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THERMODYNAMIC STABILITIES OF LANTHANIDE COMPLEXES WITH 3-HYDROXY-2-METHYL-1,4-NAPHTHOQUINONE MONOXIME (HMNQM) *

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ABSTRACT

The thermal behaviour of complexes of La(III), Pr(III), Nd(III), Sm(III), Tb(III), Dy(III) and Ho(III), with 3-hydroxy-2-methyl-1,4-naphthoquinone monoxime has been studied potentiometrically in 75% (v/v) aqueous dioxan 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 an IBM 360 computer using the weighted least-squares method. The values of S_{min} have also been calculated. The order of stability constants was found to be

La < Pr < Nd < Sm < Tb < Dy < Ho

Thermodynamic parameters (ΔG, ΔH and ΔS) of the complexation reactions have also been calculated.

INTRODUCTION

Metal chelates are very useful in analytical chemistry and industry. Oximes form an important class of analytical reagents and they react with metal ions due to the coordinating nature of the nitrogen atom of the oxime group. In the 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 lanthanon ions as a whole form far fewer complexes and yield complexes with significantly different properties [1–3]. The low stability of lanthanon complexes can be increased by means of the chelate effect, but little work has been directed towards the elucidation of the nature of lanthanon chelates of oximes. Only a few chelates of some lanthanons have been studied potentiometrically.

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The present study was undertaken to study the thermal stabilities of lanthanons with 3-hydroxy-2-methyl-1,4-naphthoquinone monoxime at different temperatures in 75% dioxan medium.

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 standardised with potassium hydrogen phthalate and phosphate buffers before performing the titrations. 3-Hydroxy-2-methyl-1,4-naphthoquinone (phthiocol) was prepared by the method of Fieser [4] and its purity was checked by elemental analysis and TLC.

The solution of HMNQM was prepared in freshly distilled dioxan. All the metal ion solutions were prepared and standardised by conventional procedures. Sodium perchlorate (Riedel) was used to keep the ionic strength constant for different sets. A solution of tetramethyl ammonium hydroxide (TMAH) (Merck) in 75% aqueous dioxan was used as the titrant. It was standardised with oxalic acid. Dioxan (Merck) was freed from peroxide by refluxing it with sodium metal for 24 h and was freshly distilled over sodium before use. All other chemicals used were of reagent grade. The titrations were carried out in an atmosphere of nitrogen, which was presaturated with 75% aqueous dioxan. All measurements were made at a definite temperature which was kept constant by using an MLW (West Germany) (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 = 19.67 ml instead of 20 ml, due to contraction in volume on mixing dioxan and water) were titrated potentiometrically against standard 0.05 M TMAH, in 75% dioxan (v/v) to determine $\bar{n}$ and pL values of the complexes.

(i) 0.8 ml $HClO_4$ (0.02 M) + 1.0 ml of $NaClO_4$ (2 M) + 3.2 ml of H_2O + 15.0 ml of dioxan.

(ii) 0.8 ml of $HClO_4$ (0.02 M) + 1.0 ml of $NaClO_4$ (2 M) + 3.2 ml of H_2O + 10.0 ml of ligand (0.01 M) + 5.0 ml of dioxan.

(iii) 0.8 ml of $HClO_4$ (0.02 M) + 1.0 ml of $NaClO_4$ (2 M) + 2.7 ml of H_2O + 0.5 ml of metal solution (0.02 M) + 10.0 ml of ligand (0.01 M) + 5.0 ml of dioxan.

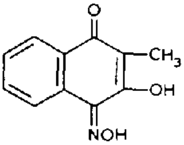
Due to the presence of an oxime group the acidity of the *ortho*-phenolic hydroxyl group is enhanced. During complexation this acidic proton is replaced by an equivalent amount of metal (**II**) and thus the ligand (**I**) acts as a mono-basic acid. This phenolic group dissociates first and the pK_1 value

TABLE 1

Stability constants of lanthanon complexes with HMNQM at $\mu = 0.1$ M $NaClO_4$ and a temperature of 50 ± 0.5°C

Metal ion	log k_1	log k_2	log β_2	S_{min}
H^+	6.70	–	–	–
La(III)	4.4437	4.1364	8.5801	1.2121
Pr(III)	4.5268	4.1831	8.7099	0.5717
Nd(III)	4.5826	4.2924	8.8750	1.0160
Sm(III)	4.6214	4.3367	8.9581	0.1530
Tb(III)	4.6923	4.3619	9.0542	0.1874
Dy(III)	4.7147	4.3814	9.0961	0.7289
Ho(III)	4.8236	4.4034	9.2270	0.1325

of the ligand will correspond to the dissociation of this group.



