

Thermodynamics of complex formation of rare earth metal ions with schiff bases in mixed solvent media

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Proton-ligand stability constants of N-phenyl-2-hydroxy-5-chloroacetophenoneimine(I) and N- α -naphthyl-2-hydroxy-5-chloroacetophenoneimine(II) and metal-ligand stability constants of their complexes with La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) and Yb(III) have been determined at 25°, 35° and 50°C ($\pm 0.02^\circ\text{C}$) and $\mu = 0.1\text{M}(\text{NaClO}_4)$ in 60% ethanol-water medium. The thermodynamic parameters for the formation of 1:1 and 1:2 complexes have been calculated. The metal complexes of the ligand(I) are observed to be enthalpy- and entropy-stabilized. However, the positive values of enthalpy and entropy changes in the case of the 1:2 complexes of ligand(II) show the predominance of the entropy effect.

In continuation of our earlier work¹ on the stability constants of Cu(II) complexes with aryl schiff bases, we report in this note the stability constants and thermodynamic parameters of rare earth complexes of ligands(I) and (II) in 60% ethanol-water medium. The temperature effect, substituent effect and the dependence of stability constants of the complexes on the atomic number of metals have been discussed.

Experimental

All the chemicals used were of AR grade. The schiff bases(I) and (II) were prepared by the condensation of 5-chloro-2-hydroxyacetophenone with aniline and α -naphthyl amine respectively. The rare earth nitrates (Indian Rare Earths Limited, Udyogmandal, Kerala) were dissolved in doubly distilled water and standardised by the method of Flaschka². 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 method of Calvin and Bjerrum as modified by Irving and Rossotti³ was used to obtain pK and $\log K$ values. The measurements were made at 25°, 35° and 50°C at $\mu = 0.1\text{M}(\text{NaClO}_4)$ in 60% aqueous ethanol.

The pK and $\log K$ values were determined by half-integral method, pointwise calculations and also by the method of least squares wherever the difference between $\log K_1$ and $\log K_2$ was less than 1.75 (ref. 4). In all the calculations, pH correction and volume correction factors have been applied for the ethanol-water mixture. The average $\log K$ values were used to calculate the free energy change (ΔG) from the Van't Hoff's isotherm. The ΔH and ΔS values were calculated from the Van't Hoff's isochore and the equation $\Delta G = \Delta H - T\Delta S$, respectively. The data are listed in Table 1.

Results and discussion

Due to the presence of azomethine nitrogen in the ligands, protonation takes place in the initial stages of titration. the proton association constant (pK_1) and proton dissociation constant (pK_2) 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 $\log \bar{n}_A/1 - \bar{n}_A$ vs B ($B = \text{pH meter reading}$) and are given below:

| | 25°C | 35°C | 50°C |
|--------|-----------|------|------|
| | Ligand I | | |
| pK_1 | 4.29 | 4.25 | 4.19 |
| pK_2 | 9.62 | 9.50 | 9.35 |
| | Ligand II | | |
| pK_1 | 3.06 | 3.03 | 2.98 |
| pK_2 | 9.90 | 9.75 | 9.62 |

The pK_2 values of ligand(II) at all the temperatures are higher than those of ligand(I). This may be due to a strong electron withdrawing effect of α -naphthyl group.

The metal-ligand titration curve deviates from the acid dissociation curve in the pH range 4.5-7.0 indicating that the complexation takes place in this pH range. The maximum value of \bar{n} is found to be 2.0 in all the complexes which suggests that the lanthanides form both 1:1 and 1:2 complexes. The value of $\log K_1$ and $\log K_2$ were determined by the half-integral method and least-squares method (Table 1).

The data in Table 1 reveal that the overall stability ($\log \beta$) of the complexes increases with increase in atomic number up to Tb(III), with a break at gadolinium. The elements heavier than gadolinium show nearly the same $\log \beta$ values. Similar observations were made for lanthanide complexes with various ligands^{5,6}.

