Separation of Alkaline Earth Metal Ions with a Strongly Acidic Cation Exchange Resin Using the Diazapolyoxabicyclic Ligand as an Ion Size Selective Masking Reagent

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An ion-exchange separation method for alkaline earth metal ions (Mg²⁺, Ca²⁺ and Sr²⁺) is described. The highly selective separation of Mg²⁺ from Ca²⁺ and Sr²⁺ has been achieved with a strongly acidic cation exchange resin (Amberlite 200CT) in the presence of cryptand [2.2.1] as the ion-size selective masking reagent. The quantitative separation of Sr²⁺ from Mg²⁺ and Ca²⁺ could be achieved using Amberlite 200CT in the presence of cryptand [2.2.2].

1. Introduction

Conventional strongly acidic cation exchange resins, such as the commercially available Amberlite 200CT and Dowex 50W, can adsorb alkaline earth metal ions. Generally, in the ion-exchange reaction, metal ions having smaller ionic radii exhibit lower distribution ratios. However, mutual separation of the alkaline earth metal ions is difficult to obtain with strongly acidic cation exchange resins. On the other hand, it is well known that crown ethers and diazapolyoxabicyclic ligands such as cryptand [2.2.1] and cryptand [2.2.2] exhibit a significant selectivity for alkali and alkaline earth metal ions [1-3]. Their selectivity for metal ions depends largely on the size of the cavity, therefore, one can choose an appropriate cryptand according to requirements. The combination of ion-exchange resins and cryptands as ion size selective masking reagents could be expected to achieve a more selective or quantitative separation system. This concept has already been applied successfully and reported in the solvent extraction systems of alkali and alkaline earth metal ions [4], and some divalent and tervalent metal ions [5].
2. Experimental

2.1 Apparatus

The concentrations of the metal ions in the aqueous phase were determined using an atomic absorption spectrophotometer (Shimadzu, Model AA-660). pH measurements were made with a Horiba (Model F-22) pH meter after shaking. A Taitec (Model BR-30LF) bioshaker was used to equilibrate the aqueous phase and the ion-exchange resin at a controlled temperature.

2.2 Reagents and the ion-exchanger

Cryptand [2.2.2] and [2.2.1] were purchased from Merck, and other chemicals were of analytical-reagent grade. Distilled and de-ionized water was used throughout. Amberlite 200CT(Na), the ion-exchanger used in this study, was purchased from Organo. Amberlite 200CT(Na) is a macroreticular strong acid cation exchange resin based on sulfonic acid groups on a polystyrenic matrix; total exchange capacity ≥ 1.70 eq/L (Na⁺ form), harmonic mean size 0.60 – 0.85 mm. This ion-exchanger was dried at 80 °C for 6 hrs after conditioning with dilute hydrochloric acid solution and sodium chloride solution in order to completely convert the resin to the sodium form.

2.3 Procedure

A 5-ml portion of an aqueous phase containing the required amount of the metal ion (2 × 10⁻⁴ M), cryptand [2.2.1] or [2.2.2] (0.02 M) and 0.02 M Good’s buffer such as tris(hydroxymethyl)aminomethane was adjusted to the desired pH with hydrochloric acid and tetramethyl ammonium hydroxide. The aqueous phase was shaken for 3-5 hrs until the reaction reached equilibrium with the required amount of ion-exchange resin (0.02 g) at 25±1 °C. After centrifugation of the mixture, the pH of the aqueous phase was measured. The metal concentration in the aqueous phase was determined by atomic absorption spectrophotometry and the amount of the metal ions adsorbed onto the ion-exchanger resin was calculated from the concentrations in the aqueous phase before and after reaction.

3. Results and Discussion

It is known that conventional strongly acidic cation exchange resins, such as the commercially available Amberlite 200CT and Dowex 50W, can readily adsorb alkaline earth metal ions. In fact, a preliminary examination showed that the alkaline earth metal ions such as Mg²⁺, Ca²⁺ and Sr²⁺ are adsorbed quantitatively onto Amberlite 200CT without mutual selectivity.

On the other hand, complex formation of the alkali, alkaline earth and lanthanide metal ions with diazapolyoxabicyclic compounds (Cryptands) exhibits a quite different tendency. Their selectivity for metal ions depends largely on the ring size, and therefore, one can choose an appropriate Cryptand according to requirements. The stability constants of cryptand [2.2.1] and [2.2.2] for alkaline earth metal ions are shown in Table 1, as already reported by J. M. Lehn et al [6].

The stability constants in Table 1 show considerable differences between Mg²⁺ and Ca²⁺ with
cryptand [2.2.1], and between Ca\(^{2+}\) and Sr\(^{2+}\) with cryptand [2.2.2]. Consequently in this study, cryptand [2.2.1] has been applied as the masking reagent in the ion exchange separation of Mg\(^{2+}\) from Ca\(^{2+}\) and Sr\(^{2+}\), and cryptand [2.2.2] for Sr\(^{2+}\) from Mg\(^{2+}\) and Ca\(^{2+}\).

