# *Characteristics of Alginic Acid as a Cation Exchanger and its Application to the Separation of Thorium(IV) and Cerium(III) Ions*

By Takeo TAKAHASHI and Shingo MIYAKE

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Alginic acid belongs to one of the poly-acids with carboxylic groups as the dissociation group. It is generally soluble in water, either neutral or basic, but can maintain a solid state in an acidic salt solution, showing an excellent cation exchange property¹⁾ and although its analytical and industrial applications have also been investigated²⁾, the characteristics as cation exchanger or situation in cation exchangers have not yet been explained clearly. It is the principle object of the present research to discuss the cation exchange property of alginic acid from the viewpoint of acidity. Alginic acid indicates somewhat stronger acidity in the aqueous solution than acetic acid³⁾ and polyacrylic acid which is also one of the polycarboxylic acids. From the viewpoint of the acidity, it is expected that the characteristics of alginic acid as cation exchanger would be placed between a strongly acidic and a weakly acidic exchanger. Thus it may be used advantageously for the ion-exchange separation of some multivalent cations, which are separated with difficulty with conventional exchangers, either strongly or weakly acidic. For example, the separation of thorium(IV) and cerium(III) with alginic acid as exchanger was briefly described in the previous communication⁴⁾. The present paper discusses the characteristics of alginic acid as cation exchanger and the same subject was described in a previous paper in some detail.

## Experimental

Alginic acid employed for the measurement of the ion exchange equilibrium was prepared by the following procedure. A commercial sodium alginate was dissolved in water to make about 0.5% solution. The insoluble residue was congelated by warming the solution to 50~60°C on a water bath, and removed by filtering through a filter bed composed of Toyo filter paper No. 2 and No. 5c. Alginic acid, coagulated by the addition of hydrochloric acid to the filtrate, was, after a few hours, collected on a piece of silk gauze of about 60 mesh, and washed with about 50% methanol until the absence of chlorine ions in the washing was confirmed. After the methanol was pressed out, the swelled alginic acid was stored in a closed container with water in the bottom.

Amberlite IR-120, a strongly acidic exchanger and IRC-50, a weakly acidic one were similarly stored in a wet state. Table I shows the properties of these exchangers available for the experiment.

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1) J. L. Monger and A. Wassermann, *Nature*, **159**, 746 (1947).

2) H. Specker and H. Hartkamp, *Z. anal. Chem.*, **140**, 167 (1953); **141**, 33 (1954).

3) S. Miyake, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 1278 (1958).

4) T. Takahashi and S. Miyake, This Bulletin, **32**, 878 (1959).

TABLE I. THE PROPERTIES OF THE EXCHANGERS

| Exchanger | Humidity % | 0.1 N NaOH (ml.) for neutralization of 1 g. of exchanger |
|---|---|---|
| IR-120 | 43.1 | 23.56 |
| H alg. | 66.6 | 18.96 |
| IRC-50 | 48.5 | 53.70 |

The alginic acid used in the column (1.5 cm. in diameter and 20 cm. in length) for the separation of thorium (IV) and cerium (III) ions was prepared from calcium alginate thread* by the procedure described in the previous paper⁴⁾.

Other reagents were all of the special grade (G. R.) available commercially.

Spectrophotometric methods were used for the analysis of thorium(IV) and cerium(III) ions, using Neo-thorone for thorium(IV) (580 m$\mu$) and hydrogen peroxide for cerium(III) (320 m$\mu$).

## Results and Discussion

**Characteristics of Alginic Acid as an Exchanger.**—*Apparent dissociation constant.*—IR-120 (0.22 g.), IRC-50 (0.10 g.) and alginic acid (0.28 g.) weighed exactly within a deviation of 1 mg. were immersed in 10 ml. of the mixed solution containing $(10-x)$ ml. of 1 N potassium chloride and $x$ ml. of potassium chloride and potassium hydroxide mixture (1 N KCl–0.1 N KOH), respectively. After the ion exchange equilibrium was achieved by allowing the mixed solution to stand for 24 hr. (for 3 days in the case of IRC-50) with occasional agitation, the pH of each supernatant solution was measured by means of Toa Denpa Model HM-3 glass electrode pH meter. Fig. 1 shows the relationship between the pH of the supernatant solution in its equilibrium state and the volume of 0.1 N potassium hydroxide added.

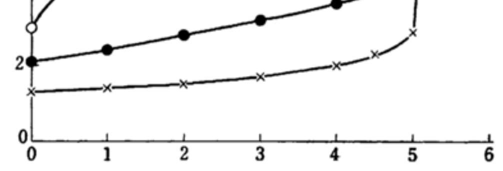

Fig. 1. Titration curves of exchangers.
○: IRC-50, ●: H alg., ×: IR-120

Such curves as those shown in Fig. 1 correspond to the titration curves of the exchangers as polyacids, and have been used for a mean in the characterization of the dissociation group of ion exchangers. For the purpose of expressing the apparent dissociation constant, p$K$, in the case of a weak polyacid, it is useful to take the value of pH at which half of the polyacid is exactly neutralized.

