

Potentiometric Study of the Lanthanide(III) Ion Complexes with Schiff Bases Derived from 2-Hydroxy-1-Naphthaldehyde and 2-Substituted Anilines

R.K. PARDESHI, S.P. BONDAGE and N.G. PALASKAR*

Department of Chemistry

Dr. Babasaheb Ambedkar Marathwada University, Aurangabad-431 004, India

A series of schiff bases derived from 2-hydroxy-1-naphthaldehyde with 2-chloroaniline, 2-ethoxyaniline, 2-methoxyaniline and 2-methylaniline have been synthesized. Their chelating tendencies towards lanthanide(III) metal ions have been investigated potentiometrically at $30 \pm 0.1^\circ\text{C}$ in 60% (v/v) dioxane-water medium and 0.1 M (NaClO_4) ionic strength. The lanthanides form 1 : 1 and 1 : 2 complexes with all the schiff bases and the trend in log K values shows a break at gadolinium.

INTRODUCTION

Schiff bases and their metal complexes have been the subject of intensive research due to their novel structural features, interesting spectral and magnetic properties and their industrial and biological importance. Extensive data on the stabilities of transition metal complexes in solution are available with various substituted schiff bases¹⁻⁴. However, there is no systematic solution study of the complexes of transition metals with the schiff bases derived from 2-hydroxy-1-naphthaldehyde. This encouraged to carry out the present investigation.

EXPERIMENTAL

All the chemicals used were of AR grade. The schiff bases were prepared by the condensation of 2-hydroxy-1-naphthaldehyde with 2-chloroaniline, 2-ethoxyaniline, 2-methoxyaniline and 2-methylaniline. The products obtained were recrystallised from ethanol and their purities were checked by TLC, elemental analysis and IR. The metal nitrates were dissolved in doubly distilled water and standardized by the known methods^{5, 6}. All the other solutions were also prepared in doubly distilled water.

A digital pH meter (Elico, model LI-120) in conjunction with a combined electrode was used for pH measurements. The Calvin-Bjerrum method modified by Irving and Rossotti⁷ was used to obtain pK and log K values. The measurements were made at $30 \pm 0.1^\circ\text{C}$ at $\mu = 0.1$ M (NaClO_4) in 60% (v/v) dioxane-water medium.

The pK and log K values were determined by half integral method, pointwise calculations and also by the method of least squares. In all the calculations, pH

correction and volume correction factors have been applied for the dioxane-water mixture.

RESULTS AND DISCUSSION

The pK_1 and pK_2 values of schiff bases which represent the deprotonation of NH group at azomethine atom and phenolic OH group were determined at $\bar{n}_A = 1.5$ and 0.5 respectively. The values were further checked from the plots of $\log [(2 - \bar{n}_A)/(\bar{n}_A - 1)]$ vs. B and $\bar{n}_A/(1 - \bar{n}_A)$ vs. B (B = pH meter reading). These proton-ligand stability constants are presented in Table-1.

TABLE-1
PROTON-LIGAND STABILITY CONSTANTS OF SCHIFF BASES

Medium: 60% (v/v) dioxane-water mixture

Temp: $30 \pm 0.1^\circ\text{C}$, $\mu = 0.1 \text{ M}$ (NaClO₄)

Ligand number	Ligand	pK_1	pK_2
L ₁	N-[2-hydroxy-1-naphthalinidine]-2-chloroaniline	—	9.56
L ₂	N-[2-hydroxy-1-naphthalinidine]-2-ethoxyaniline	4.39	10.49
L ₃	N-[2-hydroxy-1-naphthalinidine]-2-methoxyaniline	4.29	9.94
L ₄	N-[2-hydroxy-1-naphthalinidine]-2-methylaniline	4.24	9.75

The schiff base L₁ has —Cl at 2-position to azomethine nitrogen of the schiff base and it does not display pK_1 value. The absence of pK_1 value in this ligand may be due to strong electron withdrawing effect of —Cl atom present in the ligand. The electron density on the azomethine nitrogen is almost totally withdrawn by the chlorine resulting in the generation of positive charge on the azomethine nitrogen. Hence protonation of azomethine nitrogen does not take place resulting in the absence of pK_1 value.

