SHORT COMMUNICATIONS

Anion Exchange Studies of Beryllium(II), Cerium(IV), Thorium(IV) and Uranium(VI) Carbonate Complex Ions

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Ishimori and Okuno[1] studied anion exchange behavior of uranyl carbonate complex ion in a sodium carbonate solution and Saito and Sekine[2] reported that of thorium carbonate complex ion. No investigation has been reported on the behavior of beryllium and cerium(IV) carbonate complex ions toward anion exchange resins. In this paper, anion exchange behavior of macro amounts of beryllium, cerium, thorium and uranyl carbonate ions formed in ammonium carbonate solution and of tracer amounts of cerium and thorium carbonate complex ions formed in potassium carbonate were studied, using the "Dowex 1, X-8" anion exchanger (50~100 mesh) of carbonate form.

The measurements of distribution coefficients were carried out as follows: one gram of the resin was added to 200 ml. of a series of ammonium carbonate solution of various concentrations containing an equal amount of beryllium carbonate complex ions. The solution was stirred frequently by a magnetic stirrer, allowed to stand for 12 to 20 hr. at about 20°C and the resin was rapidly separated from the solution with a glass filter. The metal ion in the resin was eluted by dilute hydrochloric acid and determined gravimetrically. The distribution coefficient K_d is given by:

$$K_d = [M_r] / [M_s] \quad (\text{ml./g.}) \tag{1}$$

where M_r is the amount of metal ion in 1 g. of the resin and M_s is that in 1 ml. of the solution. The similar procedure was also applied to the cases of cerium, thorium and uranyl carbonate complex ions. The results are shown in Fig. 1.

It can be seen that beryllium and cerium ions formed the negatively-charged complex ions with ammonium carbonate in the similar manner to thorium and uranyl ions, and that the adsorbabilities of these metal carbonate complex ions decreased as the concentration of ammonium carbonate increased. It is expected from the difference of the values for K_d that

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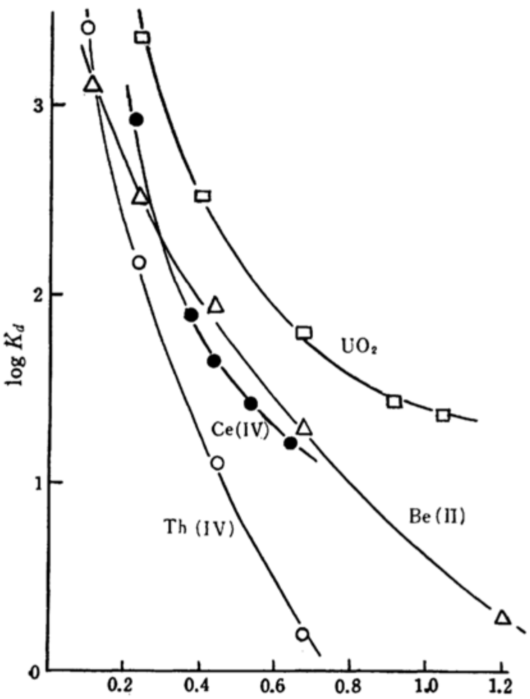
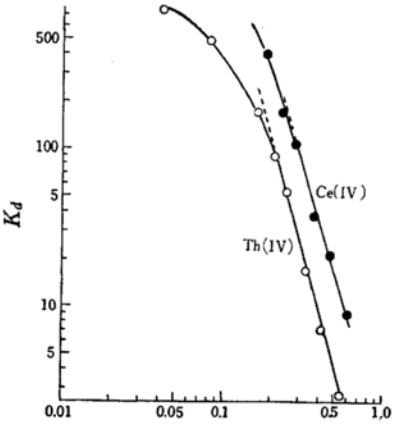
[1] T. Ishimori and H. Okuno, This Bulletin, **29**, 78 (1956).

[2] N. Saito and T. Sekine, ibid, **30**, 561 (1957).



Concentration of ammonium carbonate (M)

Fig. 1. Distribution coefficients of beryllium, cerium, thorium and uranyl ions on anion exchanger in ammonium carbonate solution.
Amounts taken,
Be^{2+}: 11.7 mg (BeO)
Ce^{4+}: 7.3 mg (CeO_2)
Th^{4+}: 26.9 mg (ThO_2)
UO_2^{2+}: 61.0 mg (U_3O_8)



Concentration of potassium carbonate (M)

Fig. 2. Distribution coefficient of cerium-144 and thorium-234 on anion exchanger in potassium carbonate solution.

thorium ions can be effectively separated from uranyl ions with the ammonium carbonate solution.

The anion exchanger was saturated with beryllium carbonate complex ions in 0.1 M ammonium carbonate solution, and then washed with dilute ammonium carbonate solution. The results obtained for the exchange capacity by this measurement showed that one mole of beryllium ion corresponds to 1.97 ($\simeq$2.0) equivalents of the resin. This may indicate that the complex anion has a formula such as $[Be(CO_3)_2]^{2-}$ in 0.1 M ammonium carbonate solution.

Distribution coefficients of thorium-234 and cerium-144 in potassium carbonate solutions were determined by a similar procedure. Thorium or cerium in the resin was eluted with hydrochloric acid and the effluent was evaporated on a water bath. The measurements of radioactivities were carried out with a G-M tube. $\log K_d - \log(CO_3^{2-})$ curves plotted in Fig. 2 show linearity for both elements from 0.25 to 0.60 M potassium carbonate solution. When only one species of negatively charged complex ion is assumed to be formed between a quadrivalent metal ion (M^{4+}) and carbonate ions, the main reaction would be

$$M^{4+} + xCO_3^{2-} = M(CO_3)_x^{4-2x} \qquad (2)$$

$$K_1 = \frac{(M(CO_3)_x^{4-2x})}{(M^{4+})(CO_3^{2-})^x} \qquad (2a)$$

Then the following equation is given as to the adsorption of the complex ion on the resin (R_2CO_3).

$$M(CO_3)_x^{4-2x} + (y/2)R_2CO_3 = R_yM(CO_3)_x + (y/2)CO_3^{2-} \qquad (3)$$

$$K_2 = \frac{(R_yM(CO_3)_x)(CO_3^{2-})^{y/2}}{(R_2CO_3)^{y/2}(M(CO_3)_x^{4-2x})} \qquad (3a)$$

Since the amount of M^{4+} is negligible compared with the amounts of "R_2CO_3", the latter can be regarded as a constant in the above equations. If the concentrations are replaced by thermodynamic activities, Eq. 1 is expressed as follows:

$$K_d = \frac{[M_r]}{[M_s]} = \frac{[R_yM(CO_3)_x]}{[M^{4+}] + [M(CO_3)_x^{4-2x}]} \qquad (4)$$

In Eq. 3, y should be equal to $2x-4$ in order to preserve electrical neutrality in the resin. From Eqs. 2a, 3a and 4, the following equation is obtained:

$$\frac{d \log K_d}{d \log(CO_3^{2-})} = 2 - x \qquad (5)$$

Since the slopes in Fig. 2 are numerically correspond to $-3.9 \sim -3.8$, the charges of thorium and cerium(IV) carbonate complex ions could be −8 (their some portions seem to have other values, e.g., −6) in the range between 0.25 and 0.60 M potassium carbonate solutions on the basis of the assumption described above. However, it is probable that these carbonate complex ions include OH^- radicals. Further, it is also supposed that more than one species of negatively charged complex ions may exist and be adsorbed on the resin in other ranges of concentrations of potassium carbonate solutions.

Details of these results will be published elsewhere.

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