Monatshefte für Chemie 117, 459—463 (1986)

Monatshefte für Chemie
Chemical Monthly

Potentiometric Studies on the Chelation Behaviour of Lanthanons with 3-Hydroxy-2-methyl-1,4-naphthoquinone (*HMNQ*)

R. K. Sharma, S. K. Singh, and **S. K. Sindhwani***

Department of Chemistry, University of Delhi, Delhi-110007, India

(Received 29 January 1985. Accepted 19 February 1985)

The chelation 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 ionic strengths. 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 and the values of S_{min} have been calculated. The order of stability constants was found to be: La < Pr < Nd < Sm < Tb.

(Keywords: Potentiometry; Stability constants; Dissociation constant; 3-Hydroxy-2-methyl-1,4-naphthoquinone; Lanthanides)

Potentiometrische Untersuchungen des Komplexierungsverhaltens von Lanthanid-Ionen mit 3-Hydroxy-2-methyl-1,4-naphthochinon (HMNQ)

Das Komplexierungsverhalten der Komplexe von La(III), Pr(III), Nd(III), Y(III), Sm(III) und Tb(III) mit 3-Hydroxy-2-methyl-1,4-naphthochinon wurde potentiometrisch in 75% (*v*/*v*) wäßrigem Dioxan bei verschiedenen Ionenstärken untersucht. Die Methode von *Bjerrum* und *Calvin* in der Modifikation nach *Irving* und *Rossotti* wurde zur Bestimmung der Werte für $\bar{n}$ und pL benutzt. Es wurden die Stabilitätskonstanten und die S_{min}-Werte berechnet; die Stabilitätskonstanten ergaben folgende Reihung: La < Pr < Nd < Sm < Tb.

Introduction

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]. Metal chelates of 3-hydroxy-2-methyl-1,4-naphthoquinone or phthiocol are well known for their analytical and biological activities. A survey of literature reveals that no work has been done on the lanthanon complexes of phthiocol. So the present study was undertaken to study the chelation behaviour of lanthanons with 3-hydroxy-2-methyl-1,4-naphthoquinone at various ionic strengths in 75% dioxan medium.

Materials and Methods

A digital *pH*-meter (EGIL 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 *HMNQ* 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 MLW (Federal Republic of Germany) (NBE type) thermostat.

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.

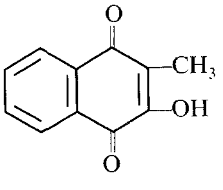
(i) 0.8 ml $HClO_4$ (0.05 *M*) + 2.0 ml $NaClO_4$ (2 *M*) + 2.2 ml of H_2O + 15.0 ml of dioxan.

(ii) 0.8 ml $HClO_4$ (0.05 *M*) + 2.0 ml $NaClO_4$ (2 *M*) + 2.2 ml H_2O + 10.0 ml of ligand + 5.0 ml of dioxan.

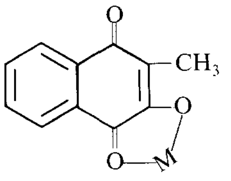
(iii) 0.8 ml $HClO_4$ (0.05 *M*) + 2.0 ml $NaClO_4$ (2 *M*) + 1.7 ml H_2O + 0.5 ml metal solution (0.02 *M*) + 10.0 ml of ligand + 5.0 ml of dioxan.

In other sets requisite amount of $NaClO_4$ was added to maintain the ionic strength at 0.1, 0.05 and 0.01 *M*.

During complexation the phenolic group dissociates first and the *pK* value of the ligand will correspond to the dissociation of this group.



I



II

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 computer (Fortran-IV). 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 the set of β_n values which makes the function $U\,[U = \sum_{n=0}^{N} (y - x - nz)\,\beta_n x^n]$ nearest to zero by minimizing $S\,[S = \sum_{i=1}^{I} U^2(x_i y_i z_i)]$ with respect to the variation in β_n.

