The Dissolution and Anion Exchange Behavior of Rare Earth and Other Metallic Elements in Potassium Bicarbonate, Potassium Carbonate and Ammonium Carbonate Solutions

By Tomitsugu TAKETATSU

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In a previous paper[1] the present author reported that rare earth ions dissolved in potassium and ammonium carbonate solutions were adsorbed on an anion exchange resin and that the amounts both dissolved and adsorbed increase with the increase in atomic number, except for cerium and yttrium.

In this paper, the state of the dissolution and anion exchange behavior of rare earth ions in a potassium bicarbonate solution, as well as that of other metallic ions (thorim, zirconium, aluminum, gallium, indium, uranyl, beryllium, zinc, cadmium, copper, nickel, cobalt and lead ions) in potassium bicarbonate, potassium carbonate and ammonium carbonate solutions, will be studied. By using the results, the application for analytical separations will be discussed.

Experimental

Standard solutions of the metallic ions investigated were prepared by dissolving the reagent grade oxides (lanthanum, prasodymium, neodymium, samarium, gadolinium, dysprosium, erbium, yttrium and gallium), the chlorides (indium, zinc, cadmium, copper, nickel and cobalt) and the nitrates (zirconium, thorium, aluminum, cerium(III), beryllium and uranium(VI)) in dilute chloric or nitric acid. The concentrations of these ions, except for beryllium, were volumetrically determined with EDTA by using xylenol orange (XO), pyrocatechol violet (PV), eriochrome black T (EBT), PAN and murexide (MX) as indicators[2]. The concentration of beryllium was determined gravimetrically as the oxide.

As the anion exchange resins, Dowex 1, X-8 in carbonate and bicarbonate forms, of 50∼100 mesh, were used.

All the other chemicals used were of a analytical reagent grade.

The measurement of the amounts of metallic ions dissolved in potassium bicarbonate, potassium carbonate and ammonium carbonate solutions, and of the distribution coefficient, K_d, of the metallic ions between an anion exchange resin and their solutions were carried out by a previously reported procedure[1]. All the experiments were

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[1] T. Taketatsu, This Bulletin, 35, 1573 (1962).

[2] K. Ueno, "Chelate Titration", Nankodo, Tokyo (1960), pp. 205-330.

carried out at room temperature, which was about 20°C.

Results and Discussion

The determination methods and the quantities of metallic ions used in this experiments are shown in Table I.

The Relation between the Concentration of Potassium Bicarbonate Added and the Amount of Rare Earth Bicarbonate Dissolved. — When an excessive amount of potassium bicarbonate in a solution was added to the rare earth chloride or nitrate, first the rare earth bicarbonate was precipitated, and then the precipitate was dissolved partially or completely by shaking. Figure 1 plots the amounts of the rare earth ions dissolved against various concentrations of potassium bicarbonate. It can be seen that the amounts of rare earth ions dissolved increase with the increase in the concentration of bicarbonate, and also with the increase in atomic number, except for cerium and yttrium. Since cerium is partially oxidized to the tetrapositive state in the bicarbonate solution, its behavior differs from that of other rare earth elements. This finding is similar to that

TABLE I. THE DETERMINATION METHODS AND THE QUANTITIES OF METALLIC IONS USED

Ion	Titration method	Indicator	pH	Taken mg.	Concn. 10^{-4} mol./l.
Th^{4+}	Direct	XO	2.5∼3.5	14.797	6.377
Zr^{4+}	Indirect (Bi^{3+})	XO	1 ∼2	4.392	4.815
La^{3+}	Direct	XO	4.5∼6	7.452	5.363
Ce^{3+}	Direct	XO	4.5∼6	7.546	5.385
Pr^{3+}	Direct	XO	4.5∼6	7.169	5.087
Nd^{3+}	Direct	XO	4.5∼6	7.056	4.891
Sm^{3+}	Direct	XO	4.5∼6	7.214	4.798
Gd^{3+}	Direct	XO	4.5∼6	7.772	4.942
Dy^{3+}	Direct	XO	4.5∼6	5.495	3.382
Er^{3+}	Direct	XO	4.5∼6	10.424	6.232
Y^{3+}	Direct	XO	4.5∼6	4.208	4.732
Ga^{3+}	Direct	PV	3.8	2.014	2.889
In^{3+}	Direct	XO	3 ∼4.5	6.814	5.933
Al^{3+}	Indirect (Zn^{2+})	XO	5 ∼6	1.854	6.870
Zn^{2+}	Direct	EBT	10	3.387	5.182
Cd^{2+}	Direct	EBT	10	6.854	6.098
Cu^{2+}	Direct	MX	8	3.241	5.101
Ni^{2+}	Direct	MX	10	2.891	4.924
Co^{2+}	Direct	XO	5 ∼6	3.092	5.246
Pb^{2+}	Direct	XO	5	11.039	5.328
UO_2^{2+}	Direct	PAN	4	18.145	6.703
Be^{2+}	Gravimetry			3.21	3.56 10^{-3}

