(5-mercapto-[1,2 3]-oxadiazol-2-yl)-phenol in DMF-water mixture.

The present work showed the influence of dielectric constant of different percentages of dioxane-water mixtures.

- pK- values of ligand L_2
- log K- values of (i) Sm (III) - L_2 (ii) Tb (III) - L_2

It could be seen from table 4 that pK values increased with the increase in the percentage of dioxane-water mixture. The variations in the values with the dielectric constants were investigated from the plots of pK *Vs* 1/ D and pK *Vs* mole fraction of organic solvent.

CONCLUSION

It is observed that there is non-linear ship between pK Vs 1/D holds good only for low percentages of organic solvent. Also, a plot of pK Vs mole fraction exhibits a linear relationship. It could be concluded that pK and log K values increase with increasing the dielectric constant that may be due to the effect of dioxane as a bulky solvent.

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