

Influence of Dielectric Constants on Complex Equilibria Eu(III)-3(2-Hydroxy-5-Methyl Phenyl)-1-Phenyl-5- (4-Methoxy-Phenyl) Pyrazoline Complexes in Different Percentages of Methanol-Water Mixture

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The interaction between Eu(III) and 3-(2-hydroxy-5-methyl phenyl)-1-phenyl-5-(4-methoxy-phenyl) pyrazoline (HMPPMPPZOLINE) in different percentages of methanol-water mixture at 0.1 M ionic strength and $27 \pm 0.1^\circ\text{C}$ has been studied potentiometrically. The data obtained can be used to study the values of proton-ligand and metal-ligand stability constants for 1 : 1 and 1 : 2 complexes. The effect of dielectric constants on stability constants of complex equilibria is studied in the present investigation.

Key Words: Dielectric constant, Complex equilibria, Eu(III), 3-(2-Hydroxy-5-methyl phenyl)-1-phenyl-5-(4-methoxy phenyl) Pyrazoline.

INTRODUCTION

Metal ligand stability constants of dicarboxylic acid (adipic acid, succinic acid, etc.) with transition metal ions have been determined in aqueous medium by many workers¹. Metal-ligand stability constants of some substituted pyrazolines and isoxazolines with transition metal ions have been determined in aqueous medium by Narwade *et al.*² and Shelke *et al.*³ have studied equilibrium constants of $\text{UO}_2(\text{II})$ and $\text{Cu}(\text{II})$ ions with dicarboxylic acids in dioxane-water mixture. Mandakmare *et al.*⁴ have determined stability constants of $\text{UO}_2(\text{II})$ complexes with some substituted coumarins by potentiometric and spectrophotometric techniques. Narwade *et al.*⁵ have investigated the interaction of $\text{Fe}(\text{III})$ with substituted chalcone at 0.1 M ionic strength potentiometrically. The interaction between $\text{Cu}(\text{II})$ -chelates with 2-hydroxy aromatic ketones and alkyl mono-amines is studied by Rabindranath⁶. Gudadhe *et al.*⁷ have investigated proton-ligand and metal-ligand stability constants of $\text{Th}(\text{IV})$ with some substituted pyrazolines. Sawalakhe *et al.*⁸ have studied the metal-ligand stability constants with 1,3-diketone, substituted pyrazolines spectrophotometrically. Sondawale *et al.*⁹ have studied the influence of dielectric constants of methanol-water media on $\text{Cu}(\text{II})$ -*o*-amino-sulphonic acid. The study of effect of dielectric constants of methanol-water media on $\text{Eu}(\text{III})$ - L_1 (HMPPMPPZOLINE) was still lacking.

In view of analytical applications, it was of interest to know the physico-chemical properties of metal ion complexes and effect of dielectric constants of methanol-water mixture. Therefore, the present work is undertaken to make a systematic study of Eu(III)-complexes with pyrazoline (HMPPMPPZOLINE).

EXPERIMENTAL

All the chemicals such as NaOH, NaClO₄, HClO₄, were of AnalaR grade.

3-(2-Hydroxy-5-methyl phenyl)-1-phenyl-5-(4-methoxy phenyl) pyrazoline (HMPPMPPZOLINE) ligand used was crystallized and its purity was checked before use. The solution of ligand (chelating agent) was prepared in aqueous medium by dissolving in an appropriate amount of it. The solution of europium nitrate (BDH) was prepared in water and its concentration was checked by EDTA. pH-meter Elico-LI-12T was used in the present investigation for measuring pH of solution. It was calibrated by standard buffer solution of pH 4.01, 7.00 and 9.12. Potentiometric titrations are carried out by using Calvin-Bjerrum titration technique in an inert atmosphere.

Experimental procedure involved potentiometric titrations of carbonate-free solutions of (i) free HClO₄ (ii) free HClO₄ (1.0×10^{-2} M) + ligand (20.001×10^{-4} M) and (iii) free HClO₄ (1.00×10^{-2} M) + ligand (20.001×10^{-4} M) + metal (4.000×10^{-4} M) against standard solution of sodium hydroxide (0.1–0.2 M) at $27 \pm 0.1^\circ\text{C}$.

Ionic strength of 0.1 M was maintained constant by adding an appropriate amount of 1 M NaClO₄; same procedure was used for 70, 75, 80 and 85% methanol-water mixture. pH values were corrected by use of Van-Uitert and Haas equation¹⁰.

RESULTS AND DISCUSSION

Proton-Ligand Formation Constants

The deviation of (acid + ligand curve) started around pH 3.50 from acid curves and increasing continuously up to pH 11.00.

The average number of protons associated with the ligand (\bar{n}_A) was determined by Irving-Rossotti's equation¹¹. The formation curves were constructed by plotting values of \bar{n}_A against pH of the system in all the percentages of methanol-water mixture.

The values of pK (dissociation constants) were estimated by noting the pH at which $\bar{n}_A = 0.5$ and accurate values were also determined by pointwise calculations.

The pK values of pyrazoline in all the percentages of methanol-water are presented in Table-1.