L₂ and L₃ are having —OC₂H₅ and —OCH₃ group at 2-position to amine group and L₄ having —CH₃ group. This can be explained on the basis of dominating nature of +M effect of —OC₂H₅/—OCH₃ group over +I effect of —CH₃. This may be attributed to the fact that ethoxy and methoxy groups increase electron density on the azomethine nitrogen to a greater extent than methyl group resulting in stronger bonding. Hence in case of L₂ and L₃ there will be decrease in acidity, *i.e.*, increase in pK_1 values as compared to L₄.

The pK_2 value of L₁ is lowest as —Cl is at 2-position, hence —I effect, *i.e.*, strong acidity. L₄ shows higher pK_2 value than L₁ as in L₄, +I effect due to —CH₃ group causes decrease in acidity. L₂ and L₃ having +M effect because of —OC₂H₅ and —OCH₃ groups, hence decrease in acidity of phenolic —OH shows higher values of pK_2 compared to L₁ and L₄.

The metal-ligand titration curve deviates from the ligand titration curve in the pH range 4.0 to 8.0. The difference between the $\log K_1$ and $\log K_2$ values calculated by pointwise calculation method and half integral method was less than one log unit, indicating simultaneous formation of 1 : 1 and 1 : 2 complexes.

Therefore least squares method was used to calculate accurate values. The values of $\log K_1$ and $\log K_2$ and $\log \beta$ are shown in Table-2.

TABLE-2
FORMATION CONSTANTS OF LANTHANIDE(III) METAL
IONS WITH SCHIFF BASES

Medium: 60% (v/v) dioxane-water mixture

Temp: $30 \pm 0.1^\circ\text{C}$, $\mu = 0.1 \text{ M (NaClO}_4\text{)}$

M^{3+}	Stability constant	Ligand			
		L_1	L_2	L_3	L_4
La	$\log K_1$	6.03	7.13	6.33	6.14
	$\log K_2$	4.98	6.17	5.15	5.14
	$\log \beta$	11.01	13.30	11.48	11.28
Ce	$\log K_1$	6.08	7.26	6.52	6.47
	$\log K_2$	5.03	6.33	5.31	5.58
	$\log \beta$	11.11	13.59	11.83	12.05
Pr	$\log K_1$	6.32	7.57	6.64	6.57
	$\log K_2$	5.57	6.81	5.52	5.84
	$\log \beta$	11.89	14.38	12.16	12.41
Nd	$\log K_1$	6.41	7.64	6.68	6.62
	$\log K_2$	5.51	7.15	5.74	5.89
	$\log \beta$	11.92	14.79	12.42	12.51
Sm	$\log K_1$	6.65	7.72	6.76	6.68
	$\log K_2$	6.06	7.11	5.87	6.03
	$\log \beta$	12.71	14.83	12.63	12.71
Eu	$\log K_1$	6.69	7.97	6.92	6.73
	$\log K_2$	6.07	7.24	6.09	6.03
	$\log \beta$	12.76	15.21	13.01	12.76
Gd	$\log K_1$	6.58	7.73	6.66	6.61
	$\log K_2$	6.08	7.20	5.80	5.98
	$\log \beta$	12.66	14.93	12.46	12.59
Tb	$\log K_1$	6.60	8.20	7.55	6.97
	$\log K_2$	6.10	7.28	6.69	6.34
	$\log \beta$	12.70	15.48	14.24	13.31
Dy	$\log K_1$	6.47	7.80	7.42	6.77
	$\log K_2$	6.02	7.20	6.61	6.22
	$\log \beta$	12.49	15.00	14.03	12.99

It is observed from Table-2 that the lanthanides show a linear increase of overall stability constants with increase in atomic number up to Eu(III) after which there is a sudden fall at Gd(III), *i.e.*, gadolinium break. The stability constant then increases at Tb(III) and Dy(III). Such behaviour was found for the most rare earth complexes with various ligands^{8,9}.

