Dissolution and Anion Exchange Behavior of the Rare Earth Elements in Potassium and Ammonium Carbonate Solutions

By Tomitsugu TAKETATSU

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It has been reported by several investigators[1-4] that tracer amounts of thorium and yttrium, as well as macro amounts of uranium(VI), thorium, cerium(IV) and beryllium, are firmly adsorbed on an anion exchange resin in a carbonate solution. No systematic studies of the dissolution of rare earth carbonates and of the anion exchange behavior of macro amounts of rare earth ions dissolved in a carbonate solution have yet been reported. In the present paper, however, the relation between the amounts of rare earth elements dissolved and the concentration of potassium or ammonium carbonate will be studied. Moreover, the minimum concentration of potassium or ammonium carbonate necessary to dissolve the precipitate of the rare earth carbonate completely will be determined, and the distribution coefficients (K_d) of rare earth ions between an anion exchange resin and a potassium or ammonium carbonate solution more concentrated than the minimum will be measured. The state of the dissolution and the anion exchange behavior of the rare earth elements will be discussed using these results.

Experimental

Standard solutions of rare earth elements were prepared by dissolving the oxides of the elements in dilute hydrochloric acid, while the concentrations of the rare earth ions were determined volumetrically with ethylenediaminetetraacetic acid (EDTA) by using Xylenol Orange as the indicator.

As the anion exchange resin, Dowex 1, X-8 in carbonate form, of a 50~100 mesh, was used.

All the other chemicals used were of analytical reagent grade.

The measurements of the amounts of rare earth elements dissolved and of the distribution coefficients K_d, of rare earth ions between an anion exchange resin and a potassium or ammonium carbonate solution were carried out as follows:

A known amount of the rare earth solution was put into a glass-stoppered conical flask, and the solution was dried on a water bath to remove any excess hydrochloric acid. One hundred milliliters of a series of potassium carbonate solutions of various concentrations was added to the residue in the flask. The precipitate of basic rare earth carbonate was thereby formed. The flask was vigorously shaken by a mechanical shaker for an hour and left to stand overnight to dissolve the precipitate.

(A) When the precipitate was not dissolved completely, it was filtered with No. 5C Toyo filter paper. The precipitate on the filter paper was dissolved in dilute hydrochloric acid, and the solution was poured into a beaker. The rare earth ion in the solution was titrated with EDTA.

(B) When the precipitate was dissolved completely, one gram of the resin was added to the carbonate solution. After the solution had been shaken by a shaker for 3 to 4 hr., the resin was rapidly separated by suction from the solution with a glass filter and transferred into a column. The rare earth element adsorbed on the resin was eluted by dilute hydrochloric acid. Although at the beginning of the elution the resin bed was disturbed by the release of carbon dioxide, it gradually settled down and was packed in the column. This disturbance did not affect the elution, since only the rare earth ion was adsorbed on the resin. The amount of rare earth ion was determined by a method similar to that described above.

All the procedures in the case of ammonium carbonate solution were similar to those used for the potassium carbonate solution, except that, because of the instability of ammonium carbonate, a magnetic stirrer was used instead of a shaker to stir the solution.

All the experiments were carried out at room temperature, which was about 20°C.

Results and Discussion

The quantities of rare earth ions used in this experiment, as well as the quantities of thorium and uranyl ions used for comparison are shown in Table I.

Relation between the Concentration of Potassium or Ammonium Carbonate Added and the Amount of Rare Earth Carbonate Dissolved.—When an excessive amount of a potassium or ammonium carbonate solution was added to the rare earth chloride, the basic rare earth carbonate was precipitated; the precipitate was then dissolved partially or completely by shaking or stirring. The plots of the amounts of the rare earth ions dissolved against various concentrations of potassium and ammonium carbonate are shown in Figs. 1 and 2. The

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[1] T. Ishimori and H. Okuno, This Bulletin, **29**, 78 (1956).
[2] N. Saito and T. Sekine, ibid., **30**, 561 (1957).
[3] S. Misumi and T. Taketatsu, ibid., **32**, 877 (1959).
[4] N. Saito and T. Sekine, *Nature*, **180**, 753 (1957).

molar concentration of ammonium carbonate is represented by the molecular formula of $NH_4CO_2NH_2 \cdot NH_4HCO_3$, but the concentration is not accurate owing to the instability of ammonium carbonate.

