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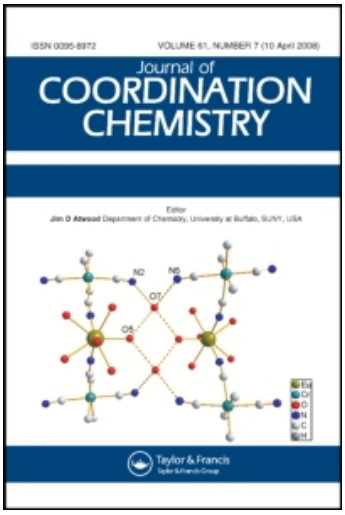

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METAL-CHELATE EQUILIBRIA IN THE REACTIONS BETWEEN RARE EARTH IONS AND THORON

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Interactions between the rare earth ions, Y(III), La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and 1-(*o*-arsonophenylazo)-2-naphthol-3, 6-disulphonic acid (thoron; abbr. APANS) have been investigated at 30° in aqueous media using *p*H-titration technique. Reactions for all the metal ions except Ce(III) were carried out in a perchlorate medium of ionic strength of 0.10 M maintained by $NaClO_4$ solution, while Ce(III) was studied in chloride medium at the same ionic strength. The formation constants of the various species have been evaluated employing a modified algebraic method of Chaberek and Martell. The formation of diprotonated 1:1 metal to ligand chelate is evident, which slowly liberates protons. The nonprotonated species of middle and heavy rare earth ions interact with hydroxyl ions to form monohydroxo chelate species.

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INTRODUCTION

1-(*o*-Arsonophenylazo)-2-naphthol-3,6-disulphonic acid (thoron, abbr. APANS) possesses a pronounced chelating tendency due to suitable geometric arrangements of its five coordinating groups,[1–3] and is capable of formation of various protonated chelate species. The values of the formation constants of the chelates of the different rare earth ions are close to one another and the study of various metal-ligand equilibria are therefore of considerable theoretical interest. The investigations of chelation reactions of APANS with the rare earth ions, Y(III), La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III) and Lu(III), in aqueous perchloric acid media and Ce(III) in hydrochloric acid media, were carried out at 30° and at ionic strength of 0.10 M maintained by $NaClO_4$ or NaCl respectively. The equilibrium constants were determined by the methods of Bjerrum,[5] Irving and Rossotti,[6] and the algebraic method of Chaberek and Martell,[7] as modified and described earlier.[3,4]

EXPERIMENTAL

Procedure

The *p*H-measurements were carried out using a mains operated *p*H-meter (Elico, Model L1-10) with a glass-calomel electrode assembly. The instrument was standardized against standard buffers. Three mixtures: (i) $HClO_4$ of known concentration, (ii) $HClO_4$ as in (i) $+5.0 \times 10^{-4}$ M APANS, (iii) mixture (ii) + 5.0×10^{-4} M metal perchlorate, were prepared, and titrated separately against standard NaOH solution keeping the total volume 50 ml. All measurements were carried out at 30° and under nitrogen atmosphere and at $\mu = 0.10$.

From the experimental data, curves were plotted between *p*H and volume of alkali. Moles of alkali required per mole of ligand, *a*, were determined at various *p*H from *p*H *vs* volume of alkali curves. Values of *a* were then plotted against *p*H (Figure 1). Information on the nature of chelation equilibria was obtained and the equilibrium constants were evaluated.

The titrations were repeated using 1:2 metal ion: ligand ratio also. The curves showed that only 1:1 species was formed and there was no indication of either 1:2 species or of polynuclear complex formation.

RESULTS AND INTERPRETATION

APANS contains five protons out of which only four are dissociated in the *p*H range employed. The values of the logarithms of the step dissociation constants evaluated are: −2.0, −2.10, −5.35, −10.50.

The titration curves of all the rare earth ions obtained for 1:1 metal to ligand systems (Figure 1)

†To whom all correspondence may be made.

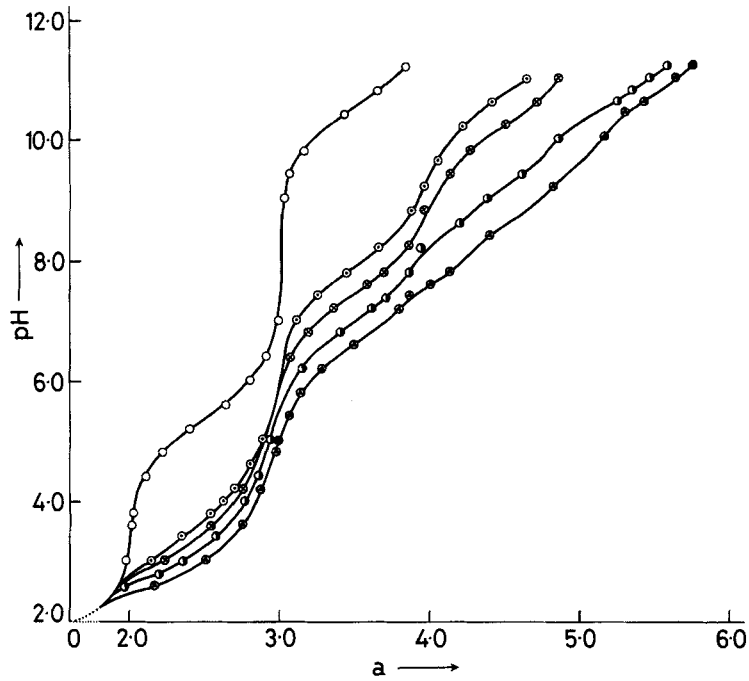

FIGURE 1 Plot of pH against moles of alkali used for per mole of ligand (a)

—○—○—, Ligand (5.0×10^{-4} M APANS)

Metal–Ligand Curves (M:L,1:1; L = 5.0×10^{-4} M)

—⊙—⊙— La; —⊗—⊗— Sm;
—◒—◒— Dy; —◉—◉— Lu

[The curves for other rare earth ions have been omitted.]

