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Stability of Strongly Acidic Rare Earth Oxalate Solutions

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Stability of strongly acidic rare earth (III) oxalate aqueous solutions was studied as a function of concentrations of oxalic acid, nitric acid, and rare earth (III) nitrate, $RE(NO_3)_3$, at 30 °C. Induction period, I_d, for precipitation of rare earth oxalate was given by $I_d = k_{RE}\ [HNO_3]_T^{\ 6}\ [RE(NO_3)_3]_T^{\ -2}\ [H_2C_2O_4]_T^{\ -3}$, where subscript T indicates the total concentration and k_{RE} is constant for rare earth metal ion. k_{RE} values for Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Yb, and Y were evaluated as 110, 14, 6.2, 2.5, 2.3, 4.8, 6.6, 13, 23, and 16/(10^{-6}sM), respectively. These results can be well explained by the simple precipitation theory based on solubility products of rare earth (III) oxalates.

A fine rare earth oxide powder can be obtained by thermal decomposition of the fine powder of its oxalate, which was produced by the rapid addition of aq. ammonia solution into the strongly acidic solution of rare earth nitrate and oxalic acid mixture. 1) In this process, use of a stable and clear solution (containing no precipitate) of the mixture is essential, because the presence of small amounts of the oxalate precipitate may course a rapid growth of crystals and it makes impossible to obtain the fine powder of the oxalate. Barrett et al.2) has reported that the solutions prepared by them were quite stable. However, we have often encountered the formation of the oxalate precipitates in the solutions. The induction period of the precipitation from the acidic solution was found to depend on the kinds and concentration of rare earth ions, as well as on the nitric acid and the oxalic acid concentrations. Based on these findings, the conditions to obtain the stable solution of the mixture was demonstrated.

Each rare earth nitrate solution was prepared by dissolving the oxides of Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Yb, and Y (99.9% purity), purchased from Rhone Poulence, into reagent grade conc. nitric acid (S.G. 1.38, 60%), and by heating the solution to remove an excess nitric acid. The rare earth concentrations were adjusted to 1.0 mol dm^{-3} with distilled water. The induction period, I_d, was determined at 30 °C by measuring the time at which turbidity of the oxalate precipitate begins to be visible after the mixture being prepared in a clean room (class 1000) in order to avoid contamination of dust particles, by the following procedure: The reagent solutions were quickly added with vigorous stirring in the order of oxalic acid, nitric acid, rare earth nitrate, and finally distilled water in order to adjust the total volume of the mixture to 100 cm^3 (in 200 cm^3 pyrex beaker). The addition order of the reagent solution is important to obtain good reproducibility and so, other orders gave irregular and very small values of I_d.

The relationship between the total concentration of oxalic acid, $[H_2C_2O_4]_T$ and I_d is given by $\log I_d = -3 \log [H_2C_2O_4]_T + \text{constant}$ (Fig. 1). The values of I_d become larger as the concentration of oxalic acid decreases. The relationship between the total concentration of nitric acid, $[HNO_3]_T$ and I_d is given by $\log I_d = 6 \log [HNO_3]_T + \text{constant}$ (Fig. 2). The values of I_d become larger as the concentration of nitric acid increases. These data clearly indicate the reason why Barrett et al.[2)] did not observe precipitate of rare earth oxalates in their solutions, because the rare earth and the oxalic acid concentrations were estimated to be less than 0.04 mol dm^{-3} and 0.1 mol dm^{-3}, respectively at the concentration of nitric acid being 1.5 mol dm^{-3}. For the production of the fine powder of rare earth oxide, optimum concentration of these reagents should also be determined by taking account of the cost and time to obtain the fine precipitate from the solutions by the addition of aqueous ammonia solution.

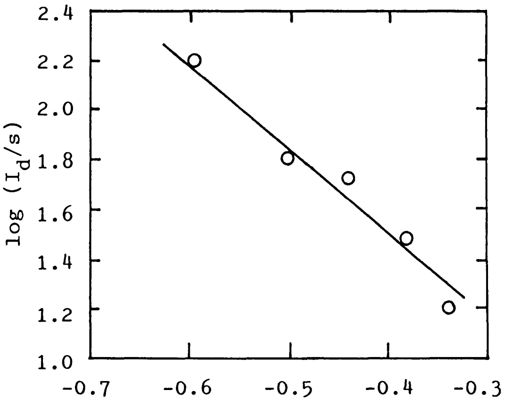

Fig. 1. Relationship between concentration of oxalic acid and I_d at $[Y(NO_3)_3]_T$ = 0.2 mol dm^{-3} and $[HNO_3]_T$ = 4.0 mol dm^{-3}.

