Potentiometric Titration of Thorium and Cerium Nitrates with Glass Electrode

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The complicating effects of hydrolysis and polymerization, together with the colloidal behavior and complex properties of thorium and cerium salts in aqueous solution cause great difficulties in the analytical procedures for the separation of thorium from cerium and other rare earths, especially, in the physico-chemical study of their electrolytic properties. The present paper reports the experimental results of potentiometric titration of thorium and cerous nitrates with glass electrode. Its purpose is two-fold: first to study the complex formation of thorium with oxalate ions; second, to determine thorium and cerium in the presence of one another with sodium hydroxide solution and to find the pH range at which thorium can be separated from cerous ions. The study of the stability of thorium complexes will be reported in a subsequent paper of this series.

Experimental

A) **Experimental Procedures.**—The change in pH during the titration was followed by means of vacuum tube potentiometer constructed in our laboratory. The titration was carried out in an oil thermostat controlled to 25°C. Approximately ten-minute intervals were allowed for the attainment of equilibrium between the addition of increments of the titrant.

The point at which the solution began to become opaque was found with the aid of a beam of light conducted to the cell vertical to the line of vision of the observer. The reproducibility of these points was of the order of 0.05 pH unit for the solution of high concentration and approximately 0.1 pH unit at the stoichiometric point.

B) **Materials.** — Conductivity water with a specific conductivity of 1.6 to 2.4 10^{-6} mho was used throughout this experiment.

Thorium nitrate of C.P. grade was purified as described in the previous paper[1].

Cerium nitrate of C.P. grade was treated with hydrogen peroxide in dilute nitric acid solution to reduce any ceric to cerous ion. An acid solution was used as the stock solution in order to prevent the hydrolysis of the salt. The concentration of the stock solution prepared above was determined by the gravimetric method. The stock solution was diluted to a desired concentration with conductivity water before each run.

Carbonate-free sodium hydroxide solution was prepared by diluting a saturated solution of pure sodium hydroxide with carbon dioxide-free water, and standardized against a standard solution of constant-boiling hydrochloric acid.

Sodium oxalate and ammonium oxalate of C.P. grade were purified by recrystallization from conductivity water.

Experimental Results and Discussion

A) **Potentiometric Titration of Thorium Nitrate with Oxalates by Using Glass Electrode as an Indicator Electrode.** — Thorium nitrate is titrated potentiometrically with sodium or ammonium oxalate by using a glass electrode as an indicator electrode. Since the activity of the free oxalate, or the non-complex oxalate, $a_{C_2O_4^{2-}}$ is a function of the hydronium ion activity, a_H, the following equation is obtained:

$$a_{C_2O_4^{2-}} = \frac{K_1K_2c}{a_H^2 + \frac{K_1}{r_1}a_H + \frac{K_1K_2}{r_2}},$$

where C is the total molar concentration of the non-complex oxalate ion, K_1 and K_2 are the primary and secondary ionization constants of oxalic acid, and r_1 and r_2 are the activity coefficients of bioxalate and oxalate ions.

The fact that thorium oxalate is soluble in a solution of ammonium or sodium oxalate was first pointed out by Bahr[2] and later used by Bunsen[3] to separate thorium from the rare earths. Brauner[4], Cleve[5] and Rosenheim, Samter and Davise[6] attributed this increased solubility to the formation of a definite ammonium and sodium or potassium thoroxalate isolated in crystalline form, such as $(NH_4)_4Th(C_2O_4)_4\cdot7H_2O$, $Na_4Th(C_2O_4)_4\cdot7H_2O$ and $2Th(C_2O_4)_2(NH_4)_2C_2O_4\cdot7H_2O$, etc., from the results of solubility measurements. Britton

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1) K. Pan and T. M. Hseu, This Bulletin, 28, 162 (1955).

2) T. Bahr, *Annalen*, 132, 231 (1864).

3) R. Bunsen, *Pogg. Ann.*, 155, 375 (1875).

4) B. Brauner, *J. Chem. Soc.*, 73, 951 (1898).

5) P. T. Cleve, *Bull. soc. chem.*, 21, 116 (1874).

6) A. Rosenheim, Samter and Davisohn, *Z. anorg. Chem.*, 35, 424, (1903).

and Maurice[7] reported the complex formation of thorium oxalate from the standpoint of the phase rule. In the present investigation the existence of these complex ions in dilute aqueous solution at 25°C was confirmed by means of potentiometric titration with glass electrode. It is found that the precipitation of thorium dioxalate is completed at pH 4.3 and the precipitate is then dissolved gradually with the addition of oxalate.

