STUDIES OF RARE EARTH METAL COMPLEXES OF HYDROXAMIC ACIDS

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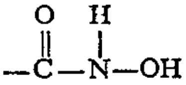
A cyclic hydroxamic acid, 2-hydroxyquinoline-N-oxide and an aromatic hydroxamic acid, benzohydroxamic acid were obtained in the form of free acids. Their acid dissociation constants and a total of seventy of the formation constants for twenty five complexes formed by these two hydroxamic acids with rare earth metals and yttrium in aqueous solution have been determined by Bjerrum potentiometric titration technique.

The titration medium was maintained at ionic strength of 0.1 *M* by sodium perchlorate and at a temperature of 25°*C*±0.1°.

In general $\log K_1 > \log K_2 > \log K_3$ for a given metal ion are observed, but the difference in the value between these three constants are not much, indicating that there is almost equal tendency for the formation of complex species.

For the trends in the series of rare earth metal complexes of these two reagents, the formation constants increase fairly regularly with decrease in ionic radius and the "gadolinium break" is also observed as usual. The trends for the elements heavier than gadolinium follows the pattern of the third group of the ligands as classified by T. Moeller *et. al.*, showing an increase with the first element beyond gadolinium and then a slight decrease toward lutetium.

A class of organic compounds containing the reactive group  $-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-OH$ and known as the hydroxamic acids has been widely studied as the useful analytical reagents recently[1~6]. In order to evaluate the usefulness and appropriate application of a chelating agent as analytical reagents, it is essential to have some physico-chemical data of reagents and their metal complexes. In spite of voluminous analytical works on hydroxamic acids, the reports of physico-chemical studies on the metal complexes of hydroxamic acids are rather limited. The data of tervalent metal complexes, especially that of rare earths are rarely found in the literature. The studies on rare earth metal complexes of some hydroxamic acids were undertaken.

Two kinds of hydroxamic acids were selected in our present investigation. The one is a cyclic hydroxamic acid, 2-hydroxyquinoline-N-oxide and the other is an aromatic hydroxamic acid, benzohydroxamic acid.

EXPERIMENTAL

A. Preparation of Reagents:

(a) Lanthanide perchlorates:

The corresponding oxides [99.9%, Fluka AG (Switzerland)] were digested in perchloric acid and the excess of perchloric acid was removed by evaporation. The solutions were diluted to

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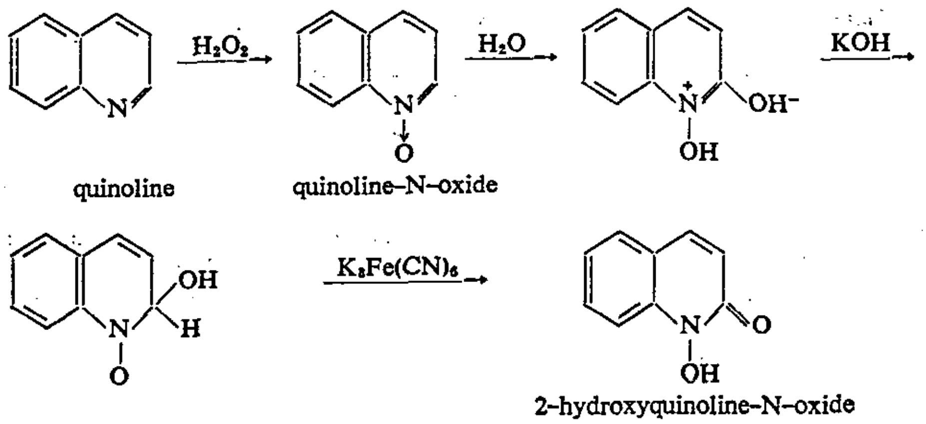
the desired concentration and were standardized by EDTA titration[6].

(b) 2-hydroxyquinoline-N-oxide:

The compound was prepared through the following steps[7]:



2-hydroxyquinoline-N-oxide was obtained as a brownish tinge scale by vacuum sublimation and recrystallization from the combining solvent of water and methanol, *m.p.* 189-190°C, which is in accordance with the literature[8].

(c) Benzohydroxamic acid (Product of Tokyo Chemical Industry Co., Ltd):

The reagent was recrystallized from ether and ethyl acetate[9].

(d) All other chemicals used in the experiment were of analytical reagent grade.

B. Instrument:

The *p*H of the solution was measured by Radiometer Titrator equipped with saturated calomel (Type K 401) and glass (Type G 200 B) electrodes, the titration curves were recorded with Raiometer Titrigraph Type SBR 2 and ABU 12 or SBU 1 and carried out in a thermostatically controlled condition at 25°C. An inert atmosphere was maintained by bubbling nitrogen through the solution during titrations.

C. Physico-chemical study of reagents and their complexes:

The Calvin-Bjerrum *p*H-titration technique as described by Rossotti[10] was employed for the determination of acid dissociation constants of chelating agents and the stability constants of metal complexes.

The following mixtures were prepared:

A: $4\times10^{-3}\,M$ $HClO_4$, $4\times10^{-3}\,M$ Reagent and $0.1\,M$ $NaClO_4$ solution
B: Mixture A$+1\times10^{-3}\,M$ Lanthanide perchlorate
C: Mixture A$+5\times10^{-4}\,M$ Lanthanide perchlorate

The appropriate mixture of the solution A, B and C were titrated with a carbonate-free standard NaOH solution and the *p*H changes were recorded against the volume of NaOH added. The titration curves are shown in Fig. 1, Fig. 2, Fig. 4, Fig. 5, Fig. 7, Fig. 8, Fig. 10, Fig. 11, Fig. 13 and Fig. 14.