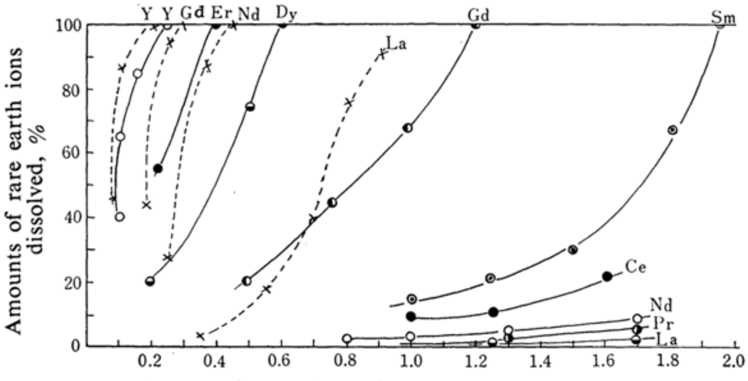

Fig. 1. Relation between the concentration of potassium bicarbonate or carbonate and the amounts of rare earth ions dissolved.

-○- Potassium bicarbonate -×- Potassium carbonate obtained by using potassium carbonate. However, the precipitates of the light lanthanons (lanthanum, praseodymium and neodymium) can scarcely be dissolved, even in 1.8 M. On the other hand, the heavy lanthanons (dysprosium, erbium and yttrium) can easily be dissolved in a bicarbonate solution of even lower concentrations. For example, the precipitates of samarium, gadolinum, dysprosium, erbium and yttrium bicarbonates are dissolved completely in a bicarbonate solution more concentrated than about 1.95, 1.20, 0.60, 0.40 and 0.25 M respectively. For comparison, the results for several rare earth ions obtained by using potassium carbonate are also plotted in Fig. 1. The variation in the amounts of rare earth ions dissolved in a potassium bicarbonate solution of a certain concentration is more remarkable than in a potassium carbonate solution. Therefore, it is expected that the separation of rare earth elements from each other can be carried out by a fractional separation using the distinct difference.

The Relation between the Adsorbabilities of the Rare Earth Ions and the Concentration of Potassium Bicarbonate.—When the precipitates of rare earth ions were dissolved completely, the anion exchange behavior of these rare earth ions was studied by the batch operation. The distribution coefficient, K_d, is given by

$$K_d = [M_r] / [M_s] \quad (\text{ml./g.})$$

where M_r and M_s are the amount of rare earth ions in one gram of the resin and in one milliliter of the solution respectively. The plot of the distribution coefficient of rare earth ions against various concentrations of potassium bicarbonate is shown in Fig. 2. It can there be seen that the adsorbability of rare earth ions decreases as the concentration of the potassium bicarbonate increases and that the order of the K_d values is yttrium> erbium>dysprosium. However, the differences in these values are very small. Although gadolinium and samarium are dissolved completely in the bicarbonate solution, these ions can only with difficulty be adsorbed on the resin because of the high concentration of the bicarbonate.

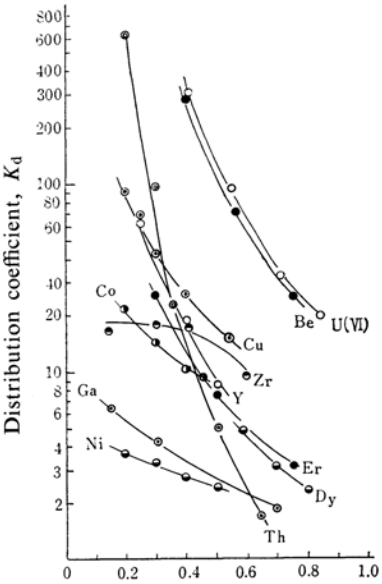

Fig. 2. Distribution coefficient of rare earth and other metallic ions between Dowex 1 and potassium bicarbonate solution.

When the logarithmic diagram of the K_d value of the rare earth ions against the concentrations of potassium bicarbonate is plotted, the slope of the log K_d vs. log(HCO_3^-) curve shows linearity and the lines are parallel to one another with a negative slope. Therefore, it may be concluded, according to a method developed by Kraus et al.[3], that each rare earth ion dissolved in a bicarbonate solution is in a state of identical negative charge.

