Potentiometric Determination of Stability Constants & Thermodynamic Parameters of Lanthanide Complexes of Acenaphthenequinone Monothiosemicarbazone (AQTS)

S K SINGH, R K SHARMA & S K SINDHWANI*

Department of Chemistry, University of Delhi,
Delhi 110 007

Stability constants of the complexes of Ho(III), Dy(III), Tb(III), Sm(III), Nd(III), Pr(III) and La(III) with acenaphthenequinone monothiosemicarbazone have been determined potentiometrically in 75% (v/v) aqueous dioxan medium at various ionic strengths and at different temperatures. The method of Bjerrum and Calvin, as modified by Irving and Rossotti, has been used to find out the values of $\bar{n}$ and pL. The stability constants have been calculated using an IBM 360 FORTRAN IV computer by the weighted least squares method. The order of the stability constants was found to be: Ho > Dy > Tb > Sm > Nd > Pr > La. Thermodynamic parameters such as ΔG, ΔH and ΔS have also been calculated.

The lanthanides exhibit remarkable similarity in chemical properties due to their nearly identical electronic configuration[1]. In the present note, chelating ability of acenaphthenequinone monothiosemicarbazone towards some lanthanide ions has been studied potentiometrically using the method of Bjerrum and Calvin[2,3] as modified by Irving and Rossotti[4]. Experiments were conducted at $0.2M$, $0.1 M$, $0.05M$ and $0.01M$ ionic strengths keeping the temperature constant at 25 C. Gibb's energy, enthalpy and entropy values for various complexation reactions have been calculated at $0.1 M$ ionic strength.

A digital pH meter (ECIL, model pH 5651) in conjunction with a glass electrode was used for pH measurements. The pH meter was standardised with potassium hydrogen phthalate and phosphate buffers before performing the titration, and constant temperature was maintained using a MLW (West Germany, NBE type) thermostat. An IBM 360 FORTRAN IV computer was used for most of the calculations.

Preparation of acenaphthenequinone monothiosemicarbazone (AQTS) has been reported earlier[5]. AQTS solution was prepared in freshly distilled dioxan.

Solutions of metal perchlorates of Ho(III), Dy(III), Tb(III), Sm(III), Nd(III), Pr(III) and La(III) were prepared from their corresponding oxides[6] (99%, Johnson Matthey). These solutions were diluted to the desired concentrations and were standardised by conventional methods.

Perchloric acid was standaridsed with sodium carbonate and diluted to the required molarity (0.02 M) by doubly distilled water. Tetramethylammonium hydroxide (TMAH) (E. Merck, A.G., Darmstadt) in 75% aqueous dioxan was used as the titrant. Its solution was standardised with oxalic acid. Sodium perchlorate (Riedel) was used to maintain the ionic strength of the medium. Dioxan (AR, BDH) was purified by the method given by Vogel[7].

Procedure

The following solutions were titrated against 0.05 M TMAH, in 75% aqueous dioxan for determining the stability constants of AQTS complexes at various ionic strengths and temperatures. First set ionic strength (μ) $= 0.2 M$ NaClO$_4$.

(i) 0.8 ml HClO$_4$ (0.02 M) + 2.0 ml NaClO$_4$ (2.0 M) + 2.2 ml doubly distilled water + 15.0 ml dioxan

(ii) 0.8 ml HClO$_4$ (0.02 M) + 2.0 ml NaClO$_4$ (2.0 M) + 2.2 ml doubly distilled water + 10.0 ml ligand (M/100) + 5.0 ml dioxan

(iii) 0.8 ml HClO$_4$ (0.02 M) + 2.0 ml NaClO$_4$ (2.0 M) + 0.5 ml metal perchlorate (0.02 M) + 1.7 ml doubly distilled water 10.0 ml ligand (M/100) + 5.0 ml dioxan.

These titrations were carried out in a closed double walled container in an atmosphere of nitrogen which was presaturated with the solvent.