From Fig. 1, the values of p$K$ for the exchangers are found to be 1.6 for IR-120, 3.1 for alginic acid and 6.0 for IRC-50. Now, attention must be paid to the fact that the values of pH cited above are of the external solution with which the exchangers are in equilibrium, and the true pH⁵⁾ in the internal body of the exchangers may show lower values. However, it is concluded that alginic acid is situated between the strongly acidic and the weakly acidic exchangers from the viewpoint of acidity. In fact, it is well known that alginic acid is one of the strongest acids among all the weak polyacids with the carboxylic group. The most valuable characteristic of alginic acid is that it has an intermediate acidity as cation exchanger.

On the other hand, in a cation exchange reaction under a given condition, the difference between the selectivity of different cations is independent in principle of the kind of functional group of exchangers, with the exception of some special exchangers, but the effect of the kind of functional group upon the property of the exchanger is due to the difference of their acidities. When the exchangers have the same functional group and different acidities, a difference in property as ion exchanger should be found. Accordingly, it is expected that alginic acid would have an intermediate property for cations, and that it may be available for the separation of several cations, which are separated with difficulty by means of conventional exchangers.

*Distribution constant of thorium(IV) and cerium(III) ions.*—Each exchanger, weighed in the same manner as that described above, is immersed in 20 ml. of $3.8\times10^{-3}$ M thorium nitrate solution or $7.1\times10^{-3}$ M cerous nitrate solution, with nitric acid of various concentrations. After equilibrium is reached through the same procedure as

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* The alginate thread was supplied from Kamogawa Kato Co., Ltd., to whom the authors are indebted and to whom they express their thanks.

5) M. Honda, *J. Am. Chem. Soc.*, **73**, 2943 (1951).

that described above, thorium(IV) or cerium(III) ions in an aliquot of the supernatant solution were determined.

The distribution constant, $K_d$, for thorium(IV) and cerium(III) ions in regard to each exchanger was calculated from the following equation.

$$K_d=\frac{\text{Concn. of cation in the exchanger (dry base) (mg./g.)}}{\text{Concn. of cation in the supernatant soln. (mg./ml.)}}$$

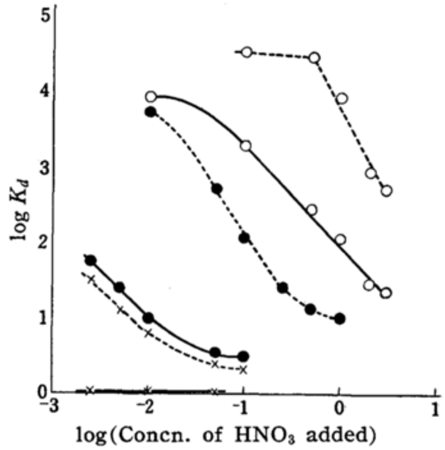

Fig. 2. Effect of concentration of nitric acid upon $K_d$ of thorium(IV) and cerium(III).
------: Th, ——: Ce
○: IR-120, ●: H alg., ×: IRC-50

Fig. 2 shows the relationship between log $K_d$ and logarithm of concentration of nitric acid in the solution. Now, for the concentrations of nitric acid, the stoichiometrical concentrations in the initial periods of the reaction were used instead of pH at the equilibrium, because of the difficulty of the measurement of pH in a concentrated nitric acid.

It is clear that IRC-50 adsorbs these cations little or not at all from an acid solution which keeps them without hydrolysis, and that these cations are adsorbed by IR-120 too tightly to be eluted fractionally with a dilute solution of conventional mineral acid. The values of $K_d$ for thorium(IV) and cerium(III) ions in regard to alginic acid is placed between those in regard to IR-120 and IRC-50.

For the separation of thorium(IV) and cerium(III) ions by cation exchanger, it has been, heretofore, usual to use strongly acidic exchangers such as Amberlite IR-120 or Dowex-50 and to use complex reagents such as EDTA[6,7], citrate[8] and oxalate[9] for the fractional elution. This is because of the difficulty with which these cations are eluted from strongly acidic exchangers with a dilute acid solution. On the other hand, it is not always easy to convert the complex ions into simple metallic ions. However, it seems likely that thorium(IV) and cerium(III) ions can be easily eluted fractionally with a conventional mineral acid as shown in Fig. 2, provided that alginic acid is used as exchanger. It has never been suggested that an intermediately acidic exchanger such as alginic acid be used for the separation of thorium(IV) and cerium(III) ions.