The Dissolution and Anion Exchange Behavior of the Various Metallic Ions in a Potassium Bicarbonate Solution. — The relation between the amounts of the various metallic ions dissolved and the concentration of potassium bicarbonate was investigated. The results are shown in Fig. 3. The precipitates of thorium, zirconium, gallium and uranyl ions were dissolved at once, while those of beryllium, copper, nickel and cobalt ions were dissolved gradually in those bicarbonate solutions more concentrated than about 0.2 M.

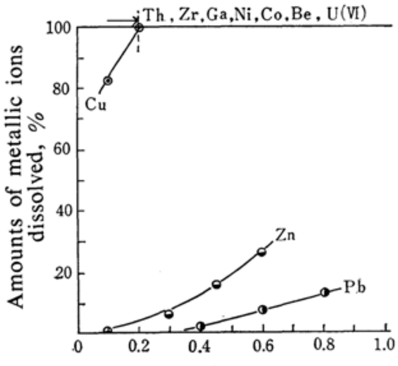

Fig. 3. Relation between the concentration of potassium bicarbonate and the amounts of various metallic ions dissolved.

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

However, the precipitates of lead, zinc and indium could not be dissolved completely, even in 1.0 M.

The plot of the K_d values of the metallic ions dissolved completely in the bicarbonate solution against the concentration of potassium bicarbonate is given in Fig. 2. The K_d values of these metallic ions decrease with the increase in the concentration of potassium bicarbonate. Uranyl and beryllium ions are adsorbed firmly on an anion exchange resin, while copper and cobalt ions are adsorbed less firmly. On the other hand, gallium and nickel ions are adsorbed weakly. The K_d value of zirconium ions is different at different time intervals in the measurement, and so it is difficult to obtain a constant value. This fact is also found in the case of using a potassium carbonate solution, as is described below. It seems that this behavior is a result of the complicated state of the soluble zirconium ion. From the distinct differences in the K_d values, it is expected that uranyl and beryllium ions can be effectively separated from other metallic ions, as well as can copper ions from cobalt and nickel ions, by an anion exchange resin, with the potassium bicarbonate solution as the eluting agent.

The Dissolution and Anion Exchange Behavior of the Various Metallic Ions in a Potassium Carbonate Solution.—The plot of the amounts of the various metallic ions dissolved against the concentration of potassium carbonate is in Fig. 4. It can be seen that uranyl, thorium, zirconium and aluminum ions are dissolved completely in a potassium carbonate solution more concentrated than about 0.2 M, while beryllium, zinc, copper and indium ions can not be dissolved completely, even in 1.0 M.

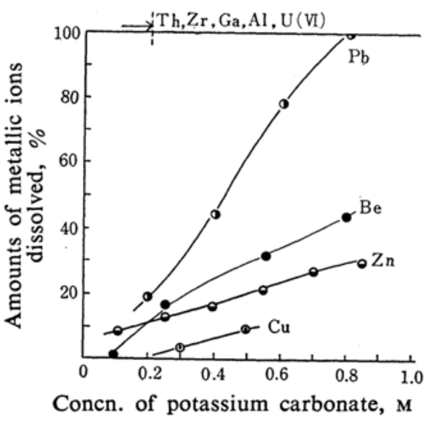

Fig. 4. Relation between the concentration of potassium carbonate and the amounts of various metallic ions dissolved.

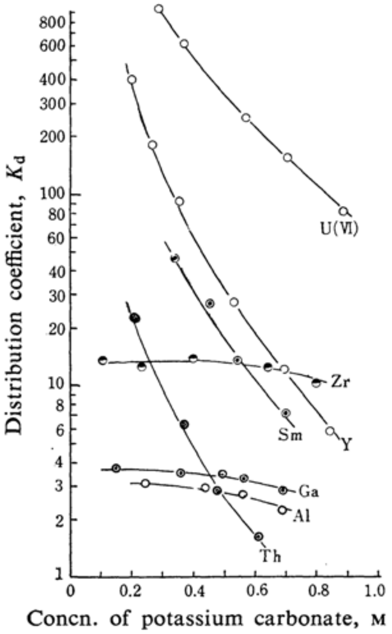

Fig. 5. Distribution coefficient of various metallic ions between Dowex 1 and potassium carbonate solution.