In all the calculations the titrant value was taken as 19.67 ml instead of 20.0 ml, due to contraction in volume on mixing dioxan and water. From the titration curves of solutions (i) and (ii) the values of n_H were calculated at various pH values. On plotting log $(\bar{n}_H/1 - \bar{n}_H)$ vs pH, straight lines having intercept equal to pK and slope equal to unity were obtained. From the titration curve of solutions (i), (ii) and (iii), $\bar{n}$ values of the metal complexes were determined at various pH values. From pK values and $\bar{n}$ values at different pH values, the corresponding values of pL were calculated. The $\bar{n}$ and pL data were subjected to the weighted least squares treatment developed by Sullivan et al.[8] on an IBM 360 FORTRAN IV computer to get β_n values. The weighted least squares treatment determined the set of β_n values which make the function,

$$U, \left\{ U = \sum_{n=0}^{n} (y - x - nz) \ \beta_n X^n \right\}$$

nearest to zero, by minimizing S,

$$\left\{ S = \sum_{i=1}^{i} \omega_i U^2(x_i, y_i, z_i^y) \right.$$

with respect to variation in β_n. S_{min} has the same statistical distribution as χ^2 with K degrees of freedom, and the weight defined in accordance with Sullivan *et al.*[9]. S_{min} can be equated to χ^2. The ΔH was calculated by the graphical method of Yatsimirskii *et al.*[10] while

ΔG and ΔS were calculated by the conventional methods.

In the present investigation it has been noticed that the value of dissociation constants pK of the ligand decreases with increasing ionic strength of the medium (Table 1) which is in agreement with Debye-Hückel equation[11]. In case of stabilities of the AQTS

Table 1—Stability Constants of Lanthanide Complexes of AQTS at Different Ionic Strengths (Temp. $= 25 \pm 0.5°C$)

Stability constant and S_{min} values	Weighted least squares method (Temp. $= 25 \pm 0.5°C$)			
	0.01 M (NaClO$_4$)	0.05 M (NaClO$_4$)	0.1 M (NaClO$_4$)	0.2 M (NaClO$_4$)
H$^+$				
	12.85	12.71	12.64	12.57
Ho^{3+}				
log K_1	10.18	9.74	9.36	9.16
log K_2	9.86	9.29	8.80	8.59
log β_2	20.04	19.03	18.16	17.75
S_{min}	0.1782	0.4705	0.3568	0.3234
Dy^{3+}				
log K_1	10.04	9.58	9.15	9.06
log K_2	9.46	9.07	8.51	8.49
log β_2	19.50	18.65	17.66	17.55
S_{min}	1.1057	0.1606	0.4108	0.2993
Tb^{3+}				
log K_1	9.85	9.44	9.11	8.96
log K_2	9.31	8.96	8.30	8.34
log β_2	19.16	18.40	17.41	17.30
S_{min}	1.3624	0.1363	0.6635	0.2850
Sm^{3+}				
log K_1	9.80	9.27	8.92	8.84
log K_2	9.17	8.73	8.27	8.13
log β_2	18.97	18.00	17.19	16.97
S_{min}	0.6217	0.1844	0.1731	0.4299
Nd^{3+}				
log K_1	9.67	9.18	8.90	8.66
log K_2	8.98	8.56	8.08	8.07
log β_2	18.65	17.74	16.98	16.73
S_{min}	0.4025	0.3246	0.3507	0.1317
Pr^{3+}				
log K_1	9.45	9.03	8.77	8.55
log K_2	8.91	8.47	7.75	7.89
log β_2	18.36	17.50	16.52	16.44
S_{min}	0.8093	0.7674	0.3794	1.0462
La^{3+}				
log K_1	9.35	8.90	8.60	8.43
log K_2	8.80	8.37	7.42	7.65
log β_2	18.15	17.27	16.02	16.08
S_{min}	0.2930	0.3917	0.1632	0.1631

Table 2—Stability Constants of Lanthanide Complexes of AQTS at Different Temperatures ($\mu = 0.1$ M NaClO$_4$)

Stability constant and S_{min} values	Weighted least squares method at		
	30 $\pm 0.5°C$	40 $\pm 0.5°C$	50 $\pm 0.5°C$
H$^+$			
	12.39	12.22	11.84
Ho^{3+}			
log K_1	9.48	9.27	8.91
log K_2	8.93	8.71	8.27
log β_2	18.41	17.98	17.08
S_{min}	0.6925	0.6353	0.2482
Dy^{3+}			
log K_1	9.37	9.11	8.81
log K_2	8.70	8.58	8.08
log β_2	18.07	17.69	16.89
S_{min}	0.7432	1.0064	0.3710
Tb^{3+}			
log K_1	9.16	9.02	8.64
log K_2	8.54	8.44	7.71
log β_2	17.70	17.46	16.35
S_{min}	0.1032	0.9966	0.6741
Sm^{3+}			
log K_1	9.12	8.91	8.48
log K_2	8.48	8.21	7.62
log β_2	17.60	17.12	16.10
S_{min}	0.3899	0.1557	0.7022
Nd^{3+}			
log K_1	8.93	8.75	8.45
log K_2	8.32	8.01	7.48
log β_2	17.25	16.76	15.93
S_{min}	0.1806	0.8759	0.1756
Pr^{3+}			
log K_1	8.82	8.47	8.32
log K_2	8.26	7.79	7.18
log β_2	17.08	16.26	15.50
S_{min}	0.8168	0.2175	1.1425
La^{3+}			
log K_1	8.75	8.28	8.20
log K_2	7.84	7.59	7.13
log β_2	16.59	15.87	15.33
S_{min}	0.3823	0.1476	1.1826

