Quantitative Separation of Alkaline Earth Metal Ions by Triple-phase Separation Method

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The triple-phase separation system has been designed for the first time combining the solvent-extraction and the ion-exchange methods. Owing to the reverse selectivity tendency of the solvent extraction and the ion exchange methods for alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}), the quantitative separation could be achieved by the triple-phase separation method.

The separation of alkaline earth metal ions has been extensively studied by the ion-exchange[1-3] and the solvent extraction[4-6] methods. However, the separation of Sr^{2+} from other alkaline earth metal ions is much more difficult; none of the known ion exchange and solvent extraction methods have been successful. This is primarily because Sr^{2+} is in the middle of selectivity series in the alkaline earth metal group. Since the selectivity of the ion exchange and the solvent extraction methods for alkaline earth metal ions is quite opposite, a highly effective separation system could be possibly designed combining these methods. A theoretical separation factor can be calculated from the ion exchange and solvent extraction data. Further, the optimum separation could be obtained adjusting the condition of the each method. In the present study, the complete separation of Sr^{2+} has been investigated for an aqueous solution containing Ca^{2+} and Sr^{2+} by a triple-phase separation technique which combines the ion exchange and the solvent extraction methods.

All of the reagents used were of an analytical grade. Layered potassium tetratitanate fibers, $K_2Ti_4O_9$ were first synthesized[7] by slow cooling method of a K_2MoO_4 flux melt containing K_2CO_3 and TiO_2 (1:3 in molar ratio). After melting the mixtures at 1423 K, the melted materials were cooled to 1223 K (cooling rate:4 K / h) and fibrous crystals of $K_2Ti_4O_9$ were obtained. Subsequently, 1 mol dm^{-3} hydrochloric acid solution was passed through the column to convert $K_2Ti_4O_9$ into the H form according to the following reaction.

$$K_2Ti_4O_9 + 2H^+ + nH_2O \leftrightarrows H_2Ti_4O_9{\cdot}nH_2O + 2K^+ \qquad (1)$$

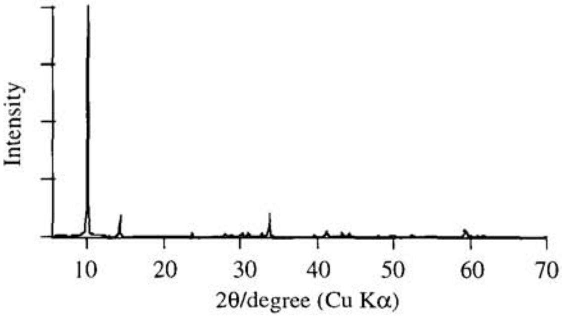

Figure 1. X-ray diffraction pattern for $K_2Ti_4O_9$.

The X-ray diffraction pattern of $K_2Ti_4O_9$ was demonstrated in Figure 1. The peak of $K_2Ti_4O_9$ is characterized by a very strong 200 reflection (d_{200} = ca.0.91 nm) which denotes a layer structure.

Stoppered glass tubes of 20 cm^3 were used to equilibrate the solid and aqueous phases containing 1×10^{-4} mol dm^{-3} of alkaline earth metal ions for ion-exchange reaction. The two phases were agitated 50 times a day by hand to establish solid-liquid equilibrium for 15 days. The contents of alkaline earth metal ions in the aqueous solution were measured by ICP. The ion exchange reaction of alkaline earth metal ions, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+},is expressed in terms of the distribution coefficient, K_d:

$$K_d = C_{M(s)}(g^{-1}) / C_M(cm^{-3}) \qquad (2)$$

where C_M represents the total concentration of metal ions in each phase and the subscript "s" denotes the solid phase.

The K_d values were given by the data obtained under the experimental conditions, 0.1g of solid and 10 cm^3 of aqueous solution. To determine the amount of the interlayer water of $H_2Ti_4O_9{\cdot}nH_2O$ in Eq. (1), the weight of the fibers was measured before and after it was heated at 1073 K for 3 h. The amount of the interlayer water of the fibers was determined as $H_2Ti_4O_9{\cdot}1.26H_2O$. The log K_d values were proportional to the pH of the aqueous solution. As the slopes of the linear relations were close to +2, this indicates that the ion exchange reaction of alkaline earth metal ions can be written as the following equation.

$$M^{2+} + H_2Ti_4O_9{\cdot}1.26H_2O_{(s)} \leftrightarrows MTi_4O_9{\cdot}1.26H_2O_{(s)} + 2H^+ \qquad (3)$$

where the subscript "s" represents the chamical species in the solid phase.

