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THERMODYNAMIC STABILITIES OF LANTHANIDE COMPLEXES OF THE BIOLOGICALLY ACTIVE COMPLEXING AGENT, 2-ACETYLPYRIDINETHIOSEMICARBAZONE (2-APT)

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ABSTRACT

Thermal equilibria of complexes of La(III), Pr(III), Nd(III), Sm(III), Tb(III), Dy(III) and Ho(III) with 2-acetylpyridinethiosemicarbazone have been investigated potentiometrically in 75% (v/v) ethanol medium at various temperatures. The method of Bjerrum and Calvin as modified by Irving and Rossotti has been used to find values of $\bar{n}$ and pL. The stability constants have been calculated on a VAX-11/750 computer using the weighted least squares method. The values of $S_{\min}$ have also been calculated. The order of stability constants has been found to be La(III) < Pr(III) < Nd(III) < Sm(III) < Tb(III) < Dy(III) < Ho(III). Thermodynamic parameters (ΔG, ΔH and ΔS) of the complexation reactions have also been calculated.

INTRODUCTION

Thiosemicarbazones form an important class of analytical reagents. In planning or selection of a chelate process for a specific purpose, the knowledge of stability or formation constants is of utmost importance. In comparison with *d*-block metal ions, the lanthanide ions as a whole form far fewer complexes and yield complexes with significantly different properties [1–3]. The low stability of lanthanide complexes can be increased by means of chelate effect. Little work has been directed towards the elucidation of the nature of lanthanide chelates of thiosemicarbazones. Only a few chelates of some lanthanides have been studied potentiometrically. The present study was undertaken to study the thermal stabilities of lanthanides with 2-acetylpyridinethiosemicarbazone, a biologically active ligand, at different temperatures in 75% ethanol in 0.1 M $NaClO_4$ medium.

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EXPERIMENTAL

A digital pH meter (ECIL model pH 5651), with a glass electrode (0–14 pH range) was used for pH measurements. The pH meter was standardized with potassium hydrogenphthalate buffer before performing the titrations. 2-Acetylpyridinethiosemicarbazone (2-APT) was synthesized by the method of Pino [4] and its purity was checked by elemental analysis, TLC, NMR, IR and UV.

The solution of 2-APT was prepared in ethanol. All the metal ion solutions were prepared and standardized by conventional procedures. Sodium perchlorate (Riedel) was used to keep the ionic strength constant for different sets. A solution of tetramethylammonium hydroxide (TMAH) (Merck) in 75% ethanol was used as the titrant. It was standardized with oxalic acid. All other chemicals used were of reagent grade. The titrations were carried out in an atmosphere of nitrogen, which was presaturated with 75% ethanol. All measurements were made at a definite temperature which was kept constant by using an MLW (F.R.G.) (NBE type) thermostat.

Procedure

The method of Bjerrum and Calvin as modified by Irving and Rossotti [5] has been used to determine $\bar{n}$ and pL values. The following solutions (total volume 19.40 ml instead of 20 ml due to contraction in volume on mixing ethanol and water) were titrated potentiometrically against standard 0.1 M TMAH, in 75% ethanol (v/v) to determine $\bar{n}$ and pL values of the complexes.

(i) 2.0 ml $HClO_4$ (0.1 M) + 1.0 ml $NaClO_4$ (2.0 M) + 15 ml ethanol + 2.0 ml water.

(ii) 2.0 ml $HClO_4$ (0.1 M) + 1.0 ml $NaClO_4$ (2.0 M) + 10.0 ml ligand (0.01 M) in ethanol + 5.0 ml ethanol + 2.0 ml water.

TABLE 1

Stability constants of lanthanide(III) complexes of 2-APT at $\mu = 0.1$ M $NaClO_4$ and at $T = 55 \pm 0.5\,°C$

Metal ion	$\log K_1$	$\log K_2$	$\log \beta_2$	S_{min}
H^+	9.90	–	–	–
La(III)	6.75	6.38	13.13	0.1725
Pr(III)	6.95	6.68	13.63	0.1986
Nd(III)	7.26	6.74	14.00	0.0750
Sm(III)	7.50	7.05	14.55	0.1687
Tb(III)	7.79	7.26	15.05	0.0645
Dy(III)	7.82	7.22	15.04	0.1486
Ho(III)	7.85	7.49	15.34	0.1129

(iii) 2.0 ml $HClO_4$ (0.1 M) + 1.0 ml $NaClO_4$ (2.0 M) + 10.0 ml ligand (0.01 M) in ethanol + 0.5 ml metal (0.02 M) + 5.0 ml ethanol + 1.5 ml water.