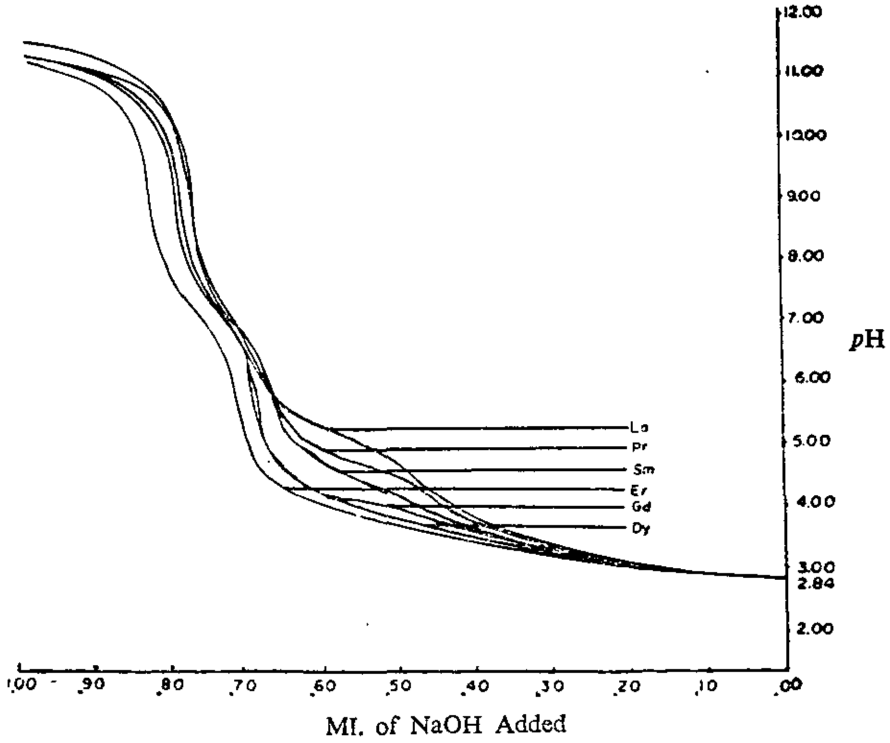


Fig. 1. Potentiometric titrations of 2-hydroxyquinoline-N-oxide with known amount of $HClO_4$ in the presence of metal ions with 0.1005 N NaOH, at $25°C\pm0.1°$, $\mu=0.1$. $T_{M^{3+}}=1\times10^{-3}M$, $T_{HL}=4\times10^{-3}M$

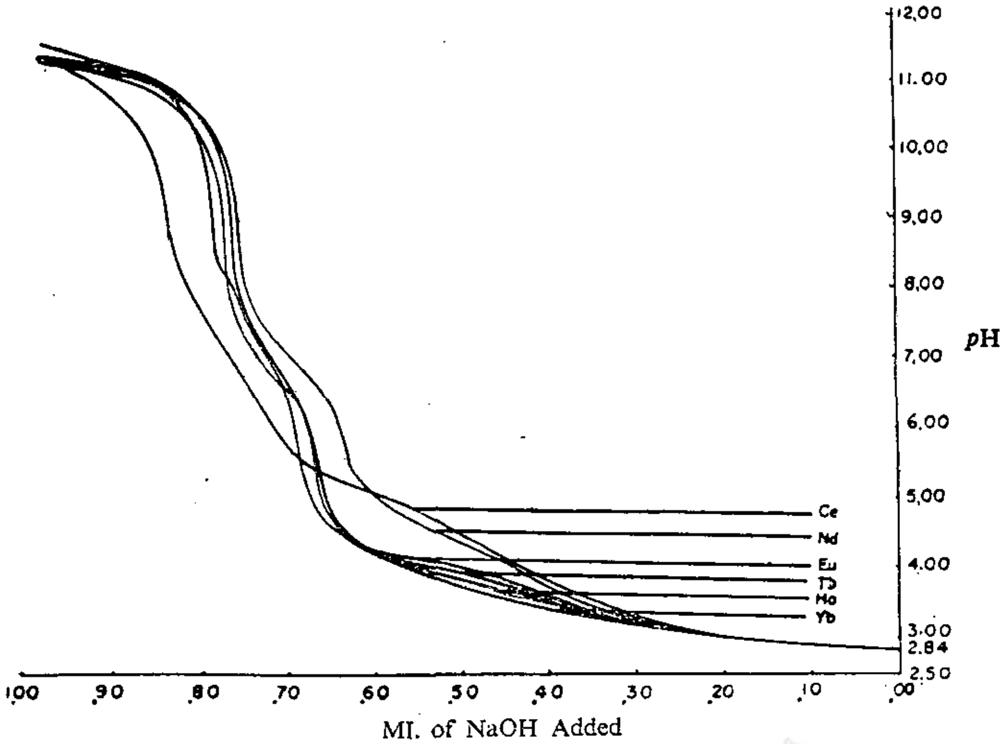


Fig. 2. Potentiometric titrations of 2-hydroxyquinoline-N-oxide with known amount of $HClO_4$ in the presence of metal ions with 0.1005 N NaOH, at $25°C\pm0.1°$, $\mu=0.1$. $T_{M^{3+}}=5\times10^{-4}M$, $T_{HL}=4\times10^{-3}M$

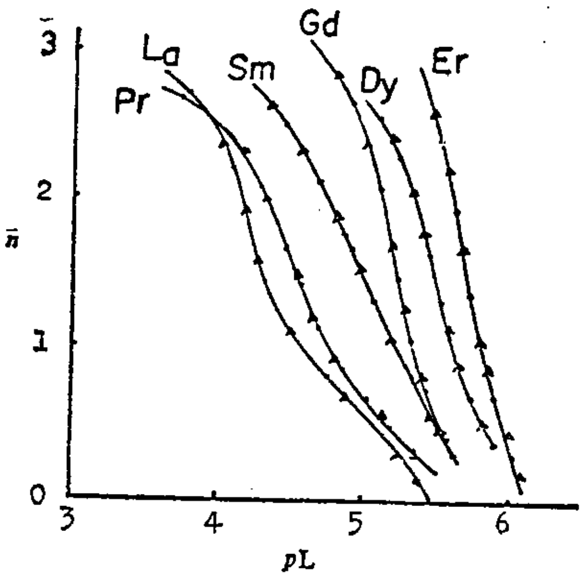


Fig. 3. Bjerrum formation curves for 2-hydroxyquinoline-N-oxide complexes with rare earth metal ions (25°C)