From these results, it can be seen that the amounts of rare earth elements dissolved increase with the increase in the concentration of carbonate, and also with the increase in atomic number, except for cerium, yttrium and scandium. For example, the precipitates of praseodymium, neodymium, samarium, gadolinium, erbium, yttrium and scandium carbonates are dissolved completely in potassium carbonate solutions more concentrated than about 0.55, 0.45, 0.35, 0.30, 0.25, 0.15 and 0.10 M respectively. The precipitate of lanthanum carbonate could not be dissolved completely even in 1.0 M. As cerium is oxidized to the tetrapositive state in a potassium or ammonium carbonate solution, its behavior differs from that of other rare earth elements. In an ammonium carbonate solution more cnocentrated than 0.2 M, cerium is able to exist as stable orange-yellowish solution; on the other hand, in a potassium carbonate solution more concentrated than 0.4 M, it is dissolved completely

TABLE I. QUANTITIES OF RARE EARTH, THORIUM AND URANYL IONS USED

Ions	Taken mg.	Concn. 10^{-4} mol./l.
La^{3+}	7.452	5.363
Ce^{3+}	7.546	5.385
Pr^{3+}	7.169	5.087
Nd^{3+}	7.056	4.891
Sm^{3+}	7.214	4.798
Gd^{3+}	7.772	4.942
Er^{3+}	10.424	6.232
Y^{3+}	4.208	4.732
Sc^{3+}	1.595	3.537
Th^{4+}	14.802	6.377
UO_2^{2+}	18.145	6.703

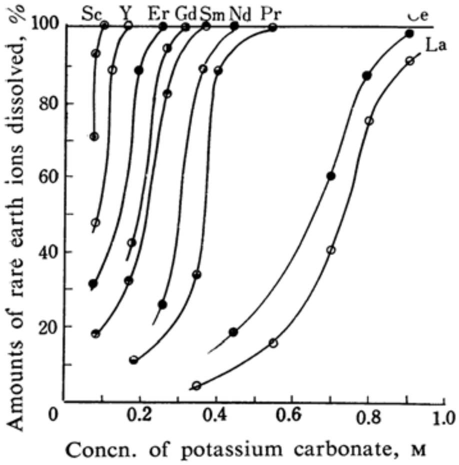

Fig. 1. Relation between the concentration of potassium carbonate and the amounts of rare earth ions dissolved.

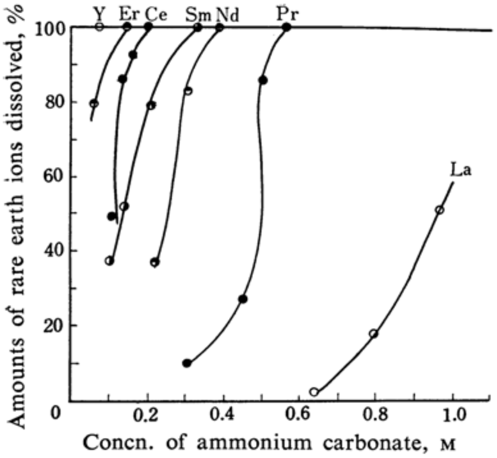

Fig. 2. Relation between the concentration of ammonium carbonate and the amounts of rare earth ions dissolved.

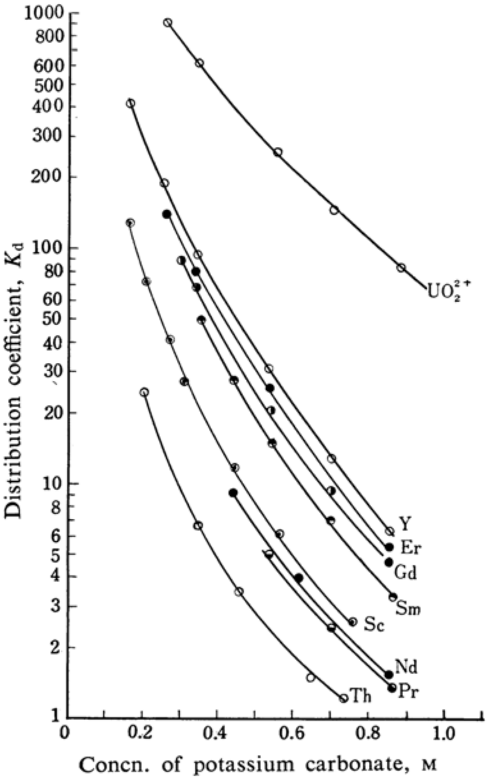

Fig.3. Distribution coefficient of rare earth and uranyl and thorium ions between Dowex 1 and potassium carbonate solution.

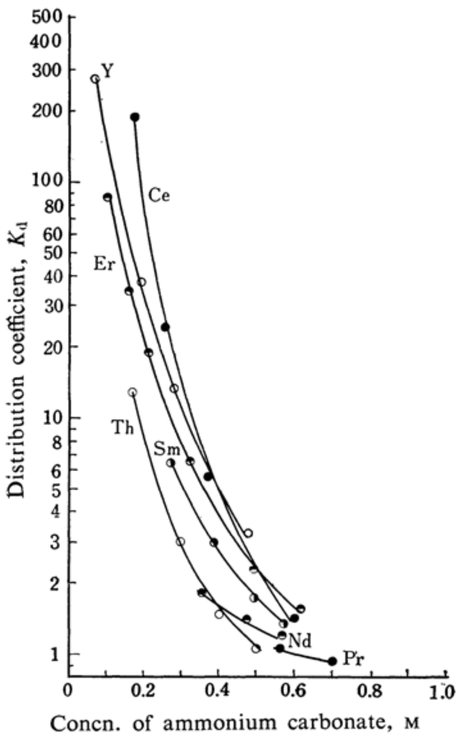

Fig. 4. Distribution coefficient of rare earth ions between Dowex 1 and ammonium carbonate solution.

at first, although the precipitate of the carbonate is formed again when the solution is left over night.