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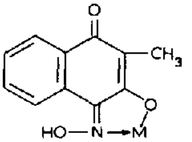

II

At high pH values (> 12.0) the hydrogen of the oxime group becomes dissociable and thus pK_2 is difficult to determine.

From the above titration curves of solutions (i), (ii) and (iii) the values of $\bar{n}$ and pL have been calculated using an IBM 360 Fortran-IV 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 $[U = \Sigma_{n=0}^{N}(y - x - nz)\beta_n X^n]$ nearest to zero, by minimizing S $[S = \Sigma_{i=1}^{I} U^2(x_1 y_i z_i)]$ with respect to the variation in β_n. We report the S_{min} values for different metal complexes. S_{min} has the same statistical distribu-

TABLE 2

Stability constants of lanthanon complexes with HMNQM at $\mu = 0.1$ M $NaClO_4$ and a temperature of 45 ± 0.5°C

Metal ion	log k_1	log k_2	log β_2	S_{min}
H^+	7.05	–	–	–
La(III)	4.5370	4.3231	8.8601	0.6095
Pr(III)	4.8127	4.5333	9.3460	0.2971
Nd(III)	4.8425	4.6279	9.4704	0.3549
Sm(III)	4.9729	4.6912	9.6641	0.2233
Tb(III)	5.0329	4.7273	9.7602	1.7102
Dy(III)	5.1014	4.7410	9.8424	1.1819
Ho(III)	5.1124	5.0731	10.1855	0.4470

tion as χ^2 with K degrees of freedom and with weights defined in accordance with Rydberg and Sullivan [7], $S_{\min}$ can be equated to χ^2. The stability constants thus calculated are given in Tables 1–3.

RESULTS AND DISCUSSION

It was observed that stability from La(III) to Dy(III) follows the same order as increasing acidity. The order of log k_1 values for HMNQM complexes is found to be

La < Pr < Nd < Sm < Tb < Dy < Ho

The same trend has also been noticed in the complexes imino diacetic acid, α-hydroxyisobutyric acid, nitrilo triacetic acid, ethylene diamine-*N*,*N*,*N'*,*N'*-tetraacetic acid, tropolone, β-isopropyl tropolone [8], and *cis*-1,2,3,4-cyclopentanetetracarboxylic acid [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 value. These results are in good agreement with those of Pitzer [10]. The thermodynamic parameters (ΔG, ΔH and ΔS) have been calculated by using the following relationship.

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

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

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

The overall free energy change, and enthalpy and entropy changes at 30 ± 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 decrease in temperature suggesting an increase in the

TABLE 3

Stability constants of lanthanon complexes with HMNQM at $\mu = 0.1$ M $NaClO_4$ and a temperature of 30 ± 0.5°C

Metal ion	log k_1	log k_2	log β_2	$S_{\min}$
H^+	7.30	–	–	–
La(III)	4.9412	4.6219	9.5631	0.7214
Pr(III)	4.9730	4.6831	9.6561	0.1729
Nd(III)	5.0113	4.7319	9.7432	0.1103
Sm(III)	5.1873	4.8064	9.9937	0.1141
Tb(III)	5.2213	4.8714	10.0927	0.4708
Dy(III)	5.4024	4.9413	10.3437	0.1444
Ho(III)	5.7917	5.2515	11.0432	0.1497

TABLE 4

Thermodynamic parameters of lanthanon complexes with HMNQM at $\mu = 0.1$ M $NaClO_4$ and a temperature of $30 \pm 0.5°C$

Metal ion	$-\Delta G$ (kcal mol^{-1})	$-\Delta H$ (kcal mol^{-1})	$-\Delta S$ (kcal K^{-1} mol^{-1})
La(III)	6.894	7.4263	0.5323
Pr(III)	6.936	7.9975	1.0615
Nd(III)	6.992	7.9975	1.0055
Sm(III)	7.229	7.9975	0.7685
Tb(III)	7.285	10.054	2.7690
Dy(III)	7.536	13.710	6.1740
Ho(III)	8.080	15.995	7.9150

extent of complex formation at lower temperature. The enthalpy changes are exothermic. The change in entropy upon complexation is related both to changes in the number of particles in the system and to changes in modes of vibration of particles in the system.

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