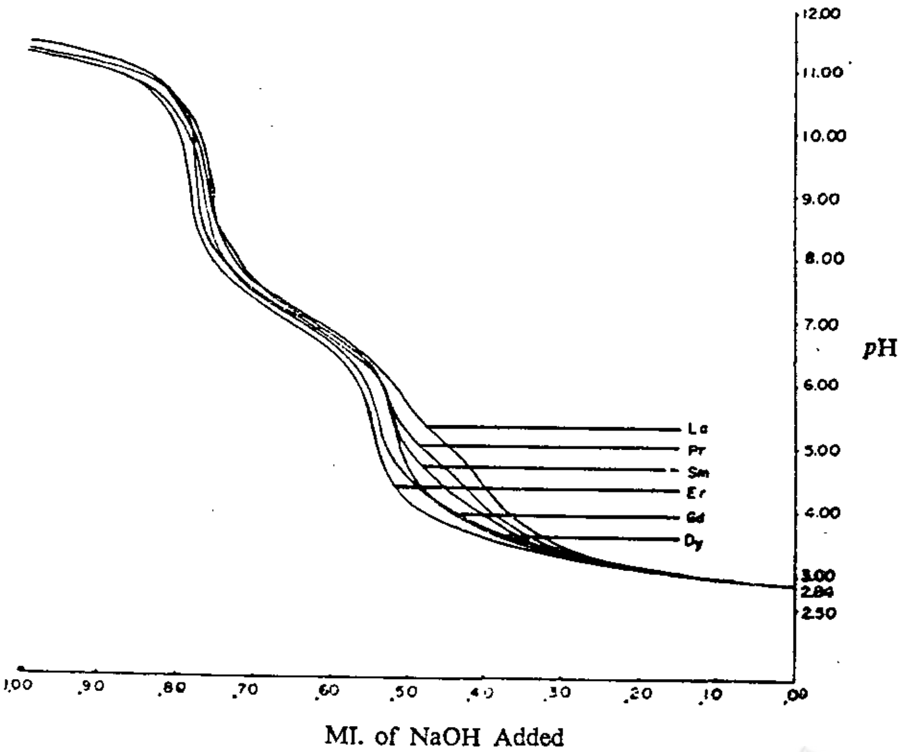


Fig. 4. Potentiometric titrations of 2-hydroxyquinoline-N-oxide with known amount of $HClO_4$ in the presence of metal ions with 0.1005 N NaOH, at 25°C±0.1°, $\mu=0.1$. $T_{M^{3+}}=1\times10^{-3}\,M$, $T_{HL}=4\times10^{-3}\,M$

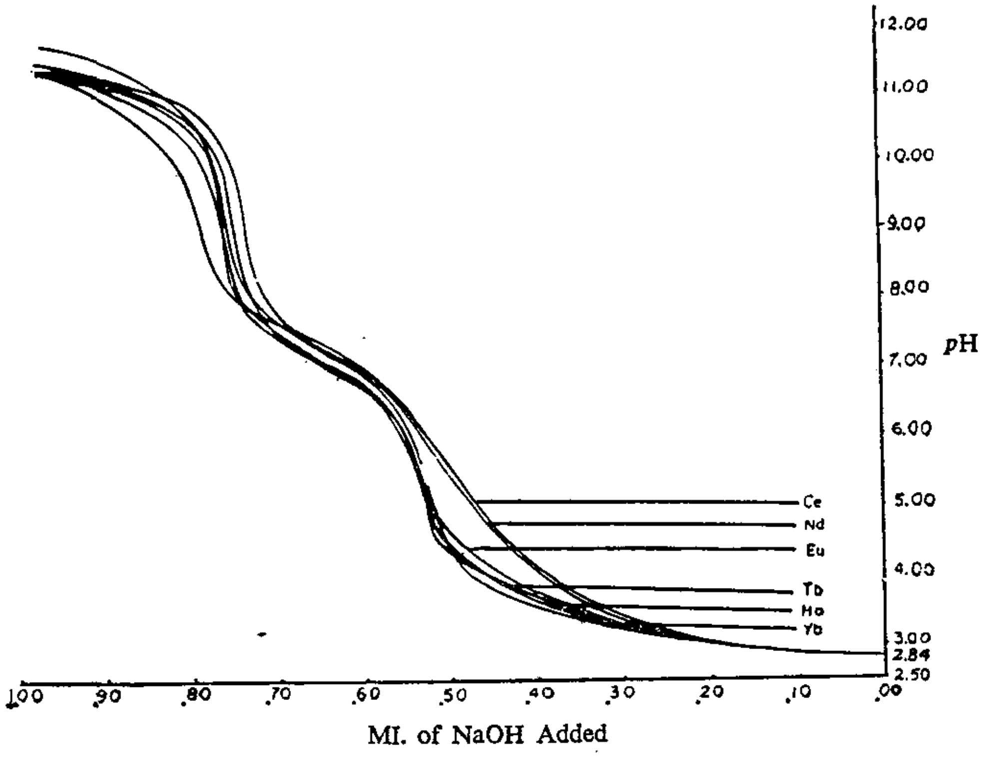


Fig. 5. Potentiometric titrations of 2-hydroxyquinoline-N-oxide with known amount of $HClO_4$ in the presence of metal ions with $0.1005\,N$ NaOH, at $25°C \pm 0.1°$, $\mu=0.1$. $T_{M^{3+}}=5\times10^{-4}\,M$, $T_{HL}=4\times10^{-3}\,M$

