

Selective Separation and Uptake of Potassium Ions from Seawater

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ABSTRACT

There are only a few inorganic cation exchangers capable of efficiently separate specific cation from systems in which analogous cations coexist. For example it is difficult to selectively take up K^+ ions in the presence of a large excess of Na^+ ions although the effective ionic size of K^+ ion in aqueous solution is different from that of Na^+ ion.

Among the synthesized inorganic ion-exchangers, sodium ion-exchanged taeniolite (Na^+T ; $NaMg_2LiSi_4O_{10}F_2 \cdot 2H_2O$), lithium ion-exchanged taeniolite (Li^+T ; $LiMg_2LiSi_4O_{10}F_2 \cdot 2H_2O$), and sodium ion-exchanged hectorite (Na^+H ; $Na_{1/3}Mg_{8/3}Li_{1/3}Si_4O_{10}F_2 \cdot 2H_2O$) were found to be promising and the removal behavior of K^+ ions from a model aqueous solution and practical seawater was examined by using normal batch-and-column methods. Quantitative analyses of the various ions were made by atomic absorption spectroscopy and EDTA titration method. Characterization of the samples was made by X-ray diffraction.

It was found that the $Na^+ \rightleftharpoons K^+$ exchange isotherm on Na^+T rises steeply and attains a plateau above the diagonal line in the initial stages, which reveals that K^+ ions are strongly preferred over Na^+ ions in the low-concentration region of K^+ ions. The order of K^+ ion selectivity was to be $Li^+T \leq Na^+H \ll Na^+T$ in the low-concentration region of K^+ ions. Moreover, the Na^+T was found to selectively take up a constant amount of K^+ ions without depending on the concentrations of Na^+ and K^+ ions in solution.

Taking the results into account we can conclude that Na^+T can be utilized in the separation and uptake of K^+ ions from seawater.

INTRODUCTION

It is difficult to selectively separate and take up small amounts of K^+ ions from seawater in the presence of a large excess of Na^+ ions with similar chemical properties in the periodic table.

During investigations of the cation-exchange characteristics of inorganic ion-exchangers, we have discovered that K^+ ions in aqueous solution are strongly held on some synthetic fluorine tetrasilicic micas by a cation-exchange reaction at room temperature, i.e., some potassium ion-memorizing inorganic ion-exchangers have been prepared (Suzuki et al., 1990).

The purposes of this paper is to examine the interesting K^+ ion-exchange characteristics in detail and to apply the obtained results to the separation and uptake of K^+ ions in seawater (K^+ : 380 ppm, Na^+ : 10,500 ppm).

EXPERIMENTAL

Na^+T , Li^+T and Na^+H samples with layer structures were synthesized by an ordinary fused state

reaction at 1400°C in a platinum crucible, using starting materials such as NaF, LiF, MgO and SiO_2 (Kitajima and Daimon, 1974; 1975). All chemicals were of analytical-reagent grade and were used without further purification. The synthesized samples were ground and repeatedly washed with distilled water and contained impurities such as α -cristobalite and other non-swelling particles which were removed by centrifugation. After this treatment the samples were dried at 80°C under vacuum and stored in a desiccator with 70% relative humidity prior to cation-exchange experiments.

The $Na^+ \rightleftharpoons K^+$ exchange experiments were made by the normal batch method with shaking at 25°C, as described elsewhere (Suzuki et al., 1984). Each 0.1 g specimen was equilibrated in 40 cm³ of NaCl + KCl solution with various ratios of the two salts for 24 h in order to determine the exchange isotherms at constant total molarities of 2.5×10^{-2} , 1.0×10^{-2} and 2.5×10^{-3} M. Na^+T (0.1 g) was also equilibrated in 40 cm³ of NaCl + KCl solution with Na^+/K^+ ratios of 10, 20, and 30 at K^+ ion concentrations of 200, 300, 400 and 500 ppm for 24 h in order to further clarify K^+ ion selectivity in the presence of a large excess of Na^+

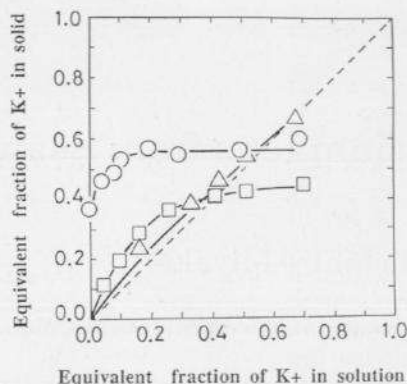


Fig. 1. $\text{Na}^+ \rightleftharpoons \text{K}^+$ exchange isotherms on Na^+T (circles), Na^+H (triangles), and Li^+H (squares) at a constant total molarity of 1.0×10^{-2} M.

ions. After the reaction, the solid and solution phases were separated by centrifugation, and an aliquot of supernatant was collected for chemical analyses. The solutions were analyzed for Li, Na and K by atomic adsorption spectroscopy. At least three replications were carried out in the cation-exchange experiments with concurrent results. The structural changes occurring in the samples before and after the uptake of K^+ ions were investigated using the powder X-ray diffraction method.