If the bonds are ionic, the Born relation $E = (e^2/2r)(1 - 1/D)$ should hold for the energy change on complexation of a gaseous ion of charge 'e' and radius 'r' in a medium of dielectric constant 'D'. Since the stability constant is related directly to this energy, the log k should increase linearly with $1/r$.

The plot of $1/r$ vs. log K_1 values of the rare earth shown in Fig. 1 indicates that the stability constants of metal complexes increase with increasing atomic number (*i.e.* decrease in ionic radius) from La(III) to Eu(III). There is, however, a discontinuity found at Gd(III). From Gd(III), the plot shows maxima and minima in log β values of these complexes indicating their greater stability, which may be attributed to the increased covalent character¹⁰.

It is also concluded from the observed nature of graphs that the present schiff base complexes with lanthanide metal ions are predominantly ionic in the first part, *i.e.*, from La(III) to Gd(III) and covalent in character in the second part, *i.e.*, from Tb(III) to Dy(III).

When log β values were plotted against pK values, no linearity could be obtained. Ionisation potential of the metal ion and donor atoms, tendency of metal ions to form π -bonds, ligand field stabilization of ligand are some of the factors which affect the linear relationship.

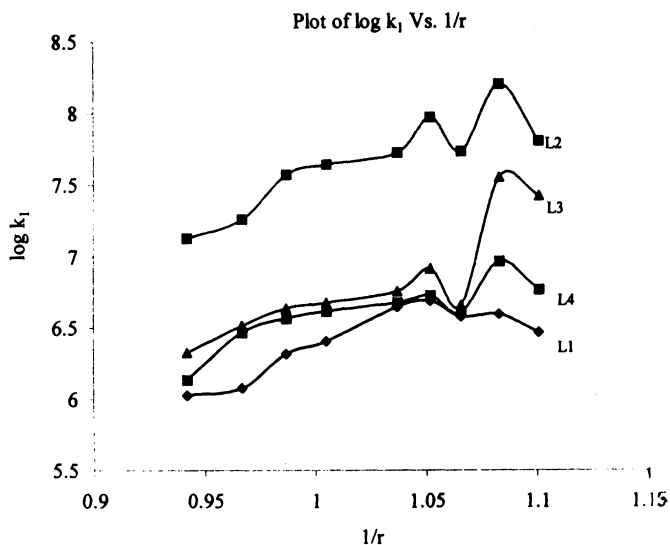


Fig. 1.

REFERENCES

1. Gotmare, R Sulekha and M.S. Mayadev, *Acta Cienc. Indica*, **17C**, 245 (1991).
2. Y.M. Issa, F.M. Abdel-Gawad, S.M. Al-Hamid and S.M. Abd, *Egypt J. Chem.*, **37**, 539 (1994).
3. M.S. Mayadev and J.V. Nalgirkar, *Indian J. Chem.*, **27A**, 456 (1998).
4. K.L. Omprakash, K. Goverdhan Reddy, A.V. Chandra Pal and M.L.N. Reddy, *Indian J. Chem.*, **23A**, 79 (1984).
5. A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, Pergamon Green and Co. Ltd., London.
6. N.V. Takhur, S.M. Jogdev and R.C. Karekar, *J. Inorg. Nucl. Chem.*, **28**, 2297 (1966).
7. S.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, 2904 (1954).
8. I. Grenthe and W.C. Fernelius, *J. Am. Chem. Soc.*, **82**, 6285 (1980).
9. S.K. Akuskar, A.G. Shnakarwar, T.K. Chondhekar and D.G. Dhuley, *Asian. J. Chem.*, **9**, 341 (1997).
10. L.C. Thomson, *J. Inorg. Nucl. Chem.*, **24**, 1089 (1962).

(Received: 19 May 2001; Accepted: 14 August 2001)

AJC-2405