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EVALUATION OF THERMODYNAMIC PARAMETERS AND STABILITY CONSTANTS FOR THE FORMATION OF LANTHANON(III) COMPLEXES WITH BIOLOGICALLY ACTIVE 2-(2′-LEPIDYLAZO)-*N*-METHYLISATIN (LAMI)

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ABSTRACT

Thermodynamic stabilities of the chelates formed between 2-(2′-lepidylazo)-*N*-methylisatin and La(III), Pr(III), Nd(III), Sm(III), Y(III), Tb(III), Dy(III) and Ho(III) were determined pH metrically in 75% (v/v) aqueous dioxan at various temperatures. The method of Bjerrum and Calvin, as modified by Irving and Rossotti, was used to evaluate $\bar{n}$ and pL. A computer was used to compute the stability constants and $S_{\min}$ values using a weighted least-squares method. The order of stability constants was found to be: La(III) < Pr(III) < Nd(III) < Sm(III) < Y(III) < Tb(III) < Dy(III) < Ho(III). Thermodynamic parameters, such as ΔG, ΔH and ΔS, have also been calculated.

INTRODUCTION

Heterocyclic azo dyes are a relatively new class of compounds, which are extensively used as analytical reagents [1]. Isatin and its derivatives have found widespread application in various fields. Knotz and Wendelin [2] have reported the antiviral and antimicrobial activity of isatin derivatives. The antineoplastic, antihypotensive, analgesic, antimicrobial, anti-inflammatory and cysticidal properties of isatin derivatives are well known [3]. They have been found to act as central nervous system depressants and are used for the prevention of smallpox, etc. [4]. A literature survey reveals that no work has been done on the lanthanon complexes of 2-(2′-lepidylazo)-*N*-methylisatin (LAMI), so the present study was undertaken to determine the stability constants of lanthanons with LAMI at different temperatures in 75% (v/v) dioxan–water medium.

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EXPERIMENTAL

Materials

A digital pH meter (ECIL model pH-5652) in conjunction with a glass electrode were used for pH measurements. The pH meter was standardised with potassium hydrogenphthalate and phosphate buffers before performing the titrations.

N-Methylisatin (1.61 g) was dissolved in aqueous ethanol to give a saturated solution. A saturated solution of 2-hydrazinolepidine (1.73 g) in ethanol was added and the mixture was refluxed for 3 h on a water bath. After completion of the reaction, the mixture was cooled and filtered, to give a reddish-orange final product. This was finally recrystallised from an ethanol–benzene (3 : 1) mixture and its purity was checked by elemental analysis and TLC.

The solution of 2-(2′-lepidylazo)-*N*-methylisatin was prepared in freshly distilled dioxan. To ensure constant ionic strength during titration an inert electrolyte, sodium perchlorate ($NaClO_4$) (Riedel), was added. Perchloric acid ($HClO_4$) was standardised with sodium carbonate. Solutions of metal perchlorates of La(III), Pr(III), Nd(III), Sm(III), Y(III), Tb(III), Dy(III) and Ho(III) were prepared from their corresponding oxides [5] (99% Johnson Matthey). These solutions were diluted to the desired concentrations and were standardised by conventional methods. A solution of tetramethylammonium hydroxide (TMAH) (Merck) in 75% aqueous dioxan was used as the titrant, and was standardised with oxalic acid. Dioxan (AR, BDH) was purified by Weissberger et al.'s [6] procedure. All other chemicals used were of reagent grade. The titrations were carried out in a nitrogen atmosphere, which was presaturated with 75% (v/v) aqueous dioxan. The measurements were made at a definite temperature which was kept constant by using an MLW (F.R.G.) (NBE type) thermostat.

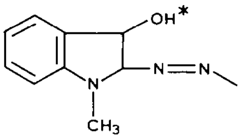
Method

The method of Bjerrum and Calvin, as modified by Irving and Rossotti [7] has been used to determine $\bar{n}$ and pL values. The following solutions (total volume = 19.67 ml instead of 20 ml, due to contraction in volume on mixing dioxan and water) were titrated potentiometrically against standard 0.04 M TMAH.

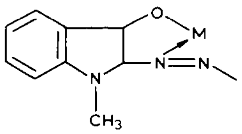
(i) 3 ml $HClO_4$ (0.02 M) + 1 ml $NaClO_4$ (2 M) + 1 ml H_2O + 15 ml dioxan.

(ii) 3 ml $HClO_4$ (0.02 M) + 1 ml $NaClO_4$ (2 M) + 1 ml H_2O + 10 ml ligand (0.01 M) + 5 ml dioxan.

(iii) 3 ml $HClO_4$ (0.02 M) + 1 ml $NaClO_4$ (2 M) + 0.5 ml H_2O + 0.5 ml metal solution (0.02 M) + 10 ml ligand (0.01 M) + 5 ml dioxan.



(I)



(II)

These titrations were repeated at 30, 40, 50 and 60 °C. The proton of LAMI (**I**), marked with an asterisk, is replaced by an equivalent amount of metal(III), i.e. M^{3+}, thereby forming a five-membered ring (**II**) during complexation.

From the titration curves of solutions (i), (ii) and (iii) the values of $\bar{n}$ and pL have been calculated using an IBM 360 computer (Fortran IV). The corresponding values of stability constants have been calculated using the weighted least-squares method of Sullivan et al. [8]. The weighted least-squares treatment determines the set of β_n values which makes eqn. (1) nearest to zero by minimizing eqn. (2) with respect to the variation in β_n.