**Separation of Thorium(IV) and Cerium(III) Ions by the Use of Alginic Acid Column.**—*Synthetic solution.*—The synthetic solutions containing thorium(IV) and cerium(III) ions in various concentrations were made pH 2 to 2.5 with aqueous ammonia and poured over the top of the column. Thorium(IV) and cerium(III) ions are adsorbed on alginic acid. After the column is washed with 100 ml. of water, cerium(III) ion is eluted with nitric acid of a concentration below 0.1 N at a flow rate of about 1 ml./min., and then the thorium(IV) ion is eluted with 1 N nitric acid. An example of the elution diagram has been shown in the previous paper[4]. Some analytical results are given in Table II.

TABLE II. SEPARATION OF THORIUM(IV) AND CERIUM(III) IONS FROM THEIR SYNTHETIC SOLUTION

| Taken mg. | | Found mg. | | Concn. and vol. of eluted soln. | | | |
|---|---|---|---|---|---|---|---|
| | | | | for Ce | | for Th | |
| Th | Ce | Th | Ce | N | ml. | N | ml. |
| 35.5 | 30.0 | 35.5 | 30.1 | 0.05 | 250 | 1 | 100 |
| 35.5 | 30.0 | 35.4 | 30.3 | 0.075 | 200 | 〃 | 〃 |
| 70.0 | 30.0 | 69.9 | 30.0 | 〃 | 〃 | 〃 | 150 |
| 35.5 | 45.0 | 35.5 | 44.8 | 0.1 | 〃 | 〃 | 100 |
| 70.0 | 45.0 | 70.1 | 44.9 | 〃 | 〃 | 〃 | 150 |
| 70.0 | 60.0 | 70.0 | 47.4 | 〃 | 300 | 〃 | 〃 |
| 105.5 | 45.0 | 105.7 | 45.0 | 〃 | 200 | 〃 | 〃 |

It is shown that the present method can be feasible for the quantitative separation of thorium(IV) and cerium(III) ions and that the column employed in this experiment has a dimension suitable for the adsorption of the cerium(III) ion below 45 mg.

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[6] L. Gordon et al., *Anal. Chem.*, **28**, 1476 (1956).

[7] T. Taketatsu, This Bulletin, **32**, 291 (1959).

[8] T. Nishi et al., *III Atomic Energy Symposium, Japan*, 69 (1959).

[9] T. Nozaki, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **76**, 996 (1955).

*Application to monazite.* — The monazite employed in this experiment was mined in 1940 at Ishikawa-yama, Fukushima-ken. Monazite ore was digested with concentrated sulfuric acid in the usual way. Mixed oxalates of thorium(IV) and rare earth metals were separated from other metallic ions through reprecipitation with oxalic acid. The oxalate mixture was converted into hydroxide by immersing into a warm sodium hydroxide solution and then dissolved in nitric acid. After the ceric ion contained in the mixed solution was reduced with a small amount of sodium nitrite to the cerous ion, and after the pH was adjusted with nitric acid to about 1, an aliquot of the solution was poured over the top of the column, which then was washed with 250 ml. of 0.1 N nitric acid at a flow rate of about 1 ml./min. Thus, the thorium(IV) ion is adsorbed entirely on alginic acid in the column, while all rare earth metal ions pass through the column. The results are shown in Table III.

TABLE III. SEPARATION OF THORIUM(IV) AND RARE EARTH IONS FROM MONAZITE

| Mixed oxide | $ThO_2$ found in the column | Oxides of R.E. found in the effluent | Other oxides eluted with 1 N $H_2SO_4$ |
|---|---|---|---|
| mg. | mg. | mg. | mg. |
| 298 | 42.5 | 237.1 | 18.3 |
| 〃 | 42.8 | 237.3 | 17.8 |
| 〃 | 43.1 | 236.8 | 19.1 |

The "other oxides" shown in the last column of Table III are the oxides not eluted with 1 N nitric acid but eluted with 1 N sulfric acid. They seem to be composed of the oxides of titanium, zirconium and hafnium. In this experiment, the mixed oxide, the oxides of rare earth elements and "other oxides" were precipitated with aqueous ammonia from respective solutions and determined gravimetrically.

## Summary

The apparent dissociation constant of alginic acid was measured by means of the neutralization with 0.1 N potassium hydroxide in 1 N potassium chloride solution and found to have a value of 3.1. This value is between that of IR-120 and of IRC-50, which is obtained by the same manner of measurement. The values of $K_d$ for thorium(IV) and cerium(III) ions in regard to these three exchangers were measured, showing that the value in regard to alginic acid is also situated between the other two.

The application of alginic acid to the fractional separation of thorium(IV) and cerium(III) ions gave a satisfactory result.

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*Institute of Industrial Science*
*The University of Tokyo*
*Yayoi-cho, Chiba*