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show a very steep inflection at $a = 3$ due to the formation of neutral diprotonated (MH_2L°) species (M = rare earth ion). The existence of this species is also evident from the precipitation of the reaction mixtures below $\mu = 0.1$ M ($NaClO_4$) in the case of middle and heavy rare earth ions. The reactions involved between $a = 0$ and 3 is:

$$M^{3+} + H_2L^{3-} \rightleftharpoons MH_2L^\circ, \qquad K = \frac{[MH_2L^\circ]}{[M^{3+}][H_2L^{3-}]} \tag{i}$$

where K is the equilibrium constant.

Beyond $a = 3$ the titration curves (Figure 1) follow another buffer region with another sharp inflection at $a = 4$ indicating the following equilibria:

$$MH_2L^\circ \rightleftharpoons MHL^- + H^+, \qquad K = \frac{[MHL^-][H^+]}{[MH_2L^\circ]} \tag{ii}$$

The turbid titration mixtures of low $NaClO_4$ concentrations ($\mu < 0.1$ M) also change into clear solutions in this buffer region and further turbidity does not appear beyond $a = 3$. The titration curves show other buffer regions between $a = 4$ and 5, following inflections at $a = 5$. Thus the last proton of metal-chelates is dissociated as under:

$$MHL^- \rightleftharpoons ML^{2-} + H^+, \qquad K = \frac{[ML^{2-}][H^+]}{[MHL^-]} \tag{iii}$$

It may be added that the proton of the above equilibrium is liberated very slowly.

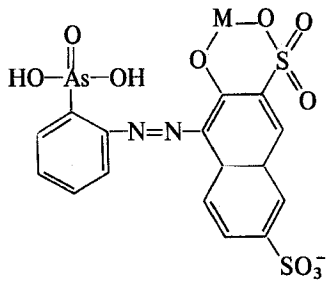
The equilibria (ii) and (iii) are similar to a ligand dissociation and therefore the equilibrium constants K were calculated by the method as described for the evaluation of dissociation constants of APANS.

Under the experimental conditions of pH another buffer region appears above $a = 5$ in the systems of

the middle and heavy rare earth ions due to the formation of hydroxo complexes. However a complete titration curve is not obtained for all the systems in the *p*H range used. The equilibrium and the formation constants are defined as below:

$$ML^{2-} + OH^- \rightleftharpoons M(OH)L^{3-}, \qquad K = \frac{[M(OH)L^{3-}]}{[ML^{2-}]\,[OH^-]} \qquad \text{(iv)}$$

The expected coordinating groups involved in neutral MH_2L° species are $-SO_3H$ and phenolic $-OH$ as shown below:



(MH_2L°)

A similar study of APANS with Th(IV) carried out in nitric acid medium shows that chelation takes place through azo and two $-OH$ groups.[3]

The formation of MH_2L° and dissociation of the two protons from MH_2L° to form a nonprotonated complex, followed by the interaction of hydroxy ions with chelates of middle and heavy rare earth ions is also evident from the gradual colour changes of various species.

The behaviour of tripositive ions in chelation equilibria with APANS has been observed to be consistent with an increase in the atomic number from lanthanum to lutetium and the chelate species (MH_2L°) have very close values of the formation constants. The chelating behaviour of yttrium lies between gadolinium and terbium. But in the dissociation of MH_2L° into monoprotonated and nonprotonated species, and association of OH^- ions with nonprotonated metal-chelate, more individualistic behaviour is observed.

It has been seen that the turbidity due to MH_2L° increases with atomic number for yttrium group systems, the same behaviour may also be followed for cerium group, La(III), Ce(III), Pr(III), Nd(III) metal-chelates which are practically soluble under the experimental conditions. The behaviour is similar to dimethyl phosphate salts of rare earth metals that fall steady in solubility from lanthanum to lutetium.

The basicities of metal-chelate species differ considerably and follow the order of atomic number like the basicities of the metal ions themselves, and may perhaps be utilized for the separation of the rare earth ions.

Equilibrium constants of rare earth-thoron complexes (30°; μ = 0.10 M).

Metal ion	Log K* for reaction (*i*)	(*ii*)	(*iii*)	(*iv*)
Y(III)	5.66	7.21	9.57	2.81
La(III)	5.30	7.89	10.75	–
Ce(III)	5.35	7.81	10.70	–
Pr(III)	5.38	7.71	10.55	–
Nd(III)	5.45	7.54	10.32	–
Sm(III)	5.51	7.44	10.20	–
Eu(III)	5.58	7.35	9.90	2.60
Gd(III)	5.59	7.30	9.74	2.70
Tb(III)	5.74	7.10	9.40	2.85
Dy(III)	5.82	6.98	9.20	2.95
Ho(III)	5.90	6.90	9.02	3.00
Er(III)	5.98	6.85	8.94	3.05
Tm(III)	6.05	6.80	8.80	3.10
Yb(III)	6.10	6.70	8.74	3.20
Lu(III)	6.17	6.60	8.54	3.26

*The error of the log K values are indicated by the standard deviation which lies between ±0.01 and ±0.03.

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