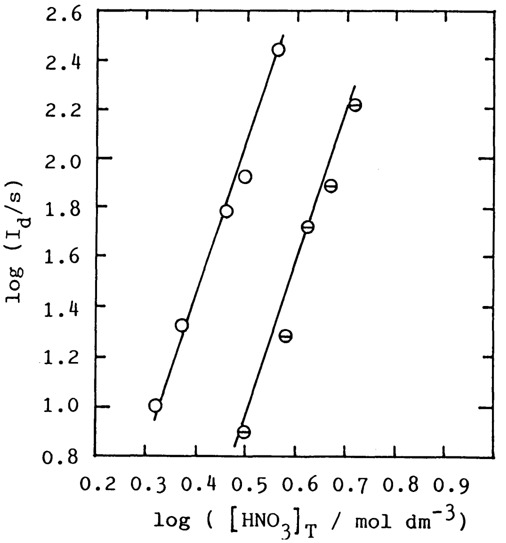

Fig. 2. Relationship between concentration of nitric acid and I_d at ○ : $[Y(NO_3)_3]_T$ = 0.1 mol dm^{-3} and $[H_2C_2O_4]_T$ = 0.175 mol dm^{-3}, and ⊖ : $[Y(NO_3)_3]_T$ = 0.2 mol dm^{-3} and $[H_2C_2O_4]_T$ = 0.35 mol dm^{-3}.

From the linear relations between the I_d and concentrations of the reagents shown in Figs. 1 and 2, an Eq. 1 can be deduced:

$$I_d = k\, [HNO_3]_T^{\,6}\, [Y(NO_3)_3]_T^{\,x}\, [H_2C_2O_4]_T^{\,-3} \qquad (1)$$

where, k is a constant and x is estimated to be about -2 from Fig. 2.

The solubility product, K_{sp} of yttrium oxalate is given by an Eq. 2.

$$K_{sp} = [Y^{3+}]^2\, [C_2O_4{}^{2-}]^3 = [Y^{3+}]^2\, K_a{}^3\, [H_2C_2O_4]^3\, [H^+]^{-6} \qquad (2)$$

where, $K_a = [H^+]^2\, [C_2O_4{}^{2-}]\, [H_2C_2O_4]^{-1} = 2.9\text{x}10^{-6}$ [6)] .

The precipitation theory tells us that when the value of the concentration product

, K', based on the total concentration of the species in the solution, is larger than that of K_{sp}, the precipitation takes place till K' reaches to that of K_{sp} (so long as the induction period of precipitation is concerned, the concentrations are well approximated by the total ones). Therefore, when K_{sp}/K' ratio ($K_{sp}/K' = K_{sp} [Y(NO_3)_3]_T^{-2} K_a^{-3} [H_2C_2O_4]_T^{-3} [HNO_3]_T^6$) is less than 1, the precipitation must occur. According to the von Weimarn's rule,[3] an initial rate of precipitation becomes higher as the ratio decreases, because the driving force of the precipitatio becomes larger. So, it is worthy of note that the concentration dependences of Eq. 1 are the same as those appeared in K_{sp}/K' ratio equation. Therefore, I_d can be deduced to be expressed as follows:

$$I_d = k' (K_{sp}/K') = k' K_{sp} K_a^{-3} [Y(NO_3)_3]_T^{-2} [H_2C_2O_4]_T^{-3} [HNO_3]_T^6 \qquad (3)$$

It can be easily deduced that x value in Eq. 1 must be -2 and k in Eq. 1 is $k' K_{sp} K_a^{-3}$ by comparing Eq. 3 and Eq. 1. The value of I_d at the constant concentrations of the term in Eq. 3 and K_{sp} for rare earth (III) ions are shown in Fig. 3.

