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Preparation of β-Diketone Resins and an Application in Separation of ^{59}Fe and ^{60}Co

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Two macroreticular resins containing β-diketone groups were prepared and their adsorptivity for nine metal ions was investigated by batch operation. Although these resins were highly selective for Fe(III) in acidic region (pH 1—4), no significant affinity was observed for Cd(II), Co(II), Cu(II), Mg(II), Mn(II), Ni(II), Zn(II), and U(VI). The β-diketone resin prepared from styrene-divinylbenzene copolymer and diketene was applicable to the separation of ^{59}Fe and ^{60}Co by a column operation.

Keywords——β-diketone resin; separation; ^{59}Fe; ^{60}Co; column operation

It is well known that some β-diketones possess the complexing affinity for a number of metal ions and have been commonly used in analytical chemistry. Some polymers containing this functional groups have also been prepared by several investigators.[2–5] Despic and Kosanovic[6] have shown that the β-diketone resins prepared by polymerization of methacrylacetone retain the complexing affinity for Fe(III).

Radioisotopes used as tracers should be radiochemically pure. Preparations of ^{59}Fe usually contain only small amount of ^{60}Co. However, owing to the long life of ^{60}Co in relation to that of ^{59}Fe, the activity of ^{60}Co in older preparations may be comparable with the activity of ^{59}Fe. Although ion exchange[7] and extraction methods[8,9] have been introduced for the separation of ^{59}Fe from ^{60}Co, application of chelating resins having high selectivity is also expected. In this paper, two new macroreticular(MR) resins containing β-diketone groups were proposed and their adsorption behavior for metal ions was investigated. The resin prepared from styrene-divinylbenzene(DVB) copolymer and diketene was successfully applicable to the separation of ^{59}Fe and ^{60}Co by a column operation.

Results and Discussion

The β-diketone resins used in this experiment were shown in Chart 1. As is shown in Fig. 1, each resin indicates characteristic absorption peaks due to the diketone groups[2] in the region of 1600—1750 cm^{-1}.

Several reaction conditions were tried for the preparation of I, but that described in the experimental section gave the maximum yield with least degradation of polymer matrix: increasing temperature tends to occur disintegration of resin beads. On the other hand, the copolymerization of methacrylacetone and DVB was carried out by regulating the frac-

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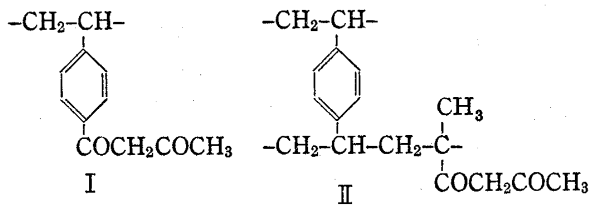

Chart 1

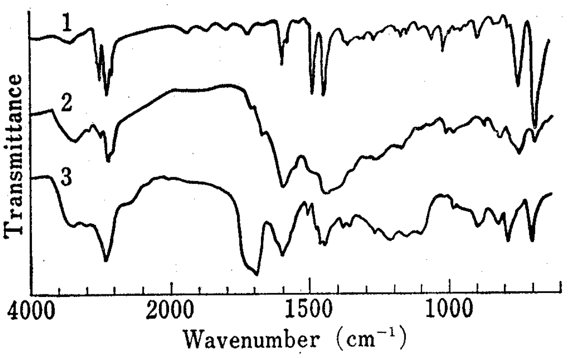

Fig. 1. Infrared Spectra of Resins (in KBr Disks)

1: styrene-DVB copolymer (DVB 7.5%).
2: resin I. 3: resin II.

tion of DVB, but the most stable MR type resin beads were obtained when DVB content was 30%.

The hydrogen-sodium exchange capacities for resins I and II were 2.4 and 2.1 meq/g, respectively. These values indicated that in the case of I, 33% of aromatic rings contained β-diketone groups based on 108 for equivalent weight of starting polymer, and II contained 27% of methacrylacetone groups. In a preliminary experiment, it was found that the equilibration rate of H-form resins in the adsorption of metal ions was too slow. Accordingly the Na-form resins whose equilibration rate is faster than that of H-form was used in the subsequent studies.

The adsorption behavior of metal ions on the resins I and II was examined by a batch operation. Figs. 2 and 3 show the experimental results for the equilibrium adsorption of metal ions at different pH. The resins demonstrate high selectivity for Fe(III) in the acidic region(pH 1—4), as would be expected from the results reported by Despic and Kosanovic,[6] whilst, no significant adsorptions were observed for the other metal ions tested.