The pH value increases with the addition of oxalate after one type of complex formation is completely in equilibrium with the other, and it is kept constant when another type of complex begins to be formed. The milky suspension was dissolved gradually and a clear solution was obtained when the mole ratio exceeded 6 : 1.

It is evident, therefore, that when an excess precipitant is added, and when the pH value exceeds 4.5, the precipitate of thorium oxalate will be partially redissolved. Consquently a negative error will be found in the analytical result from the standpoint of analytical chemistry.

As shown in Fig. 1, in titrating a dilute solution of thorium nitrate with sodium or ammonium oxalate solution, four inflections are found in each titration curve of the thorium-oxalate system. The first sharp inflection, corresponding to the complete precipitation of thorium oxalate which is expected to have the mole ratio of oxalate ion to thorium ion, viz., the "*R*" value in brief, of 2 is found at the *R* value of 1.9, and at pH ranging from 4.24 to 4.31 in each curve. The second, the third and the fourth inflections, which correspond to the formation of thoroxatale complexes, are found stepwisely in each curve at the approximate *R* values of 3, 4 and 6 respectively.

In Fig. 1, curves (A) and (B) indicate the potentiometric titrations of 50 ml. of 0.001 M $Th(NO_3)_4$ with 0.01 M $Na_2C_2O_4$ and with 0.01 M $(NH_4)_2C_2O_4$ in pure aqueous solutions, and curve (C) and (D) indicate the corresponding titrations in 0.5 M $NaClO_4$ solutions, respectively. The *R* value and pH observed at each point of inflection in these titration curves are summarized in Table I.

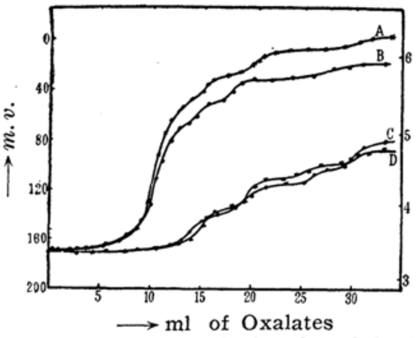

Fig. 1. Potentiometric titration of thorium nitrate with oxalates.

B) Potentiometric Titration of Thorium and Cerium Nitrates with Sodium Hydroxide Solution.—The difference between the basicities of thorium and cerium ions or between those of ceric and cerous ions has been used in the separation of the former from the latter by several investigators[8]. Britton and Maurice[9] and Bowles and Partrige[10] reported the potentiometric titration of thorium and

TABLE I

THE MOLE RATIO AND pH AT EACH MAXIMUM INFLECTION IN THE TITRATION CURVES OF THORIUM-OXALATE SYSTEM

Curve	Thorium Nitrate	Oxalate (M)		Inflect found at				
				I	II	III	IV	V
(A)	0.001 M (f=1.070) in pure water	0.01 (f=1.009) $Na_2C_2O_4$	*R* value	1.89	2.89	3.87		5.85
			pH	4.24	5.56	5.92		6.19
(B)	,,	0.01 M (f=1.003) $(NH_4)_2C_2O_4$	*R* value	1.91	2.72	3.38		5.53
			pH	4.31	5.22	5.56		5.86
(C)	0.001 M (f=1.070) in 0.5 M $NaClO_4$	0.01 M (f=1.009) $Na_2C_2O_4$	*R* value		2.89	3.68	4.91	5.66
			pH		3.76	4.14	4.39	4.66
(D)	,,	0.01 M (f=1.003) $(NH_4)_2C_2O_4$	*R* value		2.63	3.67	4.69	5.72
			pH		3.64	4.17	4.44	4.66

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[7] H. T. S. Britton and Maurice, *J. Chem. Soc.*, **1936**, 1419.

[8] Therald Moeller, George K. Schweitzer and Donald D. Star, *Chem. Rev.*, **42**, 64 (1938).

[9] H. T. S. Britton, *J. Chem. Soc.*, **127**, 2142 (1925).

[10] T. A. C. Bowles and H. M. Partridge, *Ind. Eng. Chem. Anal. Ed.*, **9**, 124 (1937).