TABLE-1
PROTON-LIGAND STABILITY CONSTANTS OF L1-(HMPPMPPZOLINE) IN
DIFFERENT PERCENTAGES OF METHANOL-WATER MIXTURE OF 0.1 M IONIC
STRENGTH

Percentage of methanol-water mixture	Dielectric constant (D)	1/D	Mole fraction	pK
70	27.20	0.0367	0.260	10.40
75	24.00	0.0416	0.295	11.00
80	19.50	0.0512	0.329	11.50
85	16.00	0.0625	0.340	11.80

It could be seen from above Table-1, for (L1) HMPPMPPZOLINE that the value of pK increases with increasing percentage of methanol in the mixture as well as log K values are found to decrease with increasing percentage of methanol-water.

The departure of (free acid + ligand + metal ion) curve from (free acid + ligand) curves was obtained around pH = 3.5 in all percentage methanol-water media.

This shows the commencement of complex formation before the hydrolysis. The value of \bar{n} (metal-ligand) formation number were calculated by Irving-Rossotti's expression¹¹.

The value of log K_1 (metal-ligand, stability constant) for 1 : 1 complex and log K_2 (metal ligand stability constant) for 1 : 2 complex were obtained from the plots of \bar{n} vs. pL, by half integral method as well as pointwise calculations in all the percentages of methanol-water mixture and these are given in Table-2. It is observed from Table-2 that log K_1 and log K_2 values decreasing with increasing the percentage of methanol-water mixture.

TABLE-2
METAL LIGAND-STABILITY CONSTANTS
System: Eu(III)-L1-HMPPMPPZOLINE; Methium: Methanol-Water

Percentage of methanol	log K_1	log K_2	log $K_1 - \log K_2$
70	10.60	9.20	1.40
75	9.55	8.66	0.89
80	8.85	8.40	0.45
85	8.10	8.05	0.05

This may be due to the fact of effect of the bulk solvent, which decreases formation constants with increase in metal-ligand stability constants.

Plots of pK vs. 1/D

The plot of pK vs. 1/D shows a nonlinear relationship in our present investigation (Fig. 1 for L₁). The linear relationship between pK vs. 1/D holds only for low percentage, i.e., 20% of methanol but at higher percentage of methanol, i.e., above 20%, i.e., 70, 75, 80 and 85% there is a nonlinear relationship which is in agreement with the observation of Aditya *et al.*¹²