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 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* $\mu = 0.2\,M$ $NaClO_4$ *and a temperature of 35° ± 0.5 °C*

Metal ion	$\log k_1$	$\log k_2$	$\log \beta_2$	S_{min}
H^+	7.4	—	—	—
La(III)	4.24	3.10	7.34	0.0021
Pr(III)	4.52	3.41	7.93	0.0028
Nd(III)	4.70	3.52	8.22	0.0051
Y(III)	4.81	3.56	8.37	0.0143
Sm(III)	5.26	3.95	9.21	0.0088
Tb(III)	5.39	4.03	9.42	0.0121

Table 2. *Stability constants of lanthanon complexes with HMNQ at* $\mu = 0.1\,M$ $NaClO_4$ *and a temperature of 35° ± 0.5 °C*

Metal ion	$\log k_1$	$\log k_2$	$\log \beta_2$	S_{min}
H^+	7.6	—	—	—
La(III)	4.50	3.58	8.08	0.0004
Pr(III)	4.76	3.87	8.63	0.0064
Nd(IIII)	4.78	3.99	8.77	0.0040
Y(III)	4.92	4.15	9.07	0.0089
Sm(III)	5.37	4.24	9.61	0.0031
Tb(III)	5.55	4.34	9.89	0.0031

Table 3. *Stability constants of lanthanon complexes with HMNQ at* $\mu = 0.05\,M$ $NaClO_4$ *and a temperature of 35° ± 0.5 °C*

Metal ion	$\log k_1$	$\log k_2$	$\log \beta_2$	S_{min}
H^+	7.70	—	—	—
La(III)	4.78	3.84	8.62	0.0016
Pr(III)	5.21	4.22	9.43	0.0070
Nd(III)	5.39	4.39	9.78	0.0031
Y(III)	5.47	4.41	9.88	0.0164
Sm(III)	5.55	4.64	10.19	0.0038
Tb(III)	5.70	5.03	10.73	0.0248

Table 4. *Stability constants of lanthanon complexes with HMNQ at* $\mu = 0.01\,M$ NaClO$_4$ *and a temperature of 35°* ± *0.5 °C*

Metal ion	$\log k_1$	$\log k_2$	$\log \beta_2$	S_{min}
H^+	7.80	—	—	—
La(III)	5.13	4.07	9.20	0.0011
Pr(III)	5.76	4.38	10.14	0.0042
Nd(III)	5.87	4.60	10.47	0.0017
Y(III)	5.98	4.89	10.87	0.0036
Sm(III)	6.18	5.18	11.36	0.0107
Tb(III)	6.41	5.24	11.65	0.0114

Results and Discussion

Complexes of lanthanon ions with *HMNQ* show an increase in stability from La(III) to Tb(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 *HMNQ* is found to be:

$$\mathrm{La} < \mathrm{Pr} < \mathrm{Nd} < \mathrm{Sm} < \mathrm{Tb}$$

The same trend has also been noticed in the complexes of α-iminodiacetic acid, α-hydroxy isobutyric acid, nitrilotriacetic acid, ethylenediamine-N,N,N′,N′-tetra acetic acid, tropolone, β-isopropyl tropolone[8] and *cis*-1,2,3,4-cyclopentane-tetracarboxylic acid[9].

The log k_1 values for yttrium lie near samarium because of the lack of ligand field stabilization. The stability constants of the complexes are found to decrease with increasing ionic strengths of the medium which is in agreement with the *Debye-Hückel* equation[10].

Acknowledgements

Grateful acknowledgement is expressed to the Centre of Advance Studies, Department of Chemistry, University of Delhi, for the award of a fellowship to *R. K. S.* and to the Computer Centre, University of Delhi, for the smooth running of programmes (Fortran IV) on an IBM 360 computer.

References

[1] *Moeller T., Martin D. F., Thompson L. G., Ferrus R., Fiestel G. R., Randall W. J.*, Chem. Rev. **65**, 1 (1965).

[2] *Moeller T., Birnbaum E. R., Forsherg J. H., Gayhart R. B.*, Progress in the Science and Technology of Rare Earths (*Eyring L.*, ed.), Vol. 3, p. 61–128. New York: Pergamon. 1968.

[3] *Sinha S. P.,* Complexes of Rare Earths. New York: Pergamon. 1966.
[4] *Fieser L. F.,* J. Biol. Chem. **133**, 391 (1940).
[5] *Irving H. M., Rossotti H. S.,* J. Chem. Soc. **1954**, 2904.
[6] *Sullivan J. C., Rydberg J., Miller W. F.,* Acta Chem. Scand. **13**, 2023 (1959).
[7] *Rydberg J., Sullivan J. C.,* Acta Chem. Scand. **13**, 2059 (1959).
[8] *Martell A. E., Smith R. M.,* Critical Stability Constant, Vol. I. New York: Plenum. 1974.
[9] *Nair P. K. R., Srinivasulu K.,* J. Inorg. Nucl. Chem. **41**, 251 (1979).
[10] *Nasanen R., Ekman A.,* Acta Chim. Scand. **6**, 1389 (1952).