Since resin I showed higher exchange capacity for Fe(III) than that of II under the experimental conditions, I was used for the subsequent experiment. The selectivity of the I for Fe(III) over Co(II) at pH of below 4.0 is of interest. At pH 3.0 the exchange capacity

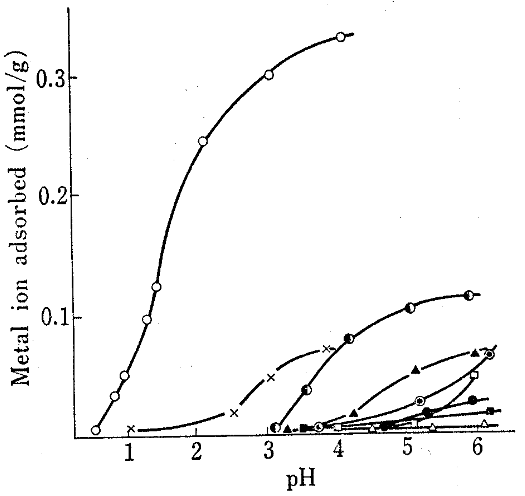

Fig. 2. Effect of pH on Adsorption of Metal Ions by Resin I(Na-form)

Shaking time: 24 hr.
—△—, Mg(II); —▲—, Mn(II); —○—, Fe(III);
—●—, Co(II); —■—, Ni(II); —◐—, Cu(II);
—⊙—, Zn(II); —□—, Cd(II); —×—, U(VI).

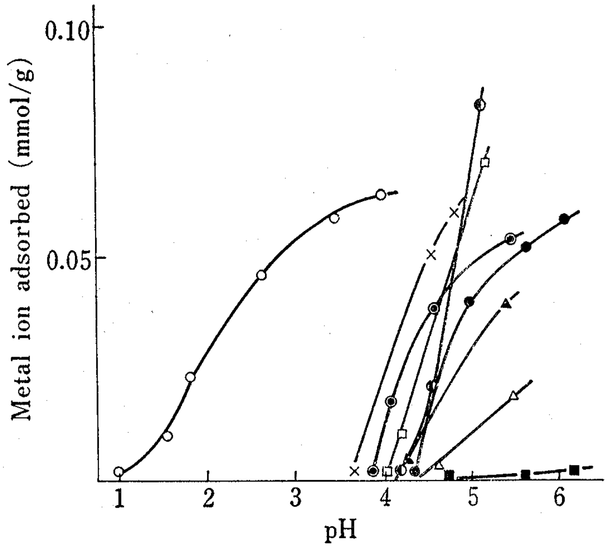

Fig. 3. Effect of pH on Adsorption of Metal Ions by Resin II(Na-form)

Shaking time: 24 hr.
Symbols are the same as those in Fig. 2.

for Fe(III) is 0.3 mmol/g, whilst that for Co(II) is negligible. Therefore, we attempted an application of I for the separation of ^{59}Fe and ^{60}Co, and a variety of experimental conditions were determined. Fig. 4 shows the effect of shaking time on the adsorption of ^{59}Fe and ^{60}Co by batch operation. The adsorption of ^{59}Fe is seriously affected by the shaking time. The effects of concentration of buffer and pH on the distribution coefficient(D) of ^{59}Fe and ^{60}Co are shown in Fig. 5. An increase in D is expected with an increase of the ionization of diketone groups. The D values increase with decreasing of the concentration of buffer. These facts are in agreement with the results reported by Sides and Kenner[10] for the adsorption of alkali earth metal ions with Dowex A-1 resin.

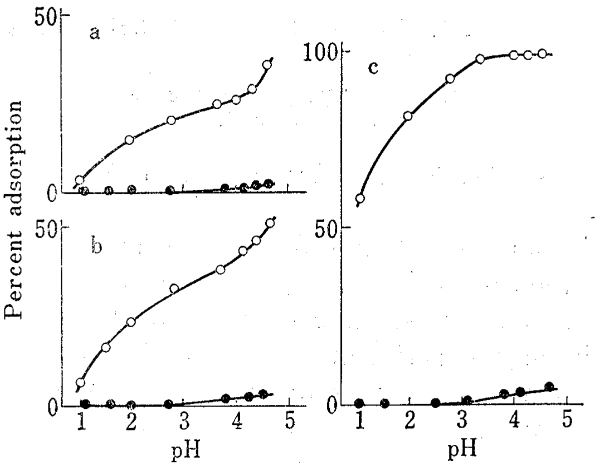

Fig. 4. Effect of pH and Shaking Time on Adsorption of ^{59}Fe and ^{60}Co

—○—, Fe^{59}; —●—, ^{60}Co.
Resin I(Na-form) 0.1 g, buffer: 0.1 M HCl-0.1 M CH_3COONH_4.
a, shaking time: 5 min. b, shaking time: 20 min.
c, shaking time: 24 hr.

