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Quantitative Extraction-Separation of Calcium and Strontium Using Cryptand [2.2.2] as a Masking Reagent

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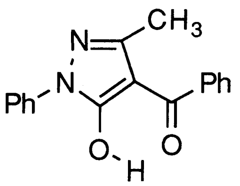
Cryptand [2.2.2] has been applied as an ion-size selective masking reagent with the aim of establishing a highly selective extraction-separation system. Calcium can be readily and quantitatively separated from strontium and barium in the synergistic solvent extraction with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) and tri-n-octylphosphine oxide (TOPO) using 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo-[8,8,8]-hexacosane (cryptand [2.2.2]) as a masking reagent.

Much attention has been devoted to a design of ligands and solvent extraction systems of high selectivity. It could possibly lead to a quantitative extraction-separation of metal ions using water-soluble ligand whose ion-size selectivity is quite opposite to conventional chelating reagents. The present work proposes for the first time a novel use of cryptands to establish a highly selective extraction system.

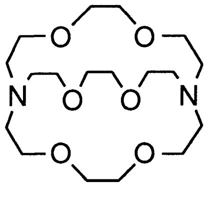
Diazapolyoxabicyclic ligands (cryptands) exhibit a prominent selectivity for alkali and alkaline earth metals. They are soluble in water and their stability in complexation is large enough for using as a practical masking reagent. Their selectivity for metal ions depends largely on the size of the ring,1) and therefore, one can choose an appropriate cryptand according to this purpose. 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. Consequently, the selection of cryptand and extraction reagents, as well as the control of the concentrations of the reagents and the pH, is significant for designing a highly selective extraction system. In the present work, the possible use of cryptand for the extraction-separation system of high selectivity has been presented with the combination of HPMBP and TOPO, which had been reported to be able to extract alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) quantitatively from a lower pH region.2,3) Cryptand [2.2.2] should be the most suitable masking reagent for separating calcium and strontium in the series of alkaline earths.1)



1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP)

$(C_8H_{17})_3P = O$

tri-n-octylphosphine oxide (TOPO)



cryptand [2.2.2]

Figure 1 shows the results for the extraction of magnesium, calcium, strontium and barium with 0.01 mol dm^{-3} HPMBP and 0.01 mol dm^{-3} TOPO into cyclohexane in the absence (blank symbols) and presence (solid symbols) of 0.01 mol dm^{-3} cryptand [2.2.2].4) Logarithm of the distribution ratio of metal ions between the organic and the aqueous phase, D, is plotted against the pH. The slopes of the straight portion of the plots are two, indicating that two protons are released through the extraction reaction. The extraction behaviors for magnesium and calcium in the presence of cryptand [2.2.2] are quite similar to those in the absence of cryptand [2.2.2]. The log D values for strontium 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 barium in the presence of cryptand [2.2.2] deviate from those in the absence of cryptand [2.2.2] over pH 4.5.

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

$$M^{2+} + 2A^- + sTOPO_o \rightleftharpoons MA_2(TOPO)_{s,o} \qquad (1)$$

$$K_{ex,s} = [MA_2(TOPO)_s]_o / [M^{2+}][A^-]^2[TOPO]_o^s$$

$$= D / [A^-]^2[TOPO]_o^s \qquad (2)$$

where subscript o denotes the species in the organic phase and D is defined as $[MA_2(TOPO)_s]_o/[M^{2+}]$. The number of TOPO units in the adduct is two per metal for magnesium, calcium and strontium and three for barium. The extraction was very poor in the absence of TOPO, for the remaining water molecules in the chelate reduces hydrophobicity. It is necessary to add TOPO in order to replace the water molecules with TOPO. The concentration of A^- can be obtained by the initial concentration of HA ($[HA]_{ini}$), the acid dissociation constant (K_a, defined as $[H^+]\,[A^-] / [HA]$), and the partition constant (P_{HA}, defined as $[HA]_o / [HA]$), as follows:

$$[A^-] = [HA]_{ini} / \{1+[H^+]\,(1+P_{HA})K_a^{-1}\} \qquad (3)$$

where K_a and P_{HA} are $10^{-3.92}$ and $10^{2.33}$.5) The log $K_{ex,s}$ values were obtained from Fig. 1 and Eq. 2 on the basis of the known s values and are summarized in Table 1. The distribution ratio of metal ion in the presence of cryptand [2.2.2] (L), D^*, can be described in Eq. 4. The formation of protonated complexes, $[MLH^{3+}]$ and $[MLH_2^{4+}]$, was reported to be negligible.1)

