

Improved Extraction-Separation Utilizing Macrocylic Ionophores as Ion-Size Selective Masking Reagents

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Improved extraction-separation could be achieved in the extraction of alkaline earths with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and tri-n-octylphosphine oxide by adding macrocylic ionophore such as 18-crown-6 or cryptand [2.2.2] to the aqueous phase as an ion-size selective masking reagent. The larger the ionic radius is, the higher pH region the extraction moved to. Consequently, the separation among the metal ions was enhanced markedly.

Keywords: Solvent extraction / Separation / Masking effect / Macrocylic ionophore / Ion-size selectivity

Application of a masking effect to the solvent extraction method is an effective means for a selective separation of metal ions. In the solvent extraction of alkali, alkaline earth and lanthanide metal ions with the chelating reagents, metal ions having smaller ionic radii exhibit higher extractability. On the other hand, the stability in the complex formation between the macrocylic ionophores and the above mentioned metal ions exhibits a quite different tendency. Thus, the solvent extraction system of high selectivity could possibly be developed by the combination of the chelating reagents and the macrocylic ionophores. 18-Crown-6 and cryptand [2.2.2] have been shown to be useful ion-size selective masking reagents in the synergistic extraction of alkaline earths into cyclohexane with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) and tri-n-octylphosphine oxide (TOPO).[1-4] In the present work, a novel macrocycle application has been proposed.

Extraction of alkaline earths in the presence of 18-

crown-6. The results for the extraction of alkaline earths with 0.05 M HPMBP and 0.01 M TOPO into cyclohexane in the absence (blank symbols) and presence (solid symbols) of 18-crown-6 (0.03 M) are shown in Figure 1. Alkaline earths were extracted in the order, $Mg > Ca > Sr > Ba$, which is the same order that the ionic radius decreases. When 0.03 M 18-crown-6 was added to the aqueous phase, the extractions were made in the higher pH region. The larger the ionic radius is, the higher pH region the extraction moved to. As a result, the separation among alkaline earths especially for Ca/Sr and Sr/Ba has been improved. It is clear that 18-crown-6 works as an ion-size selective masking reagent in the aqueous phase.

In the synergistic extraction of alkaline earths (M^{2+}) with HPMBP (HA) and TOPO (L), the extraction equilibrium and the extraction constant, $K_{ex,s}$, can be written as follows:



$$K_{ex,s} = D[H^+]^2 / [HA]_o^2 [L]_o^s \quad (2)$$

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Scope of research

Our research activities are concerned in selective complex formation systems. Major subjects of the research are followings: (1) Design and synthesis of the selective complex formation systems. Ligands that have novel functions in separation of metal ions and guest molecules are designed and synthesized. Their functions are analyzed basing on structures of the ligands and complexes. (2) Biogeochemistry of trace elements in the hydrosphere. Novel analytical methods for trace elements are developed. The behavior of trace elements in the hydrosphere is explored.



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where subscript o denotes the species in the organic phase and D is defined as $[MA_2L_s]_o/[M^{2+}]$.

The distribution ratio in the presence of 18-crown-6 (CE), D^* , can be expressed in eq 3.

$$D^* = [MA_2L_s]_o / \{[M^{2+}] + [M(CE)^{2+}]\} \\ = K_{ex,s} [HA]_o^2 [L]_o^s / [H^+]^2 \{1 + \beta[CE]\} \quad (3)$$

The separation factor, SF, between two metal ions, M1 and M2, is defined as the difference of the logarithmic value of the respective distribution ratio.

$$SF = \log (D_{M1}/D_{M2}) = \log (K_{ex,s,M1}/K_{ex,s,M2}) \quad (4)$$

The separation factor in the presence of crown ether, SF^* {(defined as $\log (D^*_{M1}/D^*_{M2})$ }, is written in eq 5 when s1 and s2 are the same and [CE] is high enough.

$$SF^* = \log (K_{ex,s,M1}/K_{ex,s,M2}) (\beta_{M2}/\beta_{M1}) \quad (5)$$

Comparing eqs 5 and 6, the separation factor can be improved as much as β_{M2}/β_{M1} . Separation factors in the presence and absence of crown ether are seen in ref. 2.