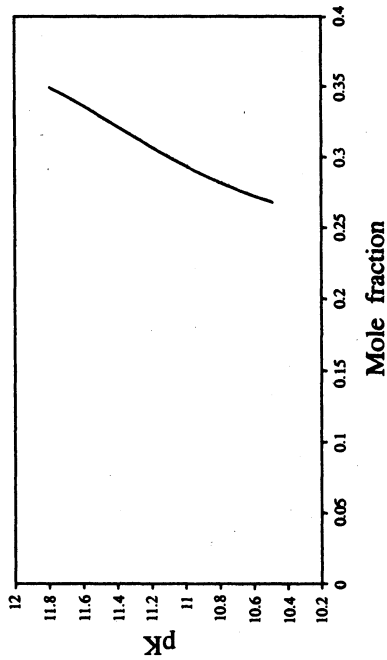


Fig. 2. Graph of pK vs. Mole fraction

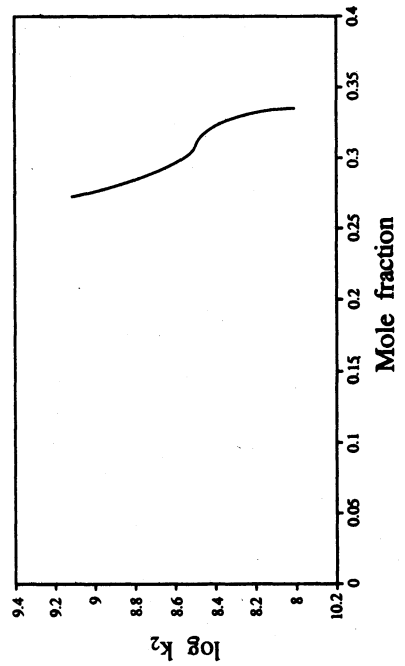


Fig. 4. Graph of log k₂ vs. Mole fraction

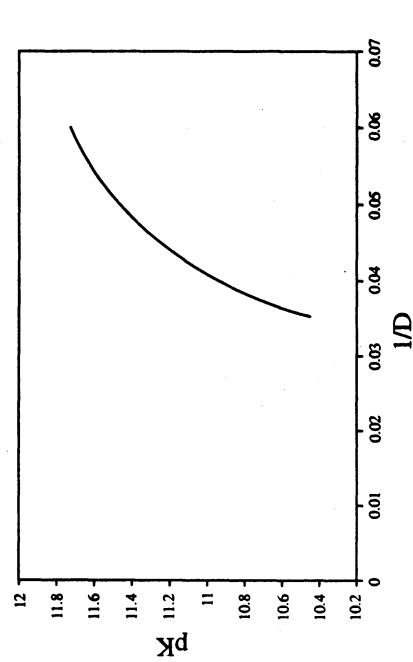


Fig. 1. Graph of pK vs. 1/D

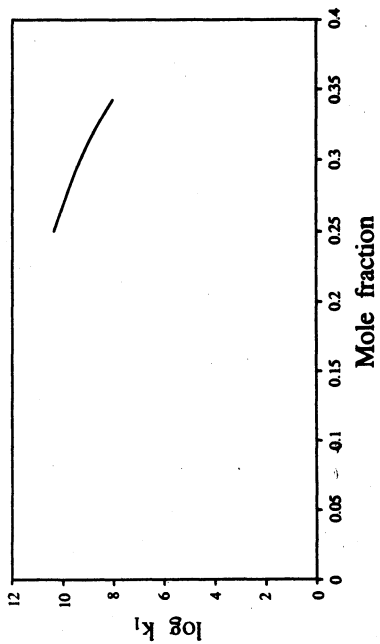


Fig. 3. Graph of log k₁ vs. Mole fraction

Plot of pK vs. Mole Fraction of Methanol

The plot of pK vs. mole fraction exhibits a linear relationship for 70, 75, 80 and 85% methanol as shown in Fig. 2 for HMPPMPPZOLINE, *i.e.*, all the points are on a straight line. Vartak and Menon¹³ reported a nonlinearity for phenol-aniline and their monosubstituted systems. According to them pK values are dependent on the solvent when electrical effects of the substituents are large.

The slope values are varying from 8 to 12. The observed slope value from the plot of pK vs. mole fraction is 3.50. The slope value is less than that of acetic acid and propionic acid. This may be due to the fact that acetic acid and propionic acid are neutral molecules while ligand HMPPMPPZOLINE is charged ion, when H^+ is displaced from the —OH group.

Log K Values of Eu(III)-L1 (HMPPMPPZOLINE)

The thermodynamic stability constants of Eu(III)-L1 (HMPPMPPZOLINE) have been determined in 70, 75, 80 and 85% methanol-water mixtures at $27 \pm 0.1^\circ C$. The data of log K values are shown in Table-2. It could be seen from Table-2 that thermodynamic stability constants decrease with increasing the percentage of methanol and that is due to bulk of solvent.

Plots of pK/log K vs. 1/D and Mole Fraction

The plots of pK/log K vs. 1/D exhibit nonlinearity and the plot of pK/log K vs. mole fraction gives a linearship for Eu(III)-L1 (HMPPMPPZOLINE) (Fig. 3 and Fig. 4). The same was observed by Pankanti *et al.*¹⁴ for Cu(II)-amino acids. The effect of dielectric constants is greater in the metal complex than in the proton-ligand complex. This may be due to the fact that the complexation equilibria involve positive and negative ions on both the sides and the number of charged particles are also remaining uncharged.

The difference between log K_1 and log K_2 values is calculated as shown in Table-2 for Eu(III)-HMPPMPPZOLINE complex in 70, 75, 80 and 85% methanol-water mixture. The difference of log K_1 and log K_2 is continuously decreasing with the increase in methanol percentage. This means that either log K_1 is relatively decreasing or log K_2 is relatively increasing as the dielectric constant is decreased. The lowering of dielectric constant would increase the electrostatic force of attraction between Eu(III) and negatively charged ligand to form 1 : 1 complex. The formation of 1 : 2 complex on the other hand is due to the reaction.

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REFERENCES

1. A.E. Martell, *Stability Constants of Metal Ion Complexes*, Special Publication Nos. 17 and 25, Chemical Society, London (1964 and 1971).
2. M.L. Narwade, Ph.D. Thesis.
3. D.N. Shelke and P.V. Jahagirdar, *Inorg. Nucl. Chem. Letters*, **14**, 925 (1979).
4. A.U. Mandakmare and M.L. Narwade, *Acta Cienc. Indica*, **21C**, 30 (1994).
5. M.L. Narwade, M.M. Chincholkar and S.U. Sathe, *J. Indian Chem. Soc.*, **62**, 194 (1985).
6. Rabindranath and R.P. Bhatnagar, *J. Indian Chem. Soc.*, **63**, 463 (1986).
7. S.K. Gudadhe, M.L. Narwade and S.V. Jamode, *Acta Cienc. Indica*, **11C**, 234 (1985).
8. P.D. Sawalakhe and M.L. Narwade, *J. Indian Chem. Soc.*, **71**, 49 (1994).
9. P.J. Sondawale and M.L. Narwade, *Acta Cienc. Indica*, **23C**, 37 (1997).
10. L.G. Van-Uitert and C.G. Haas, *J. Am. Chem. Soc.*, **75**, 451 (1953).
11. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, **54**, 3397 (1953).
12. S.K. Pal, U.C. Bhattacharya, S.C. Lahiri and S. Aditya, *Indian J. Chem.*, **7**, 497 (1969).
13. D.G. Vartak and M.G. Menon, *J. Inorg. Nucl. Chem.*, **31**, 2747 (1969).
14. Miss S. Pankanti, Ph.D. Thesis in Chemistry, Marathwada University, Aurangabad (1986).

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