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SEPARATION OF METAL IONS BY MIXED COLUMN ION-EXCHANGE CHROMATOGRAPHY

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SUMMARY

The separation of metal ions with organic hydroxy acids at a definite pH was carried out by changing the mixing ratio (γ) of the cation- and anion-exchange resins. By using 0.25 M tartaric acid, the best separation of alkaline earth metals was obtained at pH 4.1 and $\gamma = 2$. The effect of γ on the separability is discussed by considering the equation for the distribution ratio in a mixed column.

INTRODUCTION

Although mixed bed deionization is commonly used to prepare water of high purity, it had not been employed in separations by ion-exchange chromatography until we used a mixed column that contained both cation- and anion-exchange resins in 1964[1]. At first, we carried out the separation of metal ions on mixed columns with hydrochloric acid. In this process, however, we had only limited success with the separation of some heavy metal ions[2]. We then tried to use organic hydroxy acids as eluents, and we had great success by selecting a definite pH and by changing the mixing ratio (γ) of the cation- and anion-exchange resins[3–5]. In this paper, we report the separation of alkaline earth metal ions, and discuss the effect of γ on the separability by considering the equation for the distribution ratio in a mixed column.

EXPERIMENTAL

Preparation of mixed column

The cation- and anion-exchange resins used were strongly acidic and strongly basic (Diaion SK and SA, $<25\,\mu m$, respectively) and were conditioned with hydrochloric acid and sodium hydroxide solution in the usual manner. After conditioning, appropriate amounts of the resins were mixed in a concentrated electrolyte solution, such as 20% sodium chloride solution, so as to avoid violent aggregation in pure water[3].

Column operation and determination of metal ions

The total amount of the resins in the column was about 4 ml and the height of the resin in the 5-mm I.D. column was 200 mm. A 0.5-ml volume of *ca.* 10^{-3} M sample solution was added to the upper part of the column with a microsyringe and

then developed with an eluent consisting of a mixture of an organic hydroxy acid and sodium chloride at a definite pH adjusted with sodium hydroxide solution at a flow-rate of 60 ml/h (ref. 3).

The concentration of each metal ion was determined continuously by coulometry with a Hitachi Coulometric Monitor, Type 030. The principle of this instrument involves the coulometry of mercury or copper ions isolated by the reaction of metal ions with the EDTA complex of mercury or copper, and therefore the identification of a peak is achieved by comparison with the elution of a single metal ion.

RESULTS· ·

Fig. 1 shows typical elution curves of metal ions with a definite pH and various mixing ratios (γ) of cation- and anion-exchange resins.

As shown by Hayashi and Yamabe[4], for the separation of the yttrium group of rare earth elements, the best result was obtained with an eluent consisting of 0.50 M lactic acid and 0.06 M sodium chloride at pH 2.8 and $\gamma = 85/15$.

As shown in Fig. 1, for the separation of alkaline earth metals, the best result was obtained with an eluent consisting of 0.25 M tartaric acid, 0.07 M sodium chloride at pH 4.1 and $\gamma = 2$. Four metals (calcium, magnesium, strontium and barium) were almost separated within 90 min.
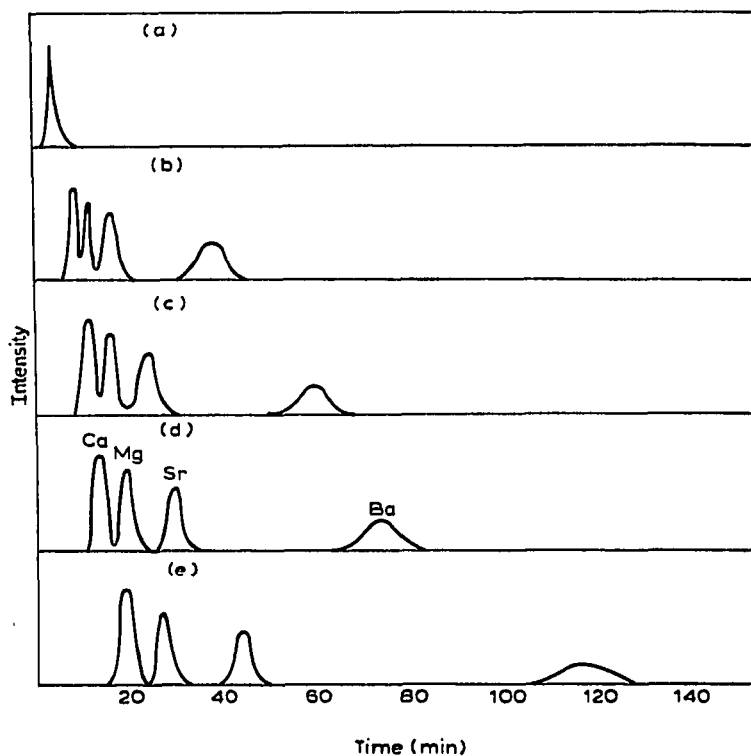

Fig. 1. Separation of alkaline earth metal ions with tartaric acid at pH 4.1 using mixed columns with Diaion SK:Diaion SA ratios of (a) 0:1; (b) 1:2; (c) 1:1; (d) 2:1; and (e) 1:0.