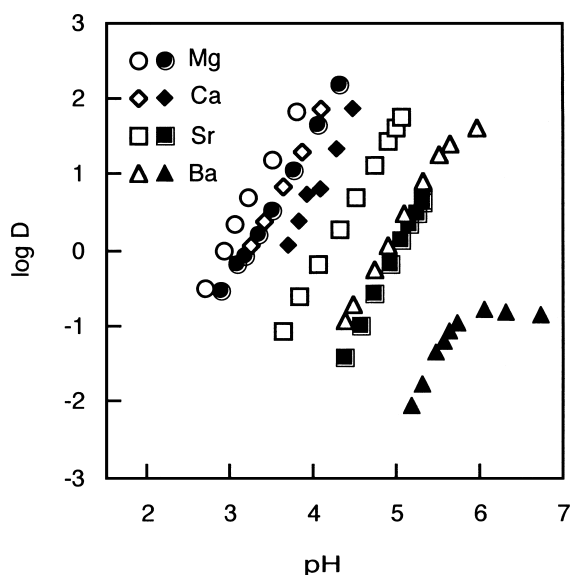


Figure 1 Extraction of alkaline earths in the absence and presence of 18-crown-6.

Extraction of alkaline earths in the presence of cryptand [2.2.2]. Diazapolyoxabicyclic ligands (cryptands) exhibit a prominent selectivity for alkali and alkaline earth metals. They are soluble in water and their stability in complexation is large enough for using as a practical masking reagent. Incorporating nitrogens as an element constituting the ring structure, the masking effect of cryptands depends on a pH unlike crown ethers such as 18-crown-6. Cryptand [2.2.2] should be the most suitable masking reagent for separating Ca and Sr in the series of alkaline earths. The extraction with 0.01 M HPMBP and 0.01 M TOPO into cyclohexane in the absence and presence of 0.01 M cryptand [2.2.2] has been examined. The extraction behaviors for Mg and Ca in the presence of cryptand [2.2.2] are quite similar to those in

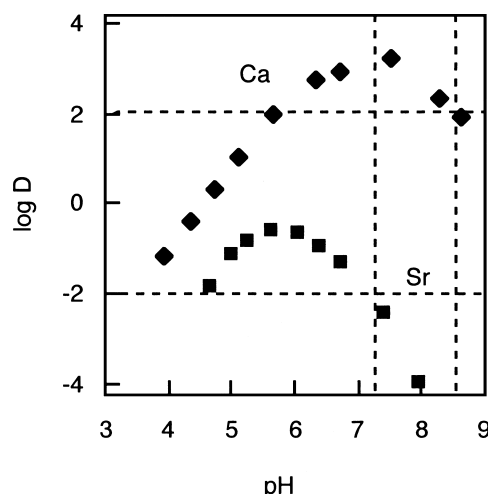


Figure 2 Quantitative extraction-separation of calcium from strontium.

the absence of cryptand [2.2.2]. The log D values for Sr in the presence of cryptand [2.2.2] increase as the pH increases similarly to those in the absence of cryptand [2.2.2], then begin to decrease over pH 5. The log D values for Ba in the presence of cryptand [2.2.2] deviate from those in the absence of cryptand [2.2.2] over pH 4.5.

The results obtained indicate that the masking effect by cryptand depends on the stability in complexation and on the pH. The extraction behaviors in the presence and absence of cryptand can be predicted by taking the above equilibrium and the concentrations of the reagents into consideration. In order to establish the quantitative extraction-separation system for Ca and Sr, the extraction was made reducing the concentrations of HPMBP and TOPO to 4×10^{-3} M keeping the initial concentration of cryptand at 1×10^{-2} M. As shown in Fig. 2, the distribution ratio of Sr decreases rapidly over pH 5.6 as expected, while that of Ca still increases by pH 7.5. Ca can be separated from Sr quantitatively at the pH range 7.2 to 8.6 where more than 99% of Ca ($\log D > 2$) is extracted into cyclohexane, while more than 99% of Sr ($\log D < -2$) remains in the aqueous phase at the same time. A careful control of pH at 7.8 could lead to the best separation; 99.9% extraction of Ca ($\log D > 3$) remaining 99.9% of Sr ($\log D < -3$) in the aqueous phase.

References

1. Umetani S, Matsui M, and Tsurubou S, *J. Chem. Soc., Chem. Commun.*, 914-916 (1993).
2. Tsurubou S, Mizutani M, Kadota Y, Yamamoto T, Umetani S, Sasaki T, Le T. H. Q, and Matsui M, *Anal. Chem.*, **67**, 1465-1469 (1995).
3. Sasaki T, Umetani S, Matsui M, and Tsurubou S, *Chem. Lett.*, 1195-1198 (1994).
4. Tsurubou S, Umetani S and Komatsu Y, *Anal. Chim. Acta*, **394**, 317-324 (1999).