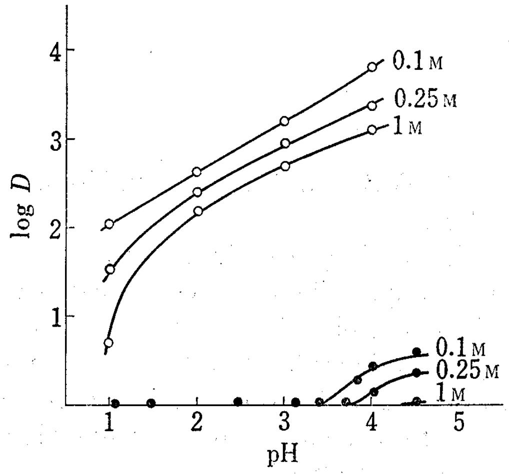

Fig. 5. Effect of Concentration of Buffer and pH on the Distribution Coefficient (D) of ^{59}Fe and ^{60}Co

—○—, ^{59}Fe; —●—, ^{60}Co.
Resin I (Na-form) 0.1 g, buffer: 0.1M, 0.25 M, and 1M HCl-CH_3COONH_4, shaking time: 24 hr.

Table I. Effect of Buffer Concentration and pH on Separation of ^{59}Fe and ^{60}Co by Column Operation

Buffer solution ($HCl-CH_3COONH_4$) concentration (M)	pH	Recovery (%)	
		^{60}Co	^{59}Fe
0.10	3.0	100	63
0.25	3.0	100	59
0.10	4.0	100	93
0.25	4.0	100	90

Flow rate: 0.5 ml/min, temperature: 24—25°.

The separation of ^{59}Fe and ^{60}Co by column operation was examined, and the results were summarized in Table I. The best separation was achieved under the following condition: concentration of buffer is 0.1 M at pH 4.0. Since leak of ^{59}Fe in the fraction of ^{60}Co was 7% under the experimental conditions, the effect of flow rate was investigated. When a flow rate is 0.1 ml/min no ^{59}Fe was observed in the fraction of ^{60}Co. A typical elution curve of the mixture of ^{59}Fe and ^{60}Co is shown in Fig. 6. To check the purity, the γ-ray spectra of the each fraction were measured with a Ge(Li) detector. As is shown in Fig. 7 both elements are entirely separated by this column. The recoveries of ^{59}Fe and ^{60}Co were 99 and 100%, respectively.

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[10] J.L. Sides and C.T. Kenner, *Anal. Chem.*, **38**, 707 (1966).

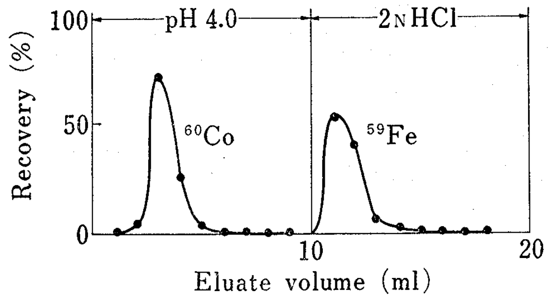

Fig. 6. A Typical Elution Curve of ^{59}Fe and ^{60}Co

Column: resin I (Na-form) 1g, 0.5 × 12.5 cm.
Buffer: 0.1 M HCl-0.1 M CH_3COONH_4.
Flow rate: 0.1 ml/min, temperature: 24—25°.