THEORETICAL

In ion-exchange chromatography, the following equation is obtained:

$$V_e = V_0 + K_d^M \cdot V_R \tag{1}$$

where V_e is the elution volume and V_0 the volume of the mobile phase, V_R the resin volume and K_d^M the distribution ratio in the mixed column. K_d^M can be defined as

$$K_d^M = \frac{V_R^+ \cdot K_d^+ + V_R^- \cdot K_d^-}{V_R} \tag{2}$$

where the distribution ratios for the cations and anions are K_d^+ and K_d^- and the volumes of the cation- and anion-exchange resins are V_R^+ and V_R^-, respectively.

If the equilibrium in the process forming a complex between a metal ion M^{3+} (for example, a rare earth metal ion) and Y^- (for example, lactate ion) is assumed to be

$$M^{3+} + 6\ Y^- \rightleftharpoons MY_6^{3-} \tag{3}$$

then the stability constant, K_c is given by

$$K_c = \frac{[MY_6^{3-}]}{[M^{3+}]\ [Y^-]^6} \tag{4}$$

If the dissociation constant of lactic acid is K_a, then $[Y^-]$ is

$$[Y^-] = C_Y \cdot \frac{K_a}{K_a + [H^+]}$$
$$\doteqdot C_Y \cdot \frac{K_a}{[H^+]} \quad \text{(if } [H^+] \gg K_a) \tag{5}$$

where C_Y is the total concentration of lactic acid. Therefore, if $K_c\ [Y^-]^6 \gg 1$, then

$$K_d^+ = \frac{[M^{3+}]}{C_M} \cdot K_d^{0+}\ (M^{3+})$$

$$= \frac{1}{1 + K_c\ [Y^-]^6} \cdot K_d^{0+}\ (M^{3+})$$

$$\doteqdot \frac{K_d^{0+}\ (M^{3+})}{K_c\ [Y^-]^6} \tag{6}$$

$$K_d^- = \frac{[MY_6^{3-}]}{C_M} \cdot K_d^{0-}\ (MY_6^{3-})$$

$$\doteqdot K_d^{0-}\ (MY_6^{3-}) \quad (K_c\ [Y^-]^6 \gg 1) \tag{7}$$

where C_M is the total concentration of metal, and K_d^{0+} and K_d^{0-} the values when only M^{3+} or MY_6^{3-} exists in the solution. Then, K_d^M is given by

$$K_d^M = K_d{}^+ - \frac{1}{V_R} \cdot (K_d{}^+ - K_d{}^-) \, V_R{}^-$$

$$= \frac{K_d^0 + (M^{3+})}{K_c \, [Y^-]^6} - \frac{1}{V_R} \left(\frac{K_d^0 + (M^{3+})}{K_c \, [Y^-]^6} - K_d^0{}^- (MY_6{}^{3-}) \right) \cdot V_R{}^- \qquad (8)$$

DISCUSSION

It is considered that the best separability is obtained with the shortest elution time under the conditions of complete separation. We will discuss the separability from the point of view of the relationship between elution time or K_d^M and the various factors.

First, we can consider the effect of pH on elution time. From eqn. 5, an increase in pH causes a large increase in $[Y^-]$ and therefore a large decrease in K_d^+. As shown earlier[3], the yttrium group of rare earths is completely separated at pH 2.8 in a single column of cation-exchange resin, but gadolinium shows considerable tailing. If we adopt a pH value of 3.0, lutetium, thulium, erbium, holmium and dysprosium show mutual interference, because an increase in pH decreases considerably K_d^+ or the elution time to similar extents for all metals[4].

For the increase in V_R^-, we must consider the difference in the K_c values of the metals in eqn. 8.

In the case of rare earth and alkaline earth metals, K_d^+ is usually larger than K_d^- and the elution behaviour resulting from an increase in V_R^- is similar to that resulting from an increase in pH. However, as shown in Fig. 1, the decrease in elution time in the case of metals of smaller K_d such as calcium, is less than that of a metal of larger K_d such as barium. Therefore, at $\gamma = 2$, complete separation is obtained because an appropriate decrease in elution time is obtained for all metals. From eqn. 7, if $K_d^{0-} (MY_6^{3-})$ is almost equal for rare earth and alkaline earth metals, the peak position in the single column of anion-exchange resin occurs at almost the same position for all metals, as shown in Fig. 1, but from the above discussion it is obvious that the anion-exchange resin in the mixed column does not act as a diluent.

In conclusion, the effects of the mixing ratio on the elution behaviour of metal ions are different from the effect of pH or a simple decrease in the content of cation-exchange resin, and therefore we can expect to obtain the best separability by using mixed columns with appropriate mixing ratios.

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