Thermochimica Acta, 155 (1989) 377–381
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

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

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(Received 3 April 1989)

ABSTRACT

The thermal behaviour of complexes of La(III), Pr(III), Nd(III), Y(III), Sm(III) and Tb(III) with 3-hydroxy-2-methyl-1,4-naphthoquinone 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. Thermodynamic parameters (ΔG, ΔH and ΔS) of the complexation reactions have also been calculated.

INTRODUCTION

In comparison with d-block metal ions, the lanthanon ions as a group form far fewer complexes and yield complexes with significantly different properties [1–3]. Metal chelates of 3-hydroxy-2-methyl-1,4-naphthoquinone or phthiocol are well known for their analytical and biological activities. A survey of the literature reveals that no work has been done on the lanthanon complexes of phthiocol. Therefore, the present study was undertaken to study the thermal stabilities of lanthanons with 3-hydroxy-2-methyl-1,4-naphthoquinone 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 standardized

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* Presented by R.K. Sharma at the 1985 World Conference on Thermal Analysis held in Badhofgastein, Austria.

0040-6031/89/$03.50

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 HMNQ was prepared in freshly distilled dioxan. 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 tetramethyl ammonium hydroxide (TMAH) (Merck) in 75% aqueous dioxan was used as the titrant. It was standardized 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 pre-saturated 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] was 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 the $\bar{n}$ and pL values of the complexes.

(1) 0.8 ml $HClO_4$ (0.05 M) + 0.1 ml $NaClO_4$ (2 M) + 4.1 ml H_2O + 15.0 ml dioxan.

(2) 0.8 ml $HClO_4$ (0.05 M) + 0.1 ml $NaClO_4$ (2 M) + 4.1 ml H_2O + 10.0 ml ligand + 5.0 ml dioxan.

(3) 0.8 ml $HClO_4$ (0.05 M) + 0.1 ml $NaClO_4$ (2 M) + 3.6 ml H_2O + 0.5 ml metal solution (0.02 M) + 10.0 ml ligand + 5.0 ml dioxan.

During complexation, the phenolic group dissociates first and the pK value of the ligand will correspond to the dissociation of this group. From the above titration curves of solutions (1), (2) and (3), the values of $\bar{n}$ and pL have been calculated using an IBM 360 Fortran IV computer. The corresponding values of the 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 $S[S = \Sigma_{i=1}^{I} W_i U^2(x_i y_i z_i)]$ with respect to the variation in β_n. We report the $S_{\min}$ values for different metal complexes. $S_{\min}$ has the same statistical 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 1–4.

TABLE 1

Stability constants of lanthanon complexes with HMNQ at $\mu = 0.01$ 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^+	7.10	–	–	–
La(III)	4.02	3.82	7.84	0.0041
Pr(III)	4.51	4.44	8.95	0.0126
Nd(III)	5.09	4.83	9.92	0.0035
Y(III)	5.13	4.62	9.75	0.0219
Sm(III)	5.25	4.88	10.13	0.0271
Tb(III)	5.54	5.02	10.56	0.0069

TABLE 2

Stability constants of lanthanon complexes with HMNQ at $\mu = 0.01$ 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^+	7.30	–	–	–
La(III)	4.55	3.92	8.27	0.0051
Pr(III)	5.11	4.46	9.57	0.0042
Nd(III)	5.35	4.13	9.48	0.0104
Y(III)	5.42	5.19	10.61	0.0289
Sm(III)	5.82	4.88	10.70	0.0087
Tb(III)	5.92	5.00	10.92	0.0218

TABLE 3

Stability constants of lanthanon complexes with HMNQ at $\mu = 0.01$ M $NaClO_4$ and a temperature of 40 ± 0.5 °C

Metal ion	log K_1	log K_2	log β_2	S_{min}
H^+	7.40	–	–	–
La(III)	4.51	4.10	8.61	0.0011
Pr(III)	5.49	4.30	9.79	0.0018
Nd(III)	5.59	4.66	10.25	0.0043
Y(III)	5.86	4.74	10.60	0.0035
Sm(III)	6.18	5.00	11.18	0.0034
Tb(III)	6.39	5.25	11.64	0.0076

TABLE 4

Thermodynamic parameters of lanthanol complexes with HMNQ at $\mu = 0.01$ M $NaClO_4$ and a temperature of 40 ± 0.5 °C

Metal ion	$-\Delta G$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (kJ K^{-1} mol^{-1})
La(III)	26.99	57.38	0.08
Pr(III)	32.89	169.79	0.42
Nd(III)	33.48	95.63	0.21
Y(III)	35.11	127.52	0.29
Sm(III)	37.04	153.00	0.38
Tb(III)	38.29	169.79	0.42

RESULTS AND DISCUSSION

Complexes of lanthanon ions with HMNQ show an increase in stability from La(III) to Tb(III) in agreement with the increasing acidity of the metal ion. The order of the stability constants for the first and second steps in the formation of lanthanide complexes with HMNQ is found to be La < Pr < Nd < Sm < Tb.

The same trend has also been noticed in the complexes of α-iminodiacetic acid, α-hydroxyisobutyric acid, nitrilotria-acetic acid, ethylenediamine-N,N,N',N'-tetraacetic acid, tropolone, β-isopropyltropolone [8] and *cis*-1,2,3,4-cyclopentanetetracarboxylic acid [9]. The log K_1 values for yttrium lie near those for samarium because of the lack of ligand field stabilization. The values of the stability constants in Tables 1–3 reveal that they decrease with increase in temperature along with the pK value. These results are in good agreement with those of Pitzer [10]. The thermodynamic parameters (ΔG, ΔH and ΔS) have been calculated 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 change, and enthalpy and entropy change at 40 ± 0.5 °C are reported in Table 4. The negative free energy change (ΔG) in each case indicates that the chelation is spontaneous. Furthermore ΔG becomes more negative with decreasing in temperature suggesting an increase in the extent of complex formation at lower temperatures. 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.

ACKNOWLEDGEMENT

Grateful acknowledgement is expressed to the C.S.I.R., New Delhi, India for the award of a Research Associateship to R.K.S. and to the Computer Centre, Delhi University for the smooth running of programmes on an IBM 360 Fortran IV computer.

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