$$D^* = [MA_2(TOPO)_s]_o / ([M^{2+}]+[ML^{2+}])$$

$$= K_{ex,s}\,[A^-]^2[TOPO]_o^s / (1+ß[L]) \qquad (4)$$

where

$$ß = [ML^{2+}] / [M^{2+}][L] \qquad (5)$$

The concentration of the neutral form of cryptand [2.2.2] at a given pH is obtained by the first and the second acid dissociation constants, K_1 and K_2, and the initial concentration of cryptand [2.2.2], $[L]_{ini}$, as follows:

$$[L] = [L]_{ini}\,K_1K_2 / (K_1K_2+K_1[H^+]+[H^+]^2) \qquad (6)$$

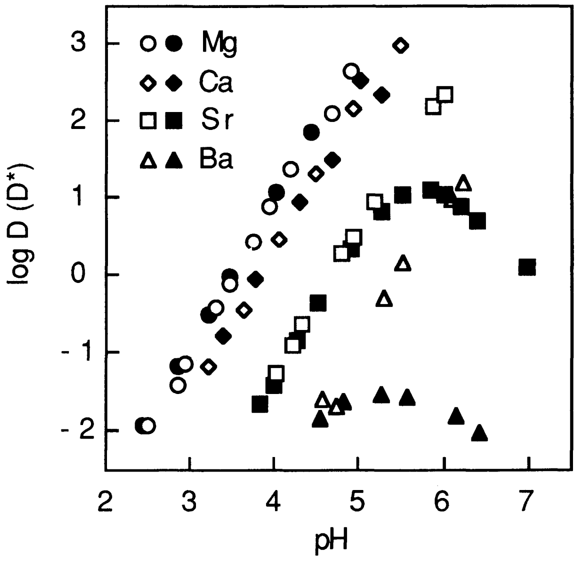


Fig. 1. Extraction of alkaline earths with HPMBP (HA) and TOPO in the absence (blank symbols) and presence (solid symbols) of cryptand [2.2.2] (L). $[HA]_o=[TOPO]_o=1\times10^{-2}$ mol dm^{-3} in cyclohexane, $[L]=1\times10^{-2}$ mol dm^{-3} in an aqueous phase.

where K_1 and K_2 are $10^{-7.28}$ and $10^{-9.60}$.1) The distribution of the neutral cryptand between the cyclohexane and aqueous phase was investigated spectrophotometrically.6) About 2% of cryptand [2.2.2] was found to distribute into the cyclohexane phase at pH 12 where the protonated species is negligible. Thus, the distribution of cryptand [2.2.2] can be considered negligible at the pH region employed in the present work where considerable part of cryptand is protonated.

Dividing D by D^* gives Eq. 7.

$$D / D^* = 1 + \beta [L] \qquad (7)$$

Figure 2 illustrates the plots of log D/D^* vs. log [L] for $[\mathrm{HPMBP}]_0 = [\mathrm{TOPO}]_0 = 0.01$ mol dm^{-3}. [L] was calculated according to Eq. 6 at each pH. The slopes of the plots increase as [L] increases and are unity in the higher [L] range. The values of log ß were obtained from the straight portion of the plots in Fig. 2 and are summarized in Table 1. These values are in good agreement with the previously reported data.1) Cryptand [2.2.2] is suitable as a masking reagent for calcium and strontium, because the log ß values increase in the order, Mg<Ca«Sr<Ba, which is the opposite order to that of the conventional chelating reagents.