Relation between the Adsorbabilities of the Rare Earth Elements and the Concentrations of Potassium and Ammonium Carbonate. — When the precipitates of rare earth carbonates were dissolved completely by the procedure described above, the anion exchange behavior of these elements was studied. The distribution coefficient, K_d, is given by:

$$K_\mathrm{d}=[\mathrm{M_r}]/[\mathrm{M_s}] \qquad (\mathrm{ml./g.})$$

where $\mathrm{M_r}$ and $\mathrm{M_s}$ represent the amount of rare earth ion in 1 g. of the resin and in 1 ml. of the solution respectively.

The plots of the distribution coefficients, K_d, of rare earth ions against various concentrations of potassium and ammonium carbonates are shown in Figs. 3 and 4. It can be seen that the adsorbability of rare earth elements decreases as the concentration of potassium or ammonium carbonate increases and that the order of the K_d values is Y > Er > Gd > Sm > Sc > Nd > Pr in a potassium carbonate solution. In an ammonium carbonate solution, the K_d value of tetrapositive cerium is larger than that of samarium and the slope of tetrapositive cerium is more similar to that of thorium than to the slopes of other rare earth elements. For purposes of comparison, the K_d values for uranyl and thorium ions in a potassium carbonate solution obtained by the same procedure as that for rare earth ion are shown in Fig. 3. From the distinct difference in the values of K_d, it is expected that the rare earth elements can be effectively separated from uranium(VI) and thorium(IV) by an anion exchange resin, with the potassium carbonate solution as the eluting agent.

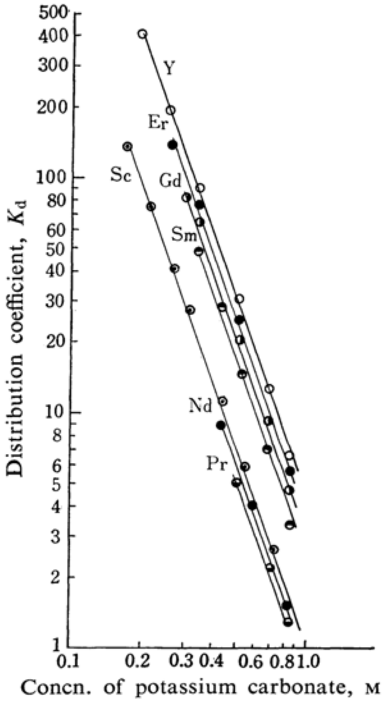

Fig. 5. Distribution coefficient of rare earth ions between Dowex 1 and potassium carbonate solution.

A logarithmic diagram of the K_d values of rare earth ions against the concentrations of potassium carbonate is given in Fig. 5. Since the slope of the curve $\log K_\mathrm{d}$ vs. $\log (\mathrm{CO_3}^{2-})$ shows linearity and since the lines are parallel to one another with a negative slope, it has been concluded, according to a method developed by Kraus et al.5) for determining the composition of metal complex species using an anion exchange resin, that the rare earth ions dissolved in a carbonate solution have an identical negative charge.

Summary

The amounts of rare earth elements dissolved in potassium and ammonium carbonate solutions of various concentrations have been

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5) K. A. Kraus and F. Nelson, "Anion Exchange Studies of the Fission Products" in "Peaceful Uses of Atomic Energy", Proceedings of the International Conference in Geneva (United Nations) Vol. VII, (1955), p. 113.

determined. These amounts increase with the increase in the concentration of the carbonate and also with the increase in atomic number, except for cerium, yttrium and scandium. When the precipitates of the rare earth elements were completely dissolved in carbonate solutions more concentrated than a certain known concentration, the distribution coefficients, K_d, of the rare earth carbonate ions between an anion exchange resin of a carbonate form and potassium or ammonium carbonate solutions of various concentrations were determined. The values of K_d increased both with the decrease in the concentration of carbonate ions and with the increasing atomic number of the rare earth elements. Since the slopes of the curve $\log K_d$ vs. $\log(CO_3^{2-})$ in a potassium carbonate solution are found to be almost the same value for all the rare earth elements investigated, it has been concluded that the soluble complex of rare earth elements possesses an identical negative charge.

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General Education Department
Kyushu University
Otsubo-machi, Fukuoka