RESULTS AND DISCUSSION

The exchange reactions of Na^+T , Na^+H and Li^+T of 1 g with 1.0×10^{-2} M KCl solutions attained to steady states within 8 h and the molar ratios of Na^+/K^+ during the reactions were found to be close to 1.0. The interlayer Na^+ ions of ca. 55% in Na^+T , 75% in Na^+H and 45% in Li^+T , whose theoretical cation exchange capacities are 235, 79 and 245 meq/100 g, respectively, were exchanged for K^+ ions at an equilibrium state. The cation exchange reactions occurred incompletely. This was considered to be due to the fact that it is impossible to synthesize solid-solutions between Na- and K- substitutions over the entire composition range.

The exchange isotherms on Na^+T , Na^+H and Li^+T at a constant total molarity of 1×10^{-2} M are shown in Fig. 1, respectively. The $\text{Na}^+ \leftrightarrow \text{K}^+$ exchange process on mica is presented by



K^+ ions are preferable to Na^+ ions if the exchange isotherm lies above the diagonal line, while Na^+ ions are preferable to K^+ ions if the exchange isotherm lies below the diagonal line and the diagonal line represents no preference between these ions. The

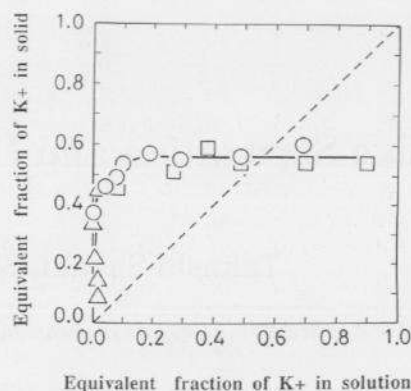


Fig. 2. $\text{Na}^+ \rightleftharpoons \text{K}^+$ exchange isotherms on Na^+T at a constant total molarities of 1.0×10^{-2} (circles), 2.5×10^{-3} (triangles), and 2.5×10^{-2} M (squares).

$\text{Na}^+ \leftrightarrow \text{K}^+$ exchange isotherm on Na^+T rises steeply and attains a plateau above the diagonal line in the initial stages, which reveals that K^+ ions are strongly preferred over Na^+ ions in the low concentration regions of K^+ ions. The $\text{Na}^+ \leftrightarrow \text{K}^+$ exchange isotherm on Na^+H lies just above the diagonal line in almost all concentration regions of K^+ ions, which reveals that K^+ ions are moderately preferred over Na^+ ions. The $\text{Na}^+ \leftrightarrow \text{K}^+$ exchange isotherm on Li^+T lies above the diagonal line in the low concentration regions of K^+ ions, but in the high concentration regions the isotherm lies below the diagonal line. The order of K^+ ions selectivity was, therefore, concluded to be $\text{Li}^+\text{T} < \text{Na}^+\text{H} < \text{Na}^+\text{T}$ in the low concentration regions of K^+ ions. The superior preference for K^+ ions over Na^+ ions on Na^+T was found to be independent of the total molarity as is shown in Fig. 2. The characteristics for the selective K^+ ions uptake of Na^+T were further examined in the presence of a large excess of Na^+ ions. From the results, Na^+T was found to selectively take up a regular amount of K^+ ions without depending on the concentrations of Na^+ and K^+ ions, as is shown in Table 1.

TABLE 1

K^+ Ion selectivity (K^+ uptake, ppm) on Na^+T (0.1 g) in 40 cm^3 of $\text{NaCl} + \text{KCl}$ solutions with an excess of Na^+ ions

Na^+/K^+ ratio	Initial K^+ concentration			
	200 ppm	300 ppm	400 ppm	500 ppm
	K^+ uptake (ppm)	K^+ uptake (ppm)	K^+ uptake (ppm)	K^+ uptake (ppm)
10	110.8	120.7	112.3	125.9
20	112.2	120.7	114.8	123.2
30	112.2	110.0	120.5	124.1

CONCLUSIONS

The order of K^+ ion selectivity was found to be $Li^+T \leq Na^+H \ll Na^+T$ in the low concentration region of K^+ ions, i.e., Na^+T was found to have superior ion-exchange selectivity for K^+ ions in the presence of a large excess of Na^+ ions.

These basic studies suggest that Na^+T has the feasibility to be an excellent ion-exchanger for the selective uptake of K^+ ions in seawater (Na^+ ; 10,500 ppm and K^+ ; 380 ppm; $Na^+/K^+ \approx 28$).

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