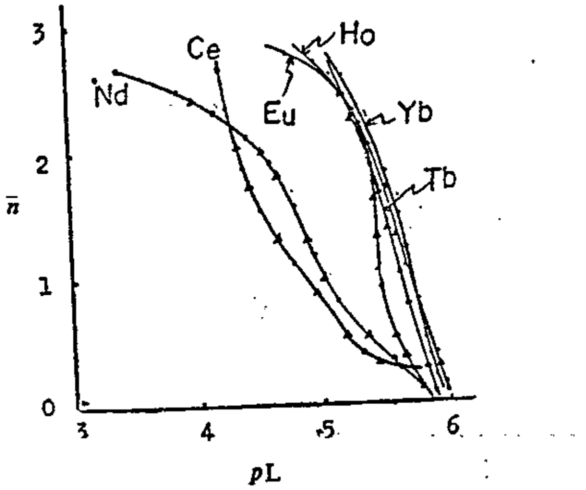


Fig. 6. Bjerrum formation curves for 2-hydroxyquinoline-N-oxide complexes with rare earth metal ions (25°C)

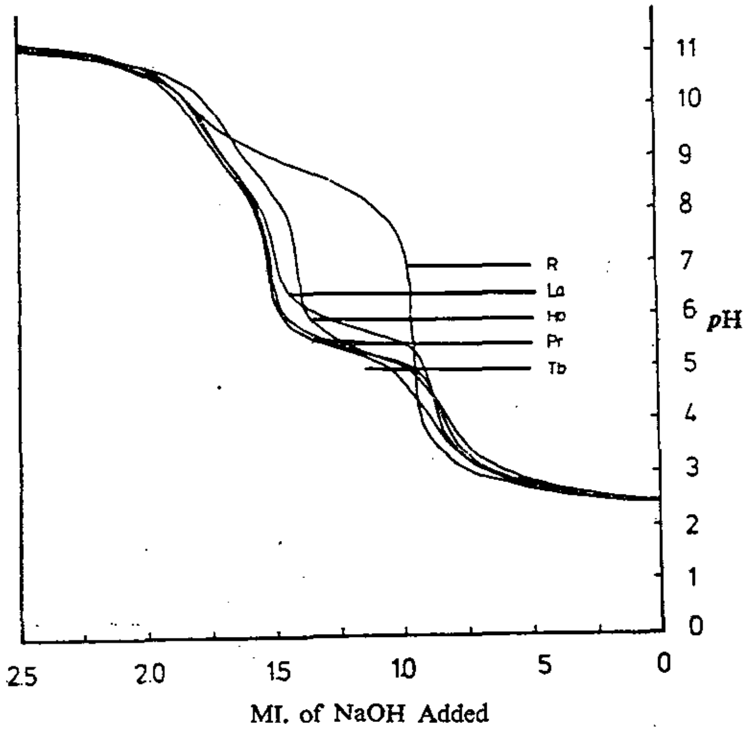


Fig. 7. Potentiometric titrations of benzohydroxamic acid with known amount of $HClO_4$ in the absence and presence of metal ions with 0.0874 N NaOH, at 25°C±0.1°, μ=0.1. $T_{M^{3+}}=1\times10^{-3}M$, $T_{HL}=4\times10^{-3}M$

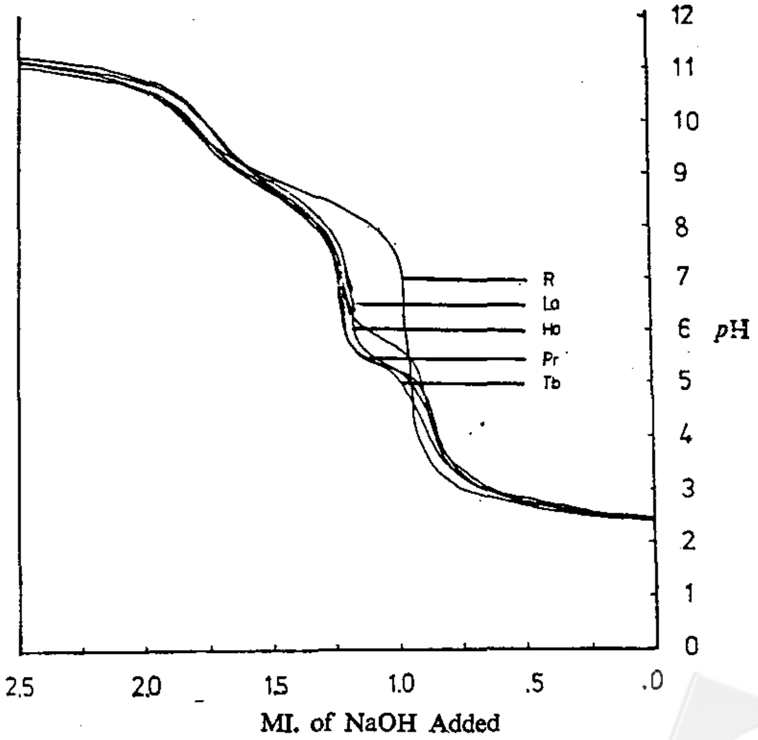


Fig. 8. Potentiometric titrations of benzohydroxamic acid with known amount of $HClO_4$ in the absence and presence of metal ions with 0.0874 N NaOH, at 25°C±0.1°, μ=0.1. $T_{M^{3+}}=5\times10^{-4}M$, $T_{HL}=4\times10^{-3}M$

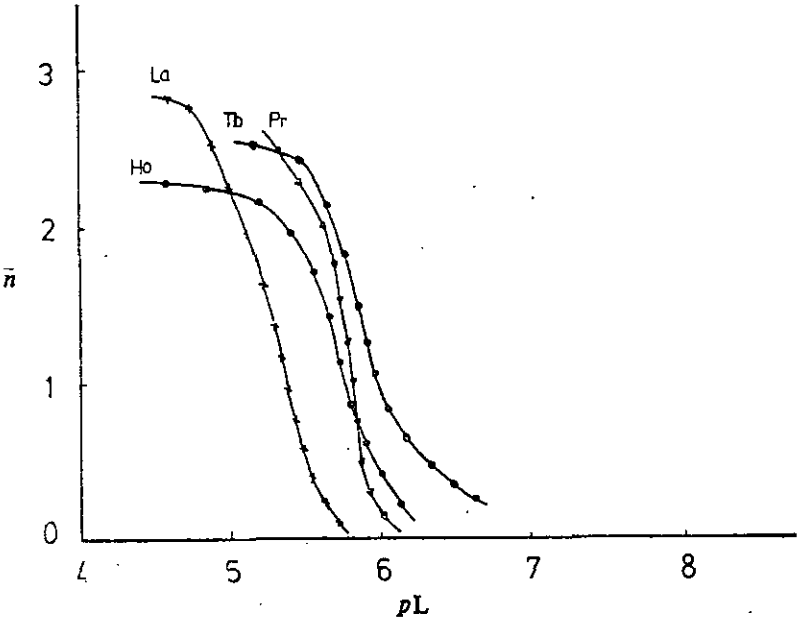


Fig. 9. Bjerrum formation curves for benzohydroxamic acid complexes with rare earth metal ions (25°C)