During complexation the acidic proton is replaced by an equivalent amount of metal(III).

From the titration curves of sets of solutions (i), (ii) and (iii) the values of $\bar{n}$ and pL have been calculated using a VAX-11/750 computer. The corresponding values of stability constants have been calculated using the weighted least-squares method of Sullivan et al. [6]. The weighted least-squares treatment determines that set of β_n values which makes the function:

$$U\left[U=\sum_{n=0}^{N}(y-x-nx)\beta_n X^n\right] \tag{1}$$

nearest to zero, by minimizing

$$S\left[S=\sum_{I=1}^{I}U^2(x_i,y_i,z_i)\right] \tag{2}$$

TABLE 2

Stability constants of lanthanide(III) complexes of 2-APT at $\mu = 0.1$ M $NaClO_4$ and at $T = 45 \pm 0.5\,°C$

Metal ion	log K_1	log K_2	log β_2	$S_{\min}$
H^+	10.06	–	–	–
La(III)	6.74	6.45	13.19	0.1894
Pr(III)	6.99	6.71	13.70	0.2133
Nd(III)	7.23	6.74	13.97	0.1368
Sm(III)	7.66	7.13	14.79	0.0642
Tb(III)	7.82	7.01	14.83	0.0576
Dy(III)	7.83	7.26	15.09	0.1233
Ho(III)	7.88	7.53	15.41	0.1435

TABLE 3

Stability constants of lanthanide(III) complexes of 2-APT at $\mu = 0.1$ M $NaClO_4$ and at $T = 35 \pm 0.5\,°C$

Metal ion	log K_1	log K_2	log β_2	$S_{\min}$
H^+	10.18	–	–	–
La(III)	6.80	6.50	13.30	0.2238
Pr(III)	7.04	6.77	13.81	0.1938
Nd(III)	7.38	6.79	14.17	0.0689
Sm(III)	7.72	6.97	14.69	0.0956
Tb(III)	7.88	7.07	14.95	0.0067
Dy(III)	7.90	7.30	15.20	0.1079
Ho(III)	7.92	7.58	15.50	0.1346

with respect to the variation in β_n. We report the $S_{\min}$ values for different metal complexes. $S_{\min}$ has the same statistical distribution as χ^2 with K degrees of freedom and with weights defined in accordance with Sullivan et al. [7]. $S_{\min}$ can be equated to χ^2. The stability constants thus calculated are given in Tables 1–3.

RESULTS AND DISCUSSION

It has been observed that stability from La(III) to Ho(III) follows the same order as increasing acidity. The order of log K_1 values for 2-APT complexes is found to be La(III) < Pr(III) < Nd(III) < Sm(III) < Tb(III) < Dy(III) < Ho(III). The same trend has also been reported by several workers [8,9]. This has been explained in terms of increasing coulombic attraction for the ligand with decreasing cationic radius. The values of stability constants in Tables 1–3 reveal that stability constants decrease with increase in temperature along with pK values of the ligand. These results are in good agreement with those of Pitzer [10]. The thermodynamic parameters (ΔG, ΔH and ΔS) have also been calculated by using the following relationships:

$$\Delta G = -RT \ln K \tag{3}$$

$$\mathrm{d} \log K/\mathrm{d}(1/T) = \Delta H/2.303R \tag{4}$$

$$\Delta S = (\Delta H - \Delta G)/T \tag{5}$$

The overall standard free energy change and standard enthalpy and standard entropy changes at 25 ± 0.5 °C are reported in Table 4. The negative free energy change (ΔG) in each case indicates that the chelation is spontaneous. Further, ΔG becomes more negative with decreasing temperature suggesting an increase in the extent of complex formation at lower temperatures. The enthalpy changes are exothermic.

TABLE 4

Thermodynamic parameters of lanthanide(III) complexes of 2-APT at $\mu = 0.1$ M and at $T = 25 \pm 0.5\,^\circ$C

Metal ion	$-\Delta G$ (kcal mol^{-1})	$-\Delta H$ (kcal mol^{-1})	$-\Delta S$ (kcal K^{-1} mol^{-1})
La(III)	9.791	5.027	0.0158
Pr(III)	10.213	4.570	0.01893
Nd(III)	10.418	4.110	0.02116
Sm(III)	10.759	5.484	0.01770
Tb(III)	10.977	3.656	0.02456
Dy(III)	11.113	5.227	0.0197
Ho(III)	11.359	5.484	0.0197

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