The $pH_{1/2}$ values, defined as pH at 50% ion exchange of alkaline earth metal ions, and the separation factors are listed in Table 1. The separation factors in logarithm for each combination can be written as follows.

$$\log S_f = 2(pH_{1/2(M1)} - pH_{1/2(M2)}) \qquad (4)$$

Table 1. Summary of the $pH_{1/2}$ values and the separation factors in logarithm given by the ion exchange reaction

	$pH_{1/2}$ values	log S_f
Ba	2.02	
		2.24
Sr	3.14	
		0.72
Ca	3.50	
		2.24
Mg	4.62	

where S_f represents separation factor. $pH_{1/2(M1)}$ and $pH_{1/2(M2)}$ denote the corresponding $pH_{1/2}$ values for metal ions.

On the other hand, the solvent extraction experiment was done between an aqueous solution (10 cm^3 containing 1×10^{-4} mol dm^{-3} alkaline earth metal ions) and an organic solution(10 cm^3 benzene containing 0.1 mol dm^{-3} 2-thenoyltrifluoroacetone (TTA) and 0.1 mol dm^{-3} trioctyl phosphine oxide(TOPO). The solvent extraction of alkaline earth metal ions is also expressed in terms of the distribution ratio, D:

$$D = C_{M(o)} / C_M \qquad (5)$$

where C_M represents the total concentration of metal ions in each solution and the subscript "o" denotes the organic solution.

The log D is proportional to the pH of the aqueous solution. The slopes of the linear relations were close to +2 and it is reported that two TOPOs were attached to one metal ion in the previous results.[5] This indicates that the solvent extraction reaction of alkaline earth metal ions can be written as follows.

$$M^{2+} + 2HA_{(o)} + 2TOPO_{(o)} \rightleftarrows MA_2(TOPO)_{2(o)} + 2H^+ \qquad (6)$$

where HA denotes TTA and the subscript "o" represents the chemical species in the organic phase.

The $pH_{1/2}$ values, defined as pH at 50% solvent extraction of the alkaline earth metal ions, are listed in Table 2. The separation factors in logarithm for each combination given by solvent extraction reaction are also summarized in Table 2.

Table 2. Summary of the $pH_{1/2}$ values and the separation factors in logarithm given by the solvent extraction reaction

	$pH_{1/2}$ values	log S_f
Mg	3.35	
		0.90
Ca	3.80	
		2.00
Sr	4.80	
		1.40
Ba	5.50	

As is shown in Table 1, the order of extraction in the ion-exchange system is $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. This selectivity series is related to the hydration energy of the alkaline earth metal ions in the aqueous solution. The order for the solvent-extraction reaction ($Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$) in Table 2, is in reverse relationship to those observed in the ion-exchange method. This order is explained in terms of several factors: the solvation effect, the charge density, or steric effect in forming the chelating ring for the solvent extraction reaction. It is obvious from Table 1 that the separation factors for Ba-Sr and Ca-Mg given by the ion-exchange method were sufficiently large to separate these pairs. On the other hand, the values of separation factor between Ca-Sr given by solvent-extraction or ion-exchange methods were too small to achieve this separation.

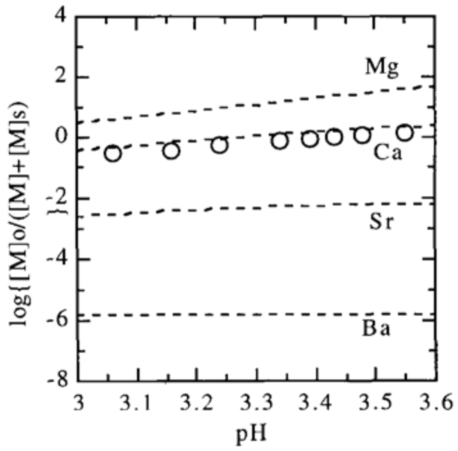

Figure 2. Distribution of Ca between benzene containing TTA and TOPO (10cm³) and aqueous solution (10 cm³) containing $H_2Ti_4O_9 \cdot nH_2O$ (0.1 g) as a function of pH. The dotted lines denote theoretical values.

Table 3. Summary of the theoretical separation factors in logarithm given by the ion exchange and solvent extraction reactions

	Mg/Ca	Ca/Sr	Sr/Ba
log Sf	3.14	2.72	3.64

To separate Ca^{2+} and Sr^{2+}, the triple phase separation system was applied to partition Ca^{2+} into the organic phase and Sr^{2+} onto the ion exchange material. Table 3 shows the theoretical values of the separation factors calculated on the basis of Tables 1 and 2. Even for the combination of Ca-Sr, the separation factor is more than 500 and it is large enough to obtain quantitative separation. Figure 2 gives the values of log $[M]_o / ([M]_{aq} + [M]_s)$ for Ca^{2+} against pH in the aqueous solution, together with the theoretical values with dotted lines for the other alkaline earth metal ions using the values in Table 3. The concentrations of TTA and TOPO in the organic phase were adjusted to 0.2 mol dm^{-3} to optimize the separation conditions. The distribution behavior of Sr^{2+} was also examined in this system. The values of log $[M]_o / ([M]_{aq} + [M]_s)$ for Sr^{2+} were found to be below -2. The concentration of Sr^{2+} in the organic and aqueous phases was too low to obtain the correct values.

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