Table 3—Thermodynamic Parameters of Lanthanide Complexes of AQTS at $\mu = 0.1\,M$ NaClO$_4$ and Temp. $= 30 \pm 0.5°C$

Metal ion	$-\Delta G$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	ΔS (J deg^{-1} mol^{-1})
Ho(III)	49.41	45.70	12.24
Dy(III)	48.77	47.99	10.13
Tb(III)	47.54	41.73	19.17
Sm(III)	47.30	43.62	12.15
Nd(III)	46.19	43.62	8.48
Pr(III)	45.54	42.65	9.54
La(III)	45.13	41.73	8.18

complexes, a similar trend is obtained. The order of stability constants of the metal complexes of AQTS is found to be: Ho > Dy > Tb > Sm > Nd > Pr > La. Moeller and Hseu[12] and Choppin and Graffeo[13] have observed similar trends. The values of log K_1, log K_2, log β_2 and S_{min} at 25°C for the complexes of lanthanides at different ionic strengths are summarised in Table 1. In the present studies it has also been observed that the stability constants decrease with the increase in temperature (Table 2) along with pK. These results are in good agreement with those of Nair and Srinivasulu[14] and Viswanath and Ananta Krishnan[15]. The values of changes in Gibb's energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying complex formation are reported in Table 3.

The stabilities of lanthanide complexes with AQTS show an increase in stability from La(III) to Ho(III) in agreement with increasing acidity. This trend suggests that metal-ligand interaction may be predominantly electrostatic.

In general, log $K_1 > $ log K_2 for a given metal ion; however, the difference in the values between the two constants is not too much, indicating that there is almost equal tendency for the formation of neutral complex species. In fact, the maximum $\bar{n}$ values observed in our present experiments are ~ 2.0 which support our assumption of 1:2 stoichiometry. Finally, in view of the very low $(5.0 \times 10^{-4}\,M)$ concentration of metal ions used in the titration, the possibility of formation of polynuclear complex is negligible.

References

1 Moeller T, *Int Rev Sci Inorg Chem Ser I*, **7** (1972) 275.
2 Bjerrum J, *Metal amine formation in aqueous solution* (Hasse, Copenhagen), 1941, 298.
3 Calvin M & Wilson K W, *J Am chem Soc*, **67** (1945) 2003.
4 Irving H M & Rossotti H S, *J chem Soc*, (1954) 2904.
5 Sah Peter P T & Daniels T C, *Recl Trav chim Phys Bas Belg*, **69** (1950) 1545.
6 Topp N E, *The chemistry of rare earth elements* (Elsevier, London), 1965, 115.
7 Vogel A I, *A text book of practical organic chemistry* (Longmans, New York), 1956, 177.
8 Sullivan J C, Rydberg J & Miller W F, *Acta chem scand*, **13** (1959) 2023.
9 Sullivan J C, Rydberg J & Miller W F, *Acta chem scand*, **13** (1959) 2059.
10 Yatsimiraskii K B & Vaslev V P, *Instability constants of complex compounds* (Van Nostrand, New York), 1960, 63.
11 Nasanen R & Ekman A, *Acta chem scand*, **6** (1952) 1389.
12 Moeller T & Hseu T M, *J inorg nucl Chem*, **24** (1962) 1635.
13 Coppin Gregory R & Graffeo Anthony J, *Inorg Chem*, **9** (1965) 1254.
14 Nair P K R & Srinivasulu K, *J inorg nucl Chem*, **41** (1979) 251.
15 Viswanath G, Menon P & Ananta Krishnan A S, *J inorg nucl Chem*, **41** (1979) 717.
16 Grenthe I, *Acta chem Scand*, **17** (1963) 2487; **18** (1964) 283, 293.