The relation between the K_d values of the metallic ions dissolved completely in a potassium carbonate solution and the concentration of the carbonate is shown in Fig. 5. Figure 5 shows that the K_d values of uranyl, rare earth and thorium ions depend upon the concentration of potassium carbonate to a remarkable extent, while, on the other hand, those of gallium and aluminum ions are scarcely affected. It is thought that the dissolution and anion exchange behavior of gallium and aluminum ions are related to the amphoteric property rather than to the formation of their carbonate complex ions. Zirconium ion did not give a constant value under these experimental conditions. Although lead ions were dissolved completely in a potassium carbonate solution more concentrated than 0.8 M, their adsorbability for an anion exchange resin is weakly. The distinct difference in K_d values between uranyl and other metallic ions will be applied to their analytical separation by a column operation.

The Dissolution and Anion Exchange Behavior of Various Metallic Ions in an Ammonium Carbonate Solution.—The molar concentration of ammonium carbonate may be represented by a molar formula of $NH_4CO_2NH_2 \cdot NH_4HCO_3$, but this formula is not accurate because of the unstable property of ammonium carbonate. The plot of the amounts of the various metallic ions dissolved against the concentration of ammonium carbonate is given in Fig. 6. Figure 6 shows that uranyl, thorium, gallium, berylliun, zinc, cadmium,

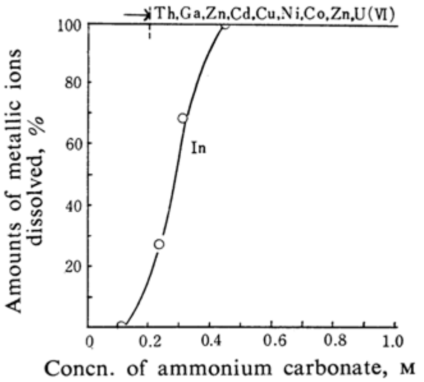

Fig. 6. Relation between the concentration of ammonium carbonate and the amounts of various metallic ions dissolved.

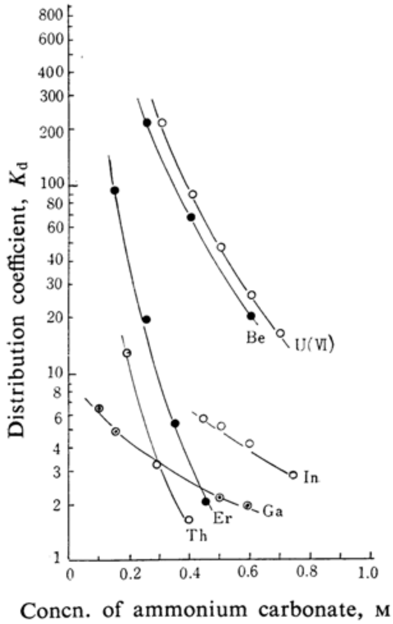

Fig. 7. Distribution coefficient of various metallic ions between Dowex 1 and ammonium carbonate.

copper, nickel and cobalt ions are dissolved completely in an ammonium carbonate solution more concentrated than about 0.2 M. Because of the formation of the ammine complexes, the macro amounts of zinc, cadmium, copper, nickel and cobalt ions are easily dissolved in an ammonium carbonate solution. Indium ions are dissolved completely in a carbonate solution more concentrated than about 0.45 M.

The relation between the K_d values of these metallic ions dissolved completely and the concentration of ammonium carbonate is shown in Fig. 7. The K_d values decrease with the increase in the concentration of ammonium carbonate. Uranyl and beryllium ions are adsorbed firmly on an anion exchange resin, while gallium, indium, thorium and rare earth ions are adsorbed less firmly. On the other hand, zinc, nickel, cobalt, cadmium and copper ions are scarcely adsorbed at all. The differences in K_d values among the metallic ions will be applied to an analytical separation; it is especially expected that the micro amounts of uranyl and beryllium ions may be separated from the macro amounts of nickel, cobalt, zinc, cadmium and copper ions.

Summary

The amounts of rare earth ions dissolved in a potassium bicarbonate solution, as well as those of other metallic ions dissolved in potassium bicarbonate, potassium carbonate and ammonium carbonate solutions, have been measured. Moreover, the minimum concentrations of potassium bicarbonate, potassium carbonate and ammonium carbonate required to dissolve the precipitates of the metallic bicarbonate and carbonate completely has been determined, and the distribution coefficients, K_d, of the completely dissolved metallic ions between an anion exchange resin and a potassium bicarbonate, potassium carbonate or ammonium carbonate solution had been measured. On the basis of those findings, the dissolution and anion exchange behavior of the metallic ions has been discussed, and the applicability to an analytical separation has been described.

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General Education Department
Kyushu University
Otsubo-machi, Fukuoka