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NOTE

Rare Earths—Schiff Base Complexes: A Potentiometric Study

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Stability constants of lanthanide chelates of Schiff bases derived from 5-chloro-2-hydroxy acetophenone and p-toluidine and m-toluidine have been determined at 25°, 35° and 50° ± 0.02°C potentiometrically in 60% ethanol-water medium and 0.1 M ($NaClO_4$) ionic strength. The lanthanides form 1 : 1 and 1 : 2 chelates and the trend in log K values show a break at gadolinium. Thermodynamic functions obtained revealed that the 1 : 1 chelates were enthalpy and entropy stabilized and 1 : 2 chelates showed predominance of entropy effect.

The present paper is a continuation of our earlier work on Cu(II)–aryl Schiff base complexes[1]. Complexation of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) and Yb(III) with 5-chloro-o⁻-hydroxy acetophenone-p-tolil and 5-chloro-o⁻-hydroxy-acetophenone-m-tolil was investigated with special emphasis on substituent effect and thermodynamic parameters.

The ligands 5-chloro-o⁻-hydroxy acetophenone-p-tolil (I) and 5-chloro-o⁻-hydroxy acetophenone-m-tolil (II) were synthesized by the method of Reddelien[2] and their purities were checked. The rare earth nitrates were obtained from Indian Rare Earths Limited, Udyogmandal, Kerala. All other reagents were of *AR* grade and the solutions were prepared in doubly distilled water.

Elico digital pH-meter was used for pH measurements. Calvin-Bjerrum[3-4] titration technique as modified by Irving and Rossotti[5] was adopted for pH-titrations and subsequent calculations of pK and log *K* values. The log *K* values were computed by (i) half $\bar{n}$ method, (ii) successive approximation method, and (iii) least squares method. The values obtained by least squares method were utilized for the calculation of ΔG from Van't Hoff's isotherm. The ΔH value was obtained from the slope of the linear plot of log *K* vs $1/T$ and ΔS values were calculated by the equation $\Delta G = \Delta H - T\Delta S$.

The present ligands contain azomethine nitrogen at 1-position and hence the association of proton takes place in the initial stages of titration. The proton association constant (pK_1) and the proton dissociation constant from —OH group (pK_2) were determined at $\bar{n}_A = 1.5$ and 0.5

respectively. The pK values obtained from the plots of log $\frac{2-\bar{n}_A}{\bar{n}_A-1}$ vs B (pH reading) and log $\frac{\bar{n}_A}{1-\bar{n}}$ vs B coincide with those obtained by half integral method and are presented below:

		25°C	35°C	50°C
Ligand I	pK_1	4.54	4.37	4.10
	pK_2	9.91	9.78	9.60
Ligand II	pK_1	4.18	4.00	3.72
	pK_2	9.82	9.72	9.56

It is evident from the above data that the pK_1 values of I at all the temperatures are higher than those of II. This is the expected trend because the electron withdrawing —CH_3 group present at meta position weaken the N–H bond at azomethine nitrogen relatively at a greater extent than when it is at para position. pK_2 values of both the ligands are seen to be unaffected by the position of the substituent which is expected because of the large distance between —OH and the substituent —CH_3 groups.

The metal-ligand titration curve deviates from the acid dissociation curve in the pH range 5.1 to 7.2 indicating the complexation in this pH range. The simultaneous formation of 1 : 1 and 1 : 2 complexes was inferred by the fact that the difference between log K_1 and log K_2 values was less than 2.5 and hence the method of least squares was adopted for the determination of these constants. The protonated nitrogen and oxygen of the phenolic group are involved in the coordination of metal with ligand molecules. The 1 : 1 complexes were found to be more established at lower pH and the results obtained are set out in Table 1.

It is evident from Table 1 that the lanthanides show a linear increase of over all stability constants with increase in atomic number up to Sm(III) after which there is a sudden fall at Gd(III) (gadolinium break). The stability constants then show an increase at Tb(III) and exhibit constancy at Dy(III) and Yb(III). Such behaviour was found for the most rare earth complexes with various ligands[6–8].

Thermodynamic parameters were obtained from the data at three different temperatures. The more negative values of ΔG_1 than ΔG_2 indicate that the 1 : 1 complex formation is energetically favoured. The negative ΔH_1 and positive ΔS_1 reveal that both the enthalpy and entropy factors favour the 1 : 1 complex formation. The large value of ΔS_2 and positive value of ΔH_2 in 1 : 2 complex formation clearly indicate that the water dipoles from their hydration shells are drastically dislodged leading to high value of positive entropy change.

TABLE 1

STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF RARE EARTH COMPLEXES OF SCHIFF BASES AT 25±0.02°C AND μ = 0.1 M

Metal ions		log K_1	log K_2	$-\Delta G_1$	$-\Delta G_2$	$-\Delta H_1$	$+\Delta H_2$	$+\Delta S_1$	$+\Delta S_2$
La(III)	I	7.38	5.38	42.11	30.70	21.65	39.68	68.66	236.18
	II	7.28	5.31	41.54	30.30	3.59	64.07	127.35	316.68
Ce(III)	I	7.41	5.60	42.28	31.95	19.53	37.38	76.34	232.68
	II	7.38	5.61	42.11	32.01	6.00	47.58	121.15	267.10
Pr(III)	I	7.48	5.78	42.68	32.98	16.06	33.70	89.33	223.76
	II	7.50	5.88	42.79	33.55	7.36	39.70	118.89	245.83
Nd(III)	I	7.51	6.01	42.85	34.29	4.50	30.82	128.68	218.50
	II	7.58	6.02	43.25	34.35	11.78	33.73	105.60	228.48
Sm(III)	I	7.53	6.14	42.96	35.03	2.29	25.70	136.47	203.81
	II	7.65	6.09	43.65	34.75	13.51	29.17	101.12	214.54
Gd(III)	I	7.48	6.08	42.68	34.69	10.21	32.97	108.95	227.08
	II	7.36	6.01	41.99	34.29	6.56	35.04	118.90	232.66
Tb(III)	I	7.65	6.28	43.65	35.83	10.07	22.84	112.66	196.89
	II	7.43	6.10	42.39	34.80	5.28	33.70	124.54	229.89
Dy(III)	I	7.54	6.38	43.02	36.40	11.38	24.02	106.17	202.76
	II	7.40	6.12	42.22	34.92	3.82	32.64	135.57	226.73
Yb(III)	I	7.41	6.50	42.28	37.09	16.52	28.29	86.44	219.39
	II	7.38	6.15	42.11	35.09	3.19	29.10	136.60	215.40

I = 5-Chloro-orthohydroxy acetophenone-p-tolil.
II = 5-Chloro-orthohydroxy acetophenone-m-tolil.

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