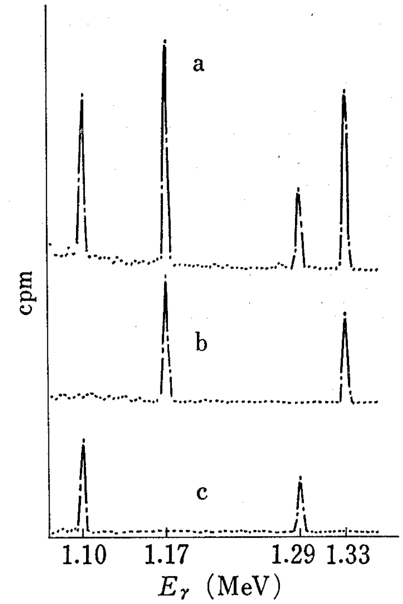

Fig. 7. γ-Ray Spectra of Each Fraction

a: original mixture of ^{59}Fe and ^{60}Co.
b: ^{60}Co fraction. c: ^{59}Fe fraction.

The resin used can be regenerated many times with no apparent loss in activity. In addition, the effluent in above process is free from the contaminants such as organic solvent and/or organic reagent which are unavoidable in solvent extraction or extraction chromatography. It should also be applicable to the separation and removal of Fe(III) in many other samples.

Experimental

The IR spectra were measured on a JASCO DS-301 spectrophotometer in KBr disks. The γ-ray spectra were obtained with a ORTEC Ge(Li) detector and 1024 channel analyzer (Nuclear Data Inc. Model 510). The radioactivity was measured by a single channel analyzer (Aloka Co., Ltd. Model NDW-351 and TDC-5U). The metal ion solutions were prepared by reagent grade nitrate except for $FeCl_3$ and $CuSO_4$ in water to produce solutions which were approximately 0.1M and were standardized by chelatometry.

Resin I——Styrene-DVB copolymer[11] (50 g, MR type, 35—60 mesh fraction) was swelled in 350 ml of 1,2-dichloroethane for 30 min and 200 g of anhydrous $AlCl_3$ was added. Freshly distilled diketene (57 ml) was added to the mixture with stirring below 10° and then the mixture was heated at 40° for 6 hr. The reaction mixture was then poured into 2 l of ice water. The resin was filtered off and washed with successive, acetone, 10% HCl, water, 5% NaOH, water, 5% HCl, water, and methanol. It was collected and dried in a vacuum. The yield of H-form resin was 52 g. The H-form resin was converted into Na-form with 2 N NaOH and washed with ethanol.

Resin II——A mixture of methacrylacetone (16 ml) prepared according to the method described by Despic and Kosanovic,[3] 24 ml of commercial DVB (about 50%), 40 ml of isooctane, and 0.6 g of benzoyl peroxide was added to 240 ml of an aqueous solution containing 2.4 g of hydroxyethyl cellulose (20—30 cp, at 20°, 2% in water), and 10 ml of 12 N HCl. The organic phase was dispersed and heated at 70° for 6 hr and then at 80° for 2 hr with stirring. The resulting polymer beads were washed with hot water and boiled with water for several hour to remove hydroxyethyl cellulose and isooctane. The resin was filtered off, and washed with hot water, acetone, 5% NaOH, water, 5% HCl, and water. After had been washed the resin was dried in a vacuum, and a 35—60 mesh fraction was collected. The yield was 32 g. The H-form resin was converted into Na-form in a similar manner as I.

Hydrogen-Sodium Exchange Capacity——This was determined by shaking 0.5 g of dry resin (H-form) with a mixture of 2 N NaOH (10 ml) and ethanol (10 ml) for 24 hr and titrating the excess alkali back to pH 8.0.

Adsorption of Metal Ions on Resins I and II——Determination of the amount of metal ions adsorbed was carried out as follows: To a glass stoppered test tube containing 0.100 g of dry resin (Na-form) 9 ml of

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[11] A. Sugii and N. Ogawa, *Chem. Pharm. Bull.* (Tokyo), 24, 1349 (1976).

0.25 M HCl–0.25 M CH_3COONH_4 buffer (pH 1—7) was added. After had been equilibrated 1 ml of 0.1 M metal ion solution was added to the test tube, then the mixture was shaken at room temperature. After shaking of a definite time the solution was filtered to separate the resin with glass wool, and the amount of metal ion remaining in filtrate was determined by chelatometry or counting of radioactivity.

Separation of ^{59}Fe and ^{60}Co by Column Operation——A column, 0.5 × 12.5 cm (Na-form resin I, 1.0 g), was equilibrated with buffer. One ml of sample solution, which was prepared by mixing ^{59}Fe and ^{60}Co solutions containing 0.3 μg of each Fe(III) and Co(II)-carrier, was charged on the column. The column was treated with buffer to remove ^{60}Co, and ^{59}Fe retained on the column was eluted with 2 N HCl.

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