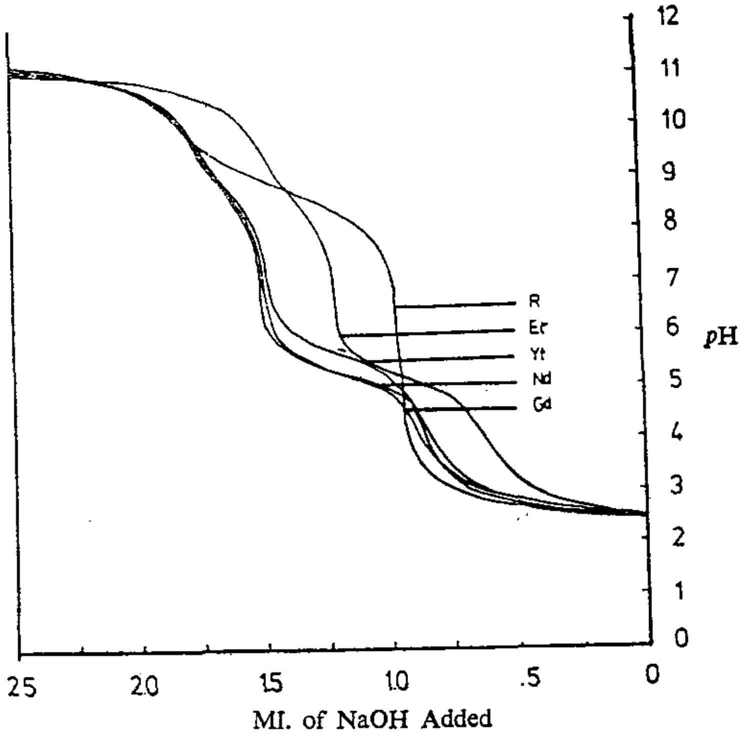


Fig. 10. Potentiometric titrations of benzohydroxamic acid with known amount of $HClO_4$ in the absence and presence of metal ions with 0.0874 N NaOH, at 25°$C\pm0.1°$, $\mu=0.1$. $T_{M^{3+}}=1\times10^{-3}\,M$, $T_{HL}=4\times10^{-3}\,M$

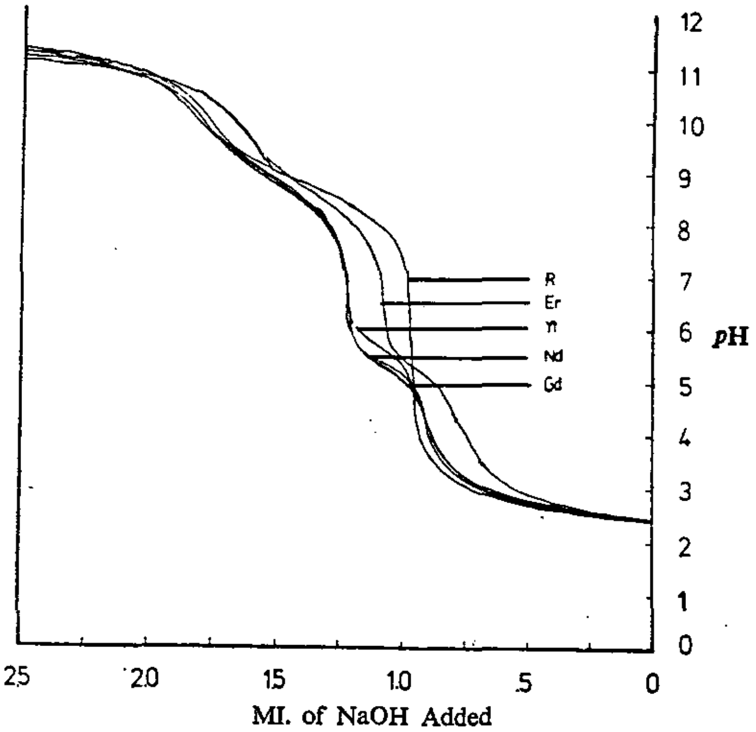


Fig. 11. Potentiometric titrations of benzohydroxamic acid with known amount of $HClO_4$ in the absence and presence of metal ions with 0.0374 *N* NaOH, at 25°*C*±0.1°, $\mu=0.1$. $T_{M^{3+}}=5\times10^{-4}\,M$, $T_{HL}=4\times10^{-3}\,M$

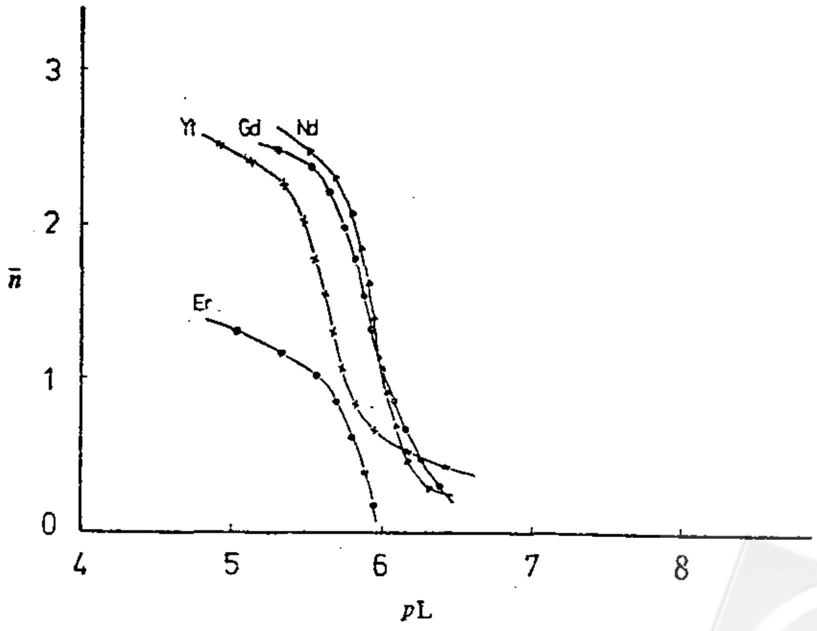


Fig. 12. Bjerrum formation curves for benzohydroxamic acid complexes with rare earth metal ions (25°*C*)