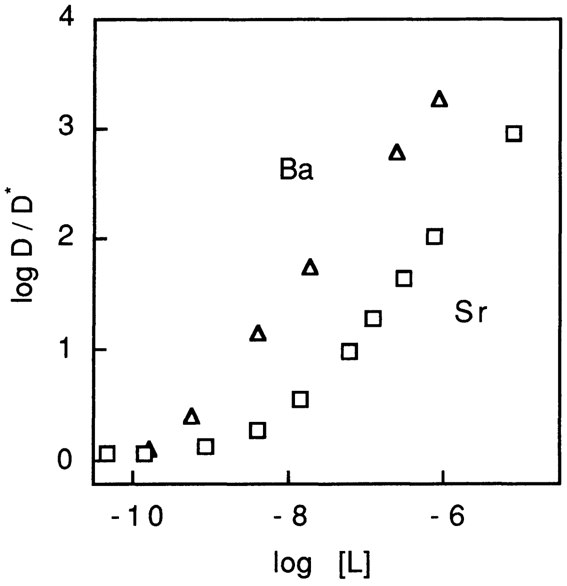


Fig. 2. Plots of log (D/D*) vs. log [L] for strontium and barium.

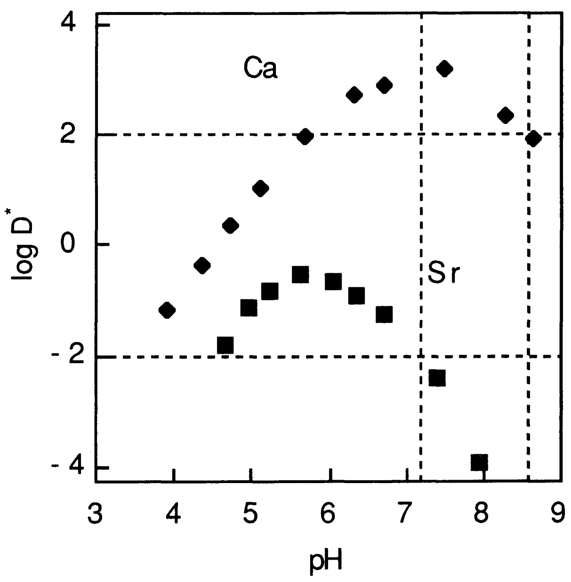


Fig. 3. Extraction of calcium and strontium with HPMBP and TOPO in the presence of cryptand [2.2.2]. $[\mathrm{HA}]_0 = [\mathrm{TOPO}]_0 = 4 \times 10^{-3}$ mol dm^{-3}, $[\mathrm{L}] = 1 \times 10^{-2}$ mol dm^{-3}.

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 calcium and strontium, the extraction was made reducing the concentrations of HPMBP and TOPO to 4×10^{-3} mol dm^{-3} keeping the initial concentration of cryptand at 1×10^{-2} mol dm^{-3}. As shown in Fig. 3, the distribution ratio of strontium decreases rapidly over pH 5.6 as expected, while that of calcium still increases by pH 7.5. Calcium can be separated from strontium quantitatively at the pH range 7.2 to 8.6 where more than 99% of calcium (log D > 2) is extracted into cyclohexane, while more than 99% of strontium (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 calcium (log D > 3) remaining 99.9% of strontium (log D < -3) in the aqueous phase.

Table 1. Extraction constants and stability constants for alkaline earths

	log $K_{ex,s}$	s	log ß	log ß[a)]
Mg^{2+}	13.45	2	—	<2
Ca^{2+}	12.85	2	—	4.4
Sr^{2+}	11.19	2	8.20	8.0
Ba^{2+}	9.70	3	9.47	9.5

a) Taken from Ref. 1.

The use of the combination of the chelating reagents and cryptand [2.2.2] having an opposite complexation tendency has been proved to be a powerful means to separate metal ions. Among the macrocyclic ligands, cryptands would be one of the most effective ligands for this purpose owing to their high selectivity for metal ions and high solubility in water. The fairy large proton affinity would prefer the extracting reagent of a weak acidity that is expected to make the extraction in a higher pH region. The extraction-separations of metal ions with a weakly acidic extractant using a variety of cryptand are now under examination. The target are also expanding, for example, to alkali and rare earths metals.

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References

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4) pH was adjusted with tetramethylammonium hydroxide and hydrochloric acid solution. 0.01 mol dm^{-3} Good's buffer was used as a buffer component. The ionic strength of the aqueous phase was controlled at 0.1 with tetramethylammonium bromide. The concentrations of metal ions were $1x10^{-5}$ to $1x10^{-4}$ mol dm^{-3}. It took several hours to reach to equilibrium for strontium and barium owing to the slow reaction with cryptand. Shaking time of 24 h was found to be long enough for equilibration.
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