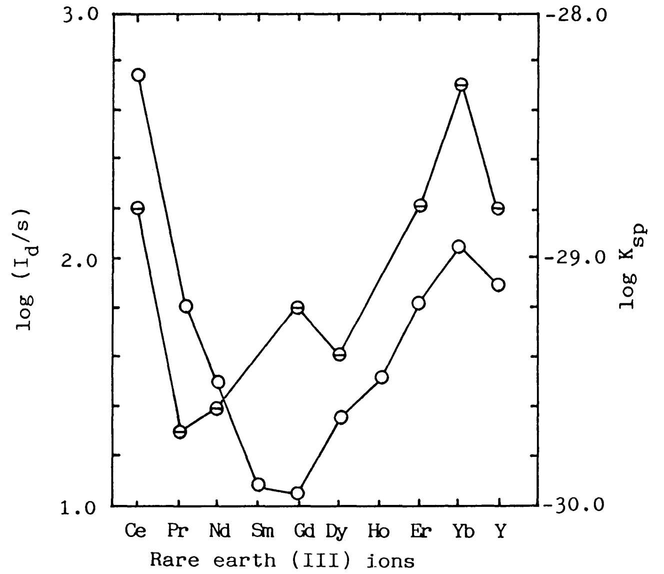

Fig. 3. I_d and K_{sp} values for rare earth (III) ions K_{sp} (⊖); after Bhat et al.[4] I_d (○); measured at $[RE(NO_3)_3]_T = 0.2$ mol dm^{-3}, $[HNO_3]_T = 4.5$ mol dm^{-3}, $[H_2C_2O_4]_T = 0.35$ mol dm^{-3}.

The relationship between the I_d values and rare earth (III) ions is similar to that between their K_{sp} values and them except for gadolinium (III). This fact is easily understood based on Eq. 3, if the change in k' values for each rare earth ion are small under the given conditions. The values of k_{RE}, shown in Table 1, corresponding to k in Eq. 1, for rare earth (III) ions were obtained by the use of Eq. 1 and the data of I_d shown in Fig. 3. Then, in order to confirm the relation between k and K_{sp} in the Eq. 1 and Eq. 3, respectively, the plots of log k_{RE} vs. log K_{sp} is shown in Fig. 4. It is given by $k_{RE} = k'' K_{sp}^{1.0}$ where k'' is a proportional constant, and by the two lines corresponding to two groups, that is, so-called, light rare earths and middle heavy ones. So, the Eq. 3 is valid for all of rare earth (III) ions and k'_{RE} values corresponding to k' in the Eq. 3 for rare earth (III) ions were estimated by the use of K_a[6] as shown in Table 1. The values of k'_{RE} being almost constant for light rare earths are different from those for middle heavy ones.

For the induction period, Kubo et al.[5] proposed the equation of $I_d S_0^n$ = constant where S_0 is concentration of supersaturation and n is a material constant.

Table 1. k_{RE} and k'_{RE} values for rare earth (III) ions

Rare earth (III)	Ce	Pr	Nd	Sm	Gd	Dy	Ho	Er	Yb	Y
$k_{RE}/(10^{-6}s/mol\ dm^{-3})$	110	14	6.2	2.5	2.3	4.8	6.6	13	23	16
$k'_{RE}/(10^{8}s)$	2.0	2.0	0.7	-	-	0.3	-	0.2	0.1	0.3

Our new equation (Eq. 3) is derived from K_{sp}/K' ratio concept which can be understood based on the simple precipitation theory. Furthermore, it can be easily used as a function of total concentration terms of the precipitate components.

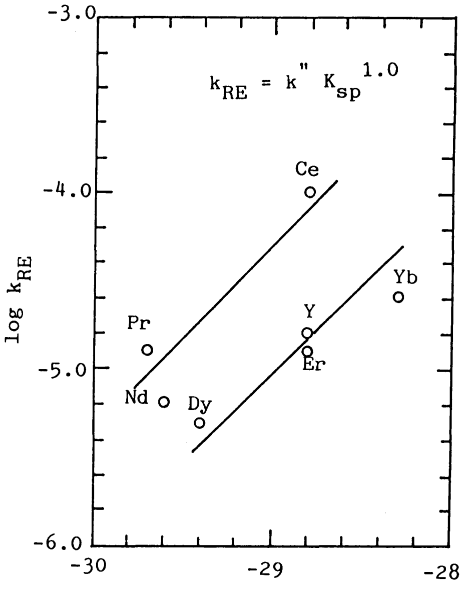

Fig. 4. Relationship between k_{RE} and K_{sp} for rare earth (III) ions.

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