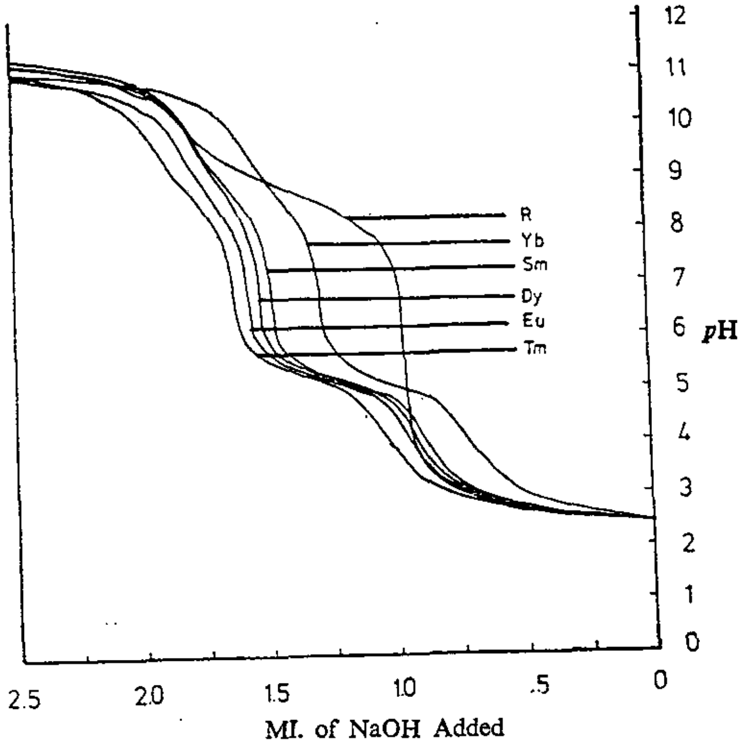


Fig. 13. Potentiometric titrations of benzohydroxamic acid with known amount of $HClO_4$ in the absence and presence of metal ions with 0.0874 N NaOH, at $25°C\pm0.1°$, $\mu=0.1$. $T_{M^{3+}}=1\times10^{-3}\,M$, $T_{HL}=4\times10^{-3}\,M$

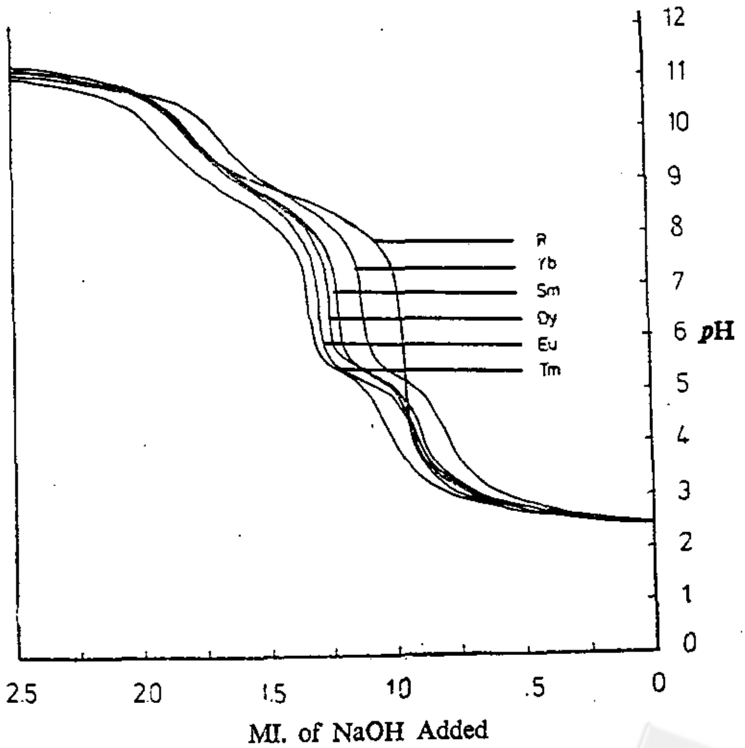


Fig. 14. Potentiometric titrations of benzohydroxamic acid with known amount of $HClO_4$ in the absence and presence of metal ions with 0.0874 N NaOH, at $25°C\pm0.1°$, $\mu=0.1$. $T_{M^{3+}}=5\times10^{-4}\,M$, $T_{HL}=4\times10^{-3}\,M$

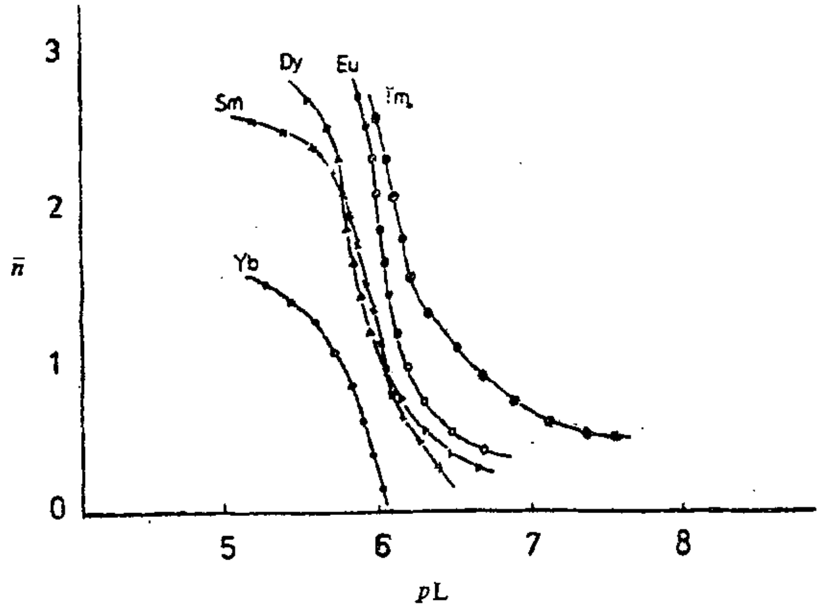


Fig. 15. Bjerrum formation curves for benzohydroxamic acid complexes with rare earth metal ions (25°C)