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

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

We report the $S_{\min}$ values for the different metal complexes. $S_{\min}$ has the same statistical distribution as χ^2 with K degrees of freedom and weights defined in accordance with Rydberg and Sullivan [9]. $S_{\min}$ can be equated to

TABLE 1

Stability constants of lanthanon complexes with LAMI at $\mu = 0.1$ M $NaClO_4$ and $T = 60 \pm 0.5$ °C

Metal ion	Weighted least-squares method			$S_{\min}$
	log K_1	log K_2	log β_2	
H^+	10.96	–	–	–
La(III)	8.56	8.21	16.77	0.0089
Pr(III)	8.86	8.12	16.98	0.0171
Nd(III)	9.08	7.93	17.01	0.0185
Sm(III)	9.36	7.41	16.77	0.0139
Y(III)	9.38	8.60	17.98	0.1211
Tb(III)	9.52	8.90	18.42	0.0032
Dy(III)	9.74	9.05	18.79	0.0113
Ho(III)	9.90	8.65	18.55	0.1445

TABLE 2

Stability constants of lanthanon complexes with LAMI at $\mu = 0.1$ M $NaClO_4$ and $T = 50 \pm 0.5$ °C

Metal ion	Weighted least-squares method			S_{min}
	log K_1	log K_2	log β_2	
H^+	11.63	–	–	–
La(III)	9.01	7.63	16.64	0.0743
Pr(III)	9.29	7.90	17.19	0.0016
Nd(III)	9.32	8.26	17.58	0.0121
Sm(III)	9.44	8.24	17.68	0.0154
Y(III)	9.74	8.09	17.83	0.0059
Tb(III)	9.85	8.56	18.41	0.0041
Dy(III)	10.01	8.54	18.55	0.0884
Ho(III)	10.24	8.76	19.00	0.0074

TABLE 3

Stability constants of lanthanon complexes with LAMI at $\mu = 0.1$ M $NaClO_4$ and $T = 40 \pm 0.5$ °C

Metal ion	Weighted least-squares method			S_{min}
	log K_1	log K_2	log β_2	
H^+	11.90	–	–	–
La(III)	9.38	7.95	17.33	0.0148
Pr(III)	9.72	8.17	17.89	0.0194
Nd(III)	9.88	8.44	18.32	0.0014
Sm(III)	9.95	8.71	18.66	0.0061
Y(III)	10.08	8.90	18.98	0.0038
Tb(III)	10.10	9.24	19.34	0.0010
Dy(III)	10.25	9.48	19.73	0.0115
Ho(III)	10.61	9.65	20.26	0.5557

TABLE 4

Stability constants of lanthanon complexes with LAMI at $\mu = 0.1$ M $NaClO_4$ and $T = 30 \pm 0.5$ °C

Metal ion	Weighted least-squares method			S_{min}
	log K_1	log K_2	log β_2	
H^+	12.78	–	–	–
La(III)	9.55	8.29	17.84	0.0770
Pr(III)	10.07	8.75	18.82	0.0138
Nd(III)	10.12	8.82	18.94	0.0175
Sm(III)	10.18	8.99	19.17	0.0037
Y(III)	10.20	9.25	19.45	0.0040
Tb(III)	10.43	9.44	19.87	0.0038
Dy(III)	10.45	9.86	20.31	0.0040
Ho(III)	10.64	9.87	20.51	1.7655

χ^2. The stability constants thus calculated are given in Tables 1–4. ΔH was calculated by the graphical method of Yatsimirskii et al. [10] while ΔG and ΔS were calculated by conventional methods.

RESULTS AND DISCUSSION

Complexes of lanthanons with LAMI show an increase in stability from La(III) to Ho(III) in agreement with increasing acidity of the metal ion. The order of stability constants for the first and second steps in the formation of lanthanide complexes with LAMI is found to be: La(III) < Pr(III) < Nd(III) < Sm(III) < Y(III) < Tb(III) < Dy(III) < Ho(III). The same trend has also been found for complexes of α-iminodiacetic acid, α-hydroxyisobutyric acid, nitrilotriacetic acid, tropolone, β-isopropyl tropolone [11] and 4,5-dimethyl-2-hydroxy acetophenone [12].

The log K_1 values for yttrium lie near to those for terbium because of the lack of ligand field stabilisation. In all cases it has been observed that log $K_1 >$ log K_2. The values of stability constants in Tables 1–4 reveal that stability constants regularly decrease with increasing temperature. pK_a values of the ligand have also been found to follow the same trend.

Thermodynamic parameters (ΔG, ΔH and ΔS) have been calculated by using the following relationships:

$$\Delta G = -RT \ln K$$

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

$$\Delta S = (\Delta H - \Delta G)/T$$

The overall free energy, enthalpy and entropy changes at 30 ± 0.5°C are reported in Table 5. The results indicate that ΔG and ΔH are negative which shows that complex reactions are favourable at ordinary temperatures. The positive ΔS values show that the system is entropy stabilized.

TABLE 5

Thermodynamic parameters for the formation of lanthanon complexes with LAMI at $\mu = 0.1$ M $NaClO_4$ and $T = 30 \pm 0.5$°C

Metal ion	$-\Delta G$ (kcal mol^{-1})	$-\Delta H$ (kcal mol^{-1})	ΔS (kcal K^{-1} mol^{-1})
La(III)	13.23	9.14	0.01349
Pr(III)	13.27	7.31	0.01967
Nd(III)	14.02	13.71	0.00102
Sm(III)	14.10	12.80	0.00420
Y(III)	14.13	11.88	0.00742
Tb(III)	14.45	13.71	0.00240
Dy(III)	14.48	11.88	0.00850
Ho(III)	14.74	14.62	0.00039

The change in entropy upon complexation of a lanthanon ion is related to both changes in the number of particles in the system and to changes in the mode of vibration of these particles. In aqueous systems, complexation by chelation is favoured by the release of bound water molecules [13].

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