TABLE II

POTENTIOMETRIC TITRATION OF THORIUM AND CEROUS NITRATES WITH SODIUM HYDROXIDE SOLUTION

Curve	Initial concentration $Th(NO_3)_4$ $Ce(NO_3)$ or the mixture	pH at which the solution becomes opaque	Maximum inflection occurs at pH	mole ratio
(A)	0.001 M $Th(NO_3)_4$ in aq. solution	4.34	6.71	3.69 : 1
(B)	0.001 M $Th(NO_3)_4$ in 0.5 M $NaClO_4$	4.78	6.61	3.94 : 1
(C)	0.001 M $Ce(NO_3)_3$ in 0.0005 M HNO_3	7.32	8.39	2.92 : 1
(D)	0.001 M $Ce(NO_3)_3$ in 0.0005 M HNO_3 and 0.5 M $NaClO_4$	6.51	7.73	2.97 : 1
(E)	0.001 M $Th(NO_3)_4$ and 0.001 M $Ce(NO_3)_3$ in 0.0005 M HNO_3	7.62	5.59 and 8.76	3.70 : 1 and 2.92 : 1
(F)	0.001 M $Th(NO_3)_4$ and 0.001 M $Ce(NO_3)_3$ in 0.0005 M HNO_3 and 0.5 M $NaClO_4$	5.86	5.08 and 8.22	3.60 : 1 and 2.97 : 1

some rare earth ions to find the pH at ranges at which these hydroxides began to precipitate. In the present investigation, the potentiometric titration was extended to extreme dilute solutions having the final concentration of 0.001 molar with respect to cerous or thorium ions. Furthermore, by reducing ceric to cerous ions in a dilute solution containing thorium ion and titrating the resulting solution with sodium hydroxide solution, thorium and cerous ions could be determined in the presence of each other.

On account of the complicating effects of polymerization and the colloidal adsorption of these hydrous oxides in the basic solution, the coagulation points that are in coincidence with the maximum inflections of the titration curve occur before the attainment of the stoichiometric points which have the R values of 4 for thorium and 3 for cerous hydroxide.

Inasmuch as the acid solution of cerous nitrate is used in the present investigation, the first inflection in the titration curve is attributed to the neutralization of the free acid and is subtracted from the total amount of the base added. The steep inflections are found at the R values of 3.7 and 2.9 and at pH 6.7 and 8.4 in the titration curves for thorium and cerous salts respectively. The presence of sodium perchlorate represses the complicating effects of polymerization and colloidal adsorption of these hydrous oxides and draws the R values in close proximity to the stoichiometric points at the R values of 4 and 3, respectively.

In titration of a mixture of thorium and cerous nitrates with sodium hydroxide solution, the pH value at the coagulation point of cerous hydroxide is little influenced by the presence of thorium hydroxide, but that of the latter is remarkably lowered by the presence of the former. This fact facilitates the separation of the one from the other and the determination of the one in the presence of the other. In applying the above method to the determination of thorium and cerous ions individually or in the presence of another one however, the experimental results obtained

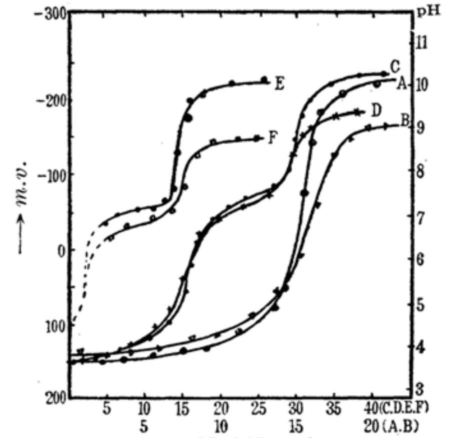

Fig. 2. Titration curves of thorium and cerous nitrates with sodium hydroxide.

from the potentiometric titration must be multiplied by experimental factors which are both greater than unity for correction, that is, 4.0/3.7 for the former and 3.0/2.9 for the latter.

Summary

1) Thorium nitrate was potentiometrically titrated with sodium and ammonium oxalates by using glass electrode as an indicator electode. Four inflections were found in the titration curves of the thorium-oxalate system. The first steep inflection, corresponding to the precipitation of thorium dioxide, was found at the mole ratio of $C_2O_4^{2-}$ to Th^{4+}, viz., the "*R*" value, 1.9 and at pH 4.3. The second the third and the fourth inflections, corresponding to the formation of thoroxalate complexes were found at the approximate *R* value of 3.4, and 6, and at pH values ranging from 5.4 to 6.3.

2) Thorium and cerium nitrates were potentiometrically titrated by sodium hydroxide in dilute solutions with glass electrode. By reducing ceric to cerous ions in a solution containing thorium ion, and by titrating the resulting solution with sodium hydroxide solution, two steps of inflection, corresponding to the precipitation of thorium and cerous hydroxides, were found respectively, in the titration curve. In applying this method to the determination of thorium and cerous ions in the presence of one another, however, the experimental results obtained from the titration curve must be multiplied by the experimental factors which are both greater than unity for accuracy.

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