D. Calculations:

The values of pKa for 2-hydroxyquinoline-N-oxide and benzohydroxamic acid were calculated from the experimental points in the buffer regions of the titration curves in absence of metal ions by using the following equation.

$$Ka=\frac{[H^+]\{[H^+]+[Na^+]-[ClO_4^-]-[OH^-]\}}{T_{HL}-[H^+]-[Na^+]+[ClO_4^-]+[OH^-]}$$

Where all the terms in square brackets are concentrations in moles per liter and T_{HL} is the analytical concentration of the reagent.

It is found that the pKa of 2-hydroxyquinoline-N-oxide and benzohydroxamic acid are respectively to be 6.74 and 8.80 at 25°C and $\mu=0.1$. These values are well in accordance with the literature[9,11]. For the evaluation of stability constant of metal complexes, the method used by Calvin and Wilson[12] was modified in our calculation.

Consider the metal chelate:

$$HL \rightleftharpoons H^+ + L^-$$

$$M^{3+} + L^- \rightleftharpoons ML^{2+}$$

$$K_1=\frac{[ML^{2+}]}{[M^{3+}][L^-]}$$

$$ML^{2}+L^- \rightleftharpoons ML_2^+$$

$$K_2=\frac{[ML_2^+]}{[ML^{2+}][L^-]}$$

$$ML_2^+ + L^- \rightleftharpoons ML_3$$

$$K_3=\frac{[ML_3]}{[ML_2^+][L^-]^3}$$

$$K=k_1k_2k_3=\frac{[ML_3]}{[M^{3+}][L^-]^3}$$

In this case, the metal ions were rare earth metals and the chelating agents were 2-hydroxyquinoline-N-oxide and benzohydroxamic acid respectively, each having one replaceable hydrogen atom. The total bound chelating agent can be calculated from the following equations.

$$T_{M^{3+}}=[M^{3+}]+[ML^{2+}]+[ML_2^+]+[ML_3] \qquad (1)$$

$$T_{HL}=[HL]+[L^-]+[ML^{2+}]+2[ML_2^+]+3[ML_3] \qquad (2)$$

Since perchloric acid and metal perchlorate were added before the titration with sodium hydroxide the electroneutrality requirement is satisfied by

$$[ML_2^+]+2[ML^{2+}]+3[M^{3+}]+[Na^+]+[H^+]=[ClO_4^-]+[OH^-]+[L^-] \qquad (3)$$

Also, for the weak acid dissociation of the chelating agent,

$$Ka=\frac{[H^+][L^-]}{[HL]}$$

If [A] represents the total moles of perchloric acid per liter added at the beginning of the titration, then

$$[ClO_4^-]=[A]+3T_{M^{3+}} \qquad (5)$$

These equations were combined to give

Total amount of the bound chelating agent

$$=[ML^{2+}]+2[ML_2^+]+3[ML_3]=[Na^+]-[A]+[H^+]-[OH^-]-[L^-] \qquad (6)$$

At any experimental point on the pH titration curve all quantities on the right-hand side of equation (6) are known, since

$$[L^-]=\frac{Ka}{[H^+]}\{T_{HL}-[Na^+]+[A]-[H^+]+[OH^-]\} \qquad (7)$$

The quantity $\bar{n}$ is defined as the average number of donor groups bound per metal ion present. To find $\bar{n}$ we need only calculate the total amount of L^- which is bound to the metal ion and divide by the total amount of metal ion present. The equation for $\bar{n}$ may be written as following.

$$\bar{n}=\frac{[Na^+]+[H^+]-[OH^-]-[L^-]-[A]}{T_{M^{3+}}} \qquad (8)$$

In calculating the values for $\bar{n}$ and $[L^-]$, the concentration was corrected for changes in volume, produced by addition of alkali during titration. In this way, a series of values for $\bar{n}$ and $[L^-]$ corresponding to different values of pH at any point of the titration curve are obtained. The Bjerrum formation curves are obtained by plotting $\bar{n}$ values against pL as they are shown by Fig. 3, Fig. 5, Fig. 9, Fig. 12 and Fig. 15.

An analysis of the Bjerrum formation curves with the application of various computational methods gives the successive formation constants for metal-ligand systems. A method of successive substitution computation technique proposed by Sen[13] has been adopted for the present work.

Let us consider the case of N=3.

$$\bar{n}=\frac{T_{HL}-[L^-]}{T_{M^{3+}}}=\frac{K_1[L^-]+2K_1K_2[L^-]^2+3K_1K_2K_3[L^-]^3}{1+K_1[L^-]+K_1K_2[L^-]^2+K_1K_2K_3[L^-]^3} \tag{9}$$

By rearrangement of (9) we obtain

$$K_1=\frac{1}{[L^-]}\left\{\frac{\bar{n}}{[1-\bar{n}]+[2-\bar{n}][L^-]K_2+[3-\bar{n}][L^-]^2K_2K_3}\right\} \tag{10}$$

$$K_2=\frac{1}{[L^-]}\left\{\frac{[\bar{n}-1]+\dfrac{\bar{n}}{[L^-]K_1}}{[2-\bar{n}]+[3-\bar{n}][L^-]K_3}\right\} \tag{11}$$

$$K_3=\frac{1}{[L^-]}\left\{\frac{[\bar{n}-2]+\dfrac{[\bar{n}-1]}{[L^-]K_2}+\dfrac{\bar{n}}{[L^-]^2K_1K_2}}{3-\bar{n}}\right\} \tag{12}$$