### Table 1. Stability constants (log β)

<table>
<thead>
<tr>
<th></th>
<th>Mg(^{2+})</th>
<th>Ca(^{2+})</th>
<th>Sr(^{2+})</th>
<th>Ba(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cryptand [2.2.1]</td>
<td>&lt; 2</td>
<td>6.95</td>
<td>7.35</td>
<td>6.30</td>
</tr>
<tr>
<td>Cryptand [2.2.2]</td>
<td>&lt; 2</td>
<td>4.4</td>
<td>8.0</td>
<td>9.5</td>
</tr>
</tbody>
</table>

At first the effect of adding 2-propanol to the aqueous phase has been examined. Figure 1 shows the effect of the percentage of 2-propanol on the adsorption of Sr\(^{2+}\) onto Amberlite 200CT as a function of pH in the presence of cryptand [2.2.1]. By adding 2-propanol to the aqueous phase, the masking effect of the cryptands is enhanced resulting in a decrease in the percent adsorption of Sr\(^{2+}\). This can be explained by the fact that lower dielectric solvents are less capable of solvating cations, thus favoring their complex formation with cryptands in the aqueous phase [7].

![Figure 1](image1.png)  
**Figure 1.** Effect of 2-propanol on the adsorption of Sr\(^{2+}\). Amberlite200CT(Na) = 0.02 g in 5 ml aqueous phase, [Sr\(^{2+}\)] = 2x10\(^{-4}\) M, [2.2.1]=0.02 M.

Figure 2 shows the results for the percent adsorption of alkaline earth metal ions onto Amberlite 200CT as a function of pH in the presence of cryptand [2.2.1]. As shown in Figure 2, the percent adsorption of Ca\(^{2+}\) and Sr\(^{2+}\) decreased sharply above pH 6, while that of Mg\(^{2+}\) was almost similar to that in the absence of cryptand [2.2.1]. The separability of Mg\(^{2+}\) from Ca\(^{2+}\) and Sr\(^{2+}\) improved in the pH range from 6 to 8 where almost 100 % of Mg\(^{2+}\) is adsorbed by the resin, while more than 75 – 85 % of Ca\(^{2+}\) and
Sr$^{2+}$ remains in the aqueous phase.

Figure 2. Adsorption of alkaline earth metal ions. Amberlite200CT(Na) = 0.02 g in 5 ml aqueous phase, \([M^{2+}] = 2 \times 10^{-4} \text{ M}, [2.2.1] = 0.02 \text{ M}, 2\text{-propanol 30\%} \).

Figure 3 shows the results for the percent adsorption of alkaline earth metal ions onto Amberlite 200CT as a function of pH in the presence of cryptand [2.2.2]. Sr$^{2+}$ can be readily separated from Mg$^{2+}$ and Ca$^{2+}$ in the pH range from 6 to 8, where more than 95\% of Mg$^{2+}$ and Ca$^{2+}$ are adsorbed onto the resin, while 100\% of Sr$^{2+}$ remains in the aqueous phase.

The masking effect with cryptands depends on the pH unlike crown ethers, because they incorporate nitrogen atoms in the ring structure. Then, cryptands exist in the protonated form at lower pH values and release hydrogens stepwise to give the neutral form, which reacts with metal ions, as the pH increases. The
pK\textsubscript{a1} and pK\textsubscript{a2} values for cryptand [2.2.1] are reported to be 7.50 and 10.53, and for cryptand [2.2.2] 7.28 and 9.60 [6]. Accordingly, the adsorption of Ca\textsuperscript{2+} and Sr\textsuperscript{2+} in Figure 2, and that of Sr\textsuperscript{2+} in Figure 3 began to decrease sharply as the pH increased. The reason why the adsorption increases again as the pH increases is not clear. The formation of metal hydroxides which would be possibly seen at higher pH values could participate in the present adsorption system.

4. Conclusion

The highly selective separation of Mg\textsuperscript{2+} and Sr\textsuperscript{2+} has been successfully developed using the ion-exchange resin, Amberlite 200CT, in the presence of cryptand [2.2.1] and cryptand [2.2.2], respectively, as the ion-size selective masking reagents. By adding 2-propanol to the aqueous phase, Mg\textsuperscript{2+} can be over 80% separated from Ca\textsuperscript{2+} and Sr\textsuperscript{2+} in the pH range 6 - 8. Sr\textsuperscript{2+} can be separated quantitatively from Mg\textsuperscript{2+} and Ca\textsuperscript{2+} in the pH range 6 - 8.

References