Table 1—Stability constants and thermodynamic parameters of lanthanide(III) complexes of schiff bases at $25^\circ \pm 0.02^\circ\text{C}$ and $\mu = 0.01\text{ M}$

| Complex | $\log K_1$ | $\log K_2$ | (kJ mol^{-1}) | | | | $(\text{JK}^{-1} \text{mol}^{-1})$ | |
|------------|------------|------------|------------------------|---------------|---------------|--------------|------------------------------------|--------------|
| | | | $-\Delta G_1$ | $-\Delta G_2$ | $-\Delta H_1$ | ΔH_2 | ΔS_1 | ΔS_2 |
| La(III)—I | 7.22 | 5.74 | 41.19 | 32.75 | 23.40 | -8.51 | 59.69 | 81.35 |
| La(III)—II | 8.02 | 5.88 | 45.76 | 33.55 | 32.13 | 3.64 | 45.73 | 124.84 |
| Ce(III)—I | 7.32 | 5.89 | 41.77 | 33.61 | 24.18 | -6.12 | 59.02 | 92.22 |
| Ce(III)—II | 8.09 | 6.05 | 46.16 | 34.52 | 26.95 | 3.06 | 64.46 | 126.12 |
| Pr(III)—I | 7.38 | 5.98 | 42.11 | 34.12 | 25.53 | -6.00 | 55.63 | 94.34 |
| Pr(III)—II | 8.11 | 6.07 | 46.27 | 34.63 | 27.43 | 7.66 | 63.22 | 141.92 |
| Nd(III)—I | 7.68 | 6.00 | 43.48 | 34.23 | 37.44 | -6.38 | 20.26 | 93.47 |
| Nd(III)—II | 8.15 | 6.17 | 46.50 | 35.20 | 27.35 | 8.12 | 64.26 | 145.40 |
| Sm(III)—I | 7.76 | 6.06 | 44.28 | 34.58 | 38.29 | -5.28 | 20.10 | 98.31 |
| Sm(III)—II | 8.17 | 6.22 | 46.62 | 35.49 | 22.84 | 9.01 | 79.79 | 149.33 |
| Gd(III)—I | 7.37 | 6.08 | 42.05 | 34.69 | 22.28 | -5.89 | 66.35 | 96.65 |
| Gd(III)—II | 7.86 | 6.20 | 44.85 | 35.37 | 33.66 | 8.20 | 37.55 | 146.25 |
| Tb(III)—I | 7.59 | 6.34 | 43.31 | 36.17 | 23.68 | -7.66 | 65.87 | 95.67 |
| Tb(III)—II | 7.97 | 6.34 | 45.47 | 36.17 | 9.92 | 7.66 | 119.29 | 147.10 |
| Dy(III)—I | 7.60 | 6.36 | 43.36 | 36.29 | 22.34 | -10.94 | 70.56 | 85.05 |
| Dy(III)—II | 7.96 | 6.36 | 45.42 | 36.29 | 13.32 | 7.61 | 107.72 | 147.31 |
| Yb(III)—I | 7.65 | 6.37 | 43.65 | 36.35 | 23.93 | -9.92 | 66.16 | 88.69 |
| Yb(III)—II | 7.94 | 6.38 | 45.30 | 36.40 | 9.24 | 6.75 | 121.00 | 144.83 |

I = N-phenyl-2-hydroxy-5-chloroacetophenoneimine

II = N- α -naphthyl-2-hydroxy-5-chloroacetophenoneimine

It is evident from Table 1 that (a) complexes of ligand(I) show negative enthalpy and positive entropy changes supporting the stabilization of these complexes, (b) a similar trend is exhibited by the 1:1 complexes of ligand(II), and (c) 1:2 complexes of ligand(II) show large positive values of ΔS_2 and ΔH_2 , which may be attributed to the drastic disruption of the coordination sphere of metal ions in the second chelation stage.

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