If we now assume that $[L^-]$ is such that $\bar{n}=n-\frac{1}{2}$, there will be equal amounts of ML_{n-1} and ML_n present, and as a first approximation

$$K_n=\frac{1}{[L^-]_{\bar{n}=n-1/2}} \tag{13}$$

Therefore,

$$K_1=\frac{1}{[L^-]_{\bar{n}=n-1/2=1/2}} \tag{14}$$

$$K_2=\frac{1}{[L^-]_{\bar{n}=n-1/2=3/2}} \tag{15}$$

$$K_3=\frac{1}{[L^-]_{\bar{n}=n-1/2=5/2}} \tag{16}$$

The values of $\log K_1$, $\log K_2$ and $\log K_3$ can be directly obtained from the Bjerrum formation curve at $\bar{n}$ equal to 0.5, 1.5 and 2.5 respectively. We may now substitute the values of the temporary constants given by (14), (15), (16) into (10), (11) and (12) to obtain

$$K_1=\frac{1}{[L^-]_{\bar{n}=1/2}}\left\{\frac{1}{1+3K_2[L^-]_{\bar{n}=1/2}+5K_2K_3[L^-]^2_{\bar{n}=1/2}}\right\} \tag{17}$$

$$K_2=\frac{1}{[L^-]_{\bar{n}=3/2}}\left\{\frac{1+\dfrac{3}{K_1[L^-]_{\bar{n}=3/2}}}{1+3K_3[L^-]_{\bar{n}=3/2}}\right\} \tag{18}$$

$$K_3=\frac{1}{[L^-]_{\bar{n}=5/2}}\left\{1+\frac{3}{K_2[L^-]_{\bar{n}=5/2}}+\frac{5}{K_1K_2[L^-]^2_{\bar{n}=5/2}}\right\} \tag{19}$$

Alternatively the values of (17), (18), (19) may be resubstituted and the process continued until constant values are obtained.

The successive formation constants of the chelates of 2-hydroxyquinoline-N-oxide and benzohydroxamic acid with rare earth metal ions are summarized in Table 1 and 2.

Table 1. Stability constants (given as the logarithms) of rare earth complexes of 2-hydroxyquinoline-N-oxide determined potentiometrically at 25°*C*±0.1° and ionic strength 0.1 in water.

Metal complexes	log K_1	log K_2	log K_3	log β_3
La-2-HQNO	5.15	4.34	3.99	13.48
Ce-2-HQNO	5.25	4.63	4.28	14.16
Pr-2-HQNO	5.30	4.71	4.18	14.19
Nd-2-HQNO	5.40	4.85	3.90	14.15
Sm-2-HQNO	5.51	5.07	4.50	15.08
Eu-2-HQNO	5.64	5.42	5.20	16.26
Gd-2-HQNO	5.58	5.32	5.11	16.01
Tb-2-HQNO	5.79	5.51	5.19	16.49
Dy-2-HQNO	5.84	5.52	5.18	16.54
Ho-2-HQNO	5.85	5.58	5.17	16.60
Er-2-HQNO	5.94	5.69	5.48	17.11
Yb-2-HQNO	5.88	5.63	5.30	16.81

Table 2. Stability constants (given as the logarithms) of rare earth complexes of benzohydroxamic acid determined potentiometrically at 25°*C* ± 0.1° and ionic strength 0.1 in water.

Metal complexes	log K_1	log K_2	log K_3	log β_3
La-BHA	5.50	5.25	4.40	15.15
Pr-BHA	5.90	5.75	5.35	17.00
Nd-BHA	6.16	5.90	5.50	17.56
Sm-BHA	6.24	5.93	5.78	17.95
Eu-BHA	6.50	6.10	5.95	18.55
Gd-BHA	6.25	5.87	5.25	17.37
Tb-BHA	6.33	5.85	5.32	17.50
Dy-BHA	6.35	5.85	5.65	17.85
Ho-BHA	6.00	5.66	*	
Er-BHA	5.85	*	*	
Tm-BHA	7.35	6.24	6.01	19.60
Yb-BHA	5.94	*	*	
Y-BHA	6.13	5.61	4.95	16.69

*: Precipitation occurs.

RESULTS AND DISCUSSION

Both 2-hydroxyquinoline-N-oxide and benzohydroxamic acid are the chelating agents that form metal chelates with ligand atom of oxygen. They form fairly stable chelates with rare earth metal ions, as it has been pointed out that the rare earth metal ions co-ordinate predominantly to oxygen donors[14].

The values of the formation constants of rare earth metal chelates determined as described above are shown in Table 1 and Table 2.

The formation constants increase fairly regularly with decrease in ionic radius, with gadolinium complex being less stable than predicted from simple ionic considerations. This behavior has been called the "gadolinium break" which is widely observed for a variety of ligands[15]. In general the relation of $\log K_1 > \log K_2 > \log K_3$ is seen for a given metal ion and the difference in the values between the three constants are not much, indicating that there is almost equal tendency for the formation of complex species.

Concerning the trends in the formation constant data for rare earth metal complexes, T., Moeller *et al.* have recently reached the following conclusion[15]. For the values of $\log K_1$ for complexes of the light rare earths, lanthanum through europium, increase with the atomic number of the rare earth metal ion and of the elements heavier than gadolinium can be divided qualitatively into three types. The first group contains those ligands for which there is a regular increase in the formation constant. The ligands in the second classification form complexes of which the formation constant for the heavy rare earths have very nearly the same value from gadolinium to lutetium. The third group contains the ligands which form complexes having formation constant increasing with first element beyond gadolinium and then showing a slight decrease to lutetium. In reviewing the results obtained for the present two series of complexes, ie. the rare earth metal chelates of 2-hydroxyquinoline-N-oxide and benzohydroxamic acids, the trend in the formation constant data are found to follow the third category.

ACKNOWLEDGEMENT

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