Solid-Phase Extraction of Lithium in Seawater with Porous Polymer Resin Impregnated with Lithium-Ion Selective Metallohost

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Abstract

The solid-phase extraction of Li⁺ in aqueous solution using a porous polymer resin (Diaion® HP2MG) impregnated with a Li⁺-selective metallohost, [Ru(DMA)(pyO₂)]₀ (DMA = 3,5-dimethylanisole, pyO₂ = 2,3-pyridinediolate), was investigated. Compared with the solvent extraction using an organic solvent solution of the same metallohost, the solid-phase method exhibited much faster extraction of Li⁺ but lower Li⁺/Na⁺ selectivity. The proposed method was applied successfully to the separation of Li⁺ in artificial seawater prior to the flame photometric determination.

Key Words: Lithium, Metallohost, Solid-phase extraction, Seawater

1. Introduction

In recent years, lithium (Li) has attracted much attention as a material for use in secondary batteries, and demand has increased rapidly. At present, Li is mainly extracted from natural brines or saline waters. Seawater is also expected as a future source. In relation, the determination of Li⁺ in saline waters becomes an important matter. It is, however, often difficult because saline waters generally contain high concentrations of Na⁺ that causes not only analytical interference but also damage to the instruments used. We recently reported a new metallohost compound, [Ru(DMA)(pyO₂)]₀ (Fig. 1), which captures Li⁺ with extremely high selectivity. We also developed an extraction-spectrophotometric method using this metallohost for the separation and determination of sub-ppm level Li⁺ in saline waters. However, this method has a few problems, i.e., the use of a flammable and harmful organic solvent and the slow extraction rate. In this study, we prepared a solid-phase extractant by impregnating a porous polymer resin with the metallohost to develop a rapid and safe separation method for Li⁺ in saline waters.

2. Experimental

[Ru(DMA)(pyO₂)]₀ was prepared as described previously. Diaion® HP2MG, a macroporous methacrylate resin, was purified by immersing in a MeOH: 4 M HCl (1:1, v/v) solution for 24 h, washing with water, and drying. The resin (1.6 g) was immersed in an EtOH solution (40 cm³) of 0.016 M metallohost for 1 h. After evaporation, the residue was washed with water and dried in vacuo on P₂O₅. The metallohost in the dry resin was 18 ± 2 % (0.16 ± 0.02 mmol/g).

The extraction was conducted by mechanically shaking a stoppered test tube in which a solution (1.5-2.0 cm³) containing 1.0 mM Li picrate or Na picrate and the resin (0.050-0.24 g) impregnated with the metallohost were placed. The metals in the aqueous phase were determined by flame photometry and the extraction percentage was calculated.

The washing of the resin after the extraction was performed in a syringe with a glass fiber filter of 1-µm pore size for several times; 3 cm³ of deionized water was used for each washing. The elution of the metal ions from the resin was done in a similar way; 3 cm³ of MeOH was used for each elution.

3. Results and Discussion

First, the solid-phase extraction experiments were conducted at 25 ºC for a 1.0 mM Li picrate solution with different shaking times (1-6 h). The amount of the resin used was 0.033 g per 1.0 cm³ of the aqueous solution. The result is
shown in Fig. 2. The extraction percentage of \( \text{Li}^+ \) becomes a constant value (ca. 85%) with 3 h or more of shaking time. The shaking time required for equilibrium is much shorter than that for the solvent extraction using an organic solvent solution of the same metallohost (\( > 8 \) h)\(^2,3\)). The fast extraction in the solid-phase extraction may be explained based on the metallohost concentration at the two-phase interface where the complex formation with \( \text{Li}^+ \) occurs. All the metallohost molecules exist on the surface of the macroporous resin in the solid-phase extraction, whereas they are mostly in the bulk organic phase in the solvent extraction. Furthermore, the solid-phase extraction was conducted at 50 °C, keeping the other conditions unchanged; the result is shown in Fig. 2. Equilibrium is attained within 1 h of shaking.

In order to enhance the extraction percentage, the amount of the resin was increased to 0.12 g per 1.0 cm\(^3\) of the aqueous solution. A shorter shaking time region (5-60 min) was examined at 50 °C. The extraction of \( \text{Na}^+ \) picrate was also conducted. The results are shown in Fig. 3. As expected, \( \text{Li}^+ \) is quantitatively extracted by only 15-min shaking. On the other hand, the extractability of \( \text{Na}^+ \) decreases with increasing shaking time, and the extraction percentage is 14% by 60-min shaking. Considering the \( \text{Li}^+ /\text{Na}^+ \) separation efficiency, the following experiments were conducted by shaking the resin with a sample solution (ratio: 0.12 g/1.0 cm\(^3\)) for 30 min at 50 °C. Under these conditions, the \( \text{Li}^+ /\text{Na}^+ \) separation factor is 66, which is much lower than that observed for the solvent extraction (\( > 10^4 \))\(^2,3\). The lowered selectivity was found to be mainly caused by the \( \text{Na}^+ \) extraction with the HP2MG resin itself.

To remove the \( \text{Na}^+ \) extracted on the solid phase, the solid phase (0.24 g) was washed with water; about 50% of \( \text{Na}^+ \) was removed after three-times washing with water (3 cm\(^3\) for each washing step). At this time, the loss of \( \text{Li}^+ \) was negligibly small. The selective removal of \( \text{Na}^+ \) suggests that \( \text{Li}^+ \) and \( \text{Na}^+ \) are captured at different sites of the metallohost\(^4\).

The elution of \( \text{Li}^+ \) from the resin was also examined; \( \text{Li}^+ \) was nearly quantitatively eluted after three-times elution with MeOH (3 cm\(^3\) for each elution step).

The method of the solid-phase extraction followed by the washing and elution steps was applied to the separation of \( \text{Li}^+ \) from artificial seawater (JIS K 2510). As a sample solution, a mixture of 0.8 cm\(^3\) of the artificial seawater containing 0.18 ppm \( \text{LiCl} \) and 1.2 cm\(^3\) of 0.020 M aqueous \( \text{Na}^+ \) picrate solution was used. Based on flame photometric analysis of the eluted solution, the \( \text{Li}^+ \) concentration in the artificial seawater was determined to be 0.20 ± 0.01 ppm, showing quantitative extraction and elution of \( \text{Li}^+ \). Therefore, this solid-extraction method has a potential to be applied as a separation method prior to the instrumental analysis of \( \text{Li}^+ \) in saline waters.

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**References**


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