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Cesium Ion Sieve Effect of Sodium-Substituted Hectorite

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The cation selectivity of Na-substituted fluormicas, which are swellable with water, has been investigated. Consequently, Na-substituted taeniolite (NaT) has been found to exhibit a remarkable K^+ ion sieve effect in the low-concentration region of K^+ ions.[1,2] In this paper, we report the discovery of an excellent Cs^+ ion sieve effect of Na-substituted hectorite (NaH) with no dependence on the concentration of Cs^+ ions. The Cs^+ ion selectivities of NaT and Na-substituted tetrasilicic mica (NaTS) are also determined and compared with that of NaH. It is of special importance to separate and collect ^{137}Cs from radioactive waste and circulating water in nuclear reactors, because it has a long half-life period and dissolves easily in water.

Na-substituted fluormicas are built by the stacking of complex layers and interlayer sheets. The former consist of two SiO_4 tetrahedral sheets and one (Mg,Li)-$(O,F)_6$ octahedral sheet, and the latter are made by exchangeable Na^+ ions and water molecules. Although the fundamental structures of NaH, NaT, and NaTS are similar to one another, the atomic ratios of Li/Mg in the octahedral sheet are different among these systems. Basal spacings of NaH, NaT, and NaTS, which are estimated from basal reflections, are 12.3 Å at room temperature in 70% relative humidity (rh), and their chemical compositions are ideally as follows: NaH, $Na_{1/3}Mg_{8/3}Li_{1/3}Si_4O_{10}F_2{\cdot}2H_2O$; NaT, $NaMg_2LiSi_4O_{10}F_2{\cdot}2H_2O$; NaTS, $NaMg_{5/2}Si_4O_{10}F_2{\cdot}2H_2O$.[3-5]

NaH, NaT (Topy Ind. Co.), and NaTS (Coop Chemical Ind. Co.) were repeatedly washed with distilled water, and most impurities, namely small amounts of α-cristobalite and other nonswelling particles, were removed by centrifugation prior to cation-exchange experiments. The specimens were dried at 80 °C under vacuum and stored in a desiccator with rh = 70%. The $Na^+ \rightarrow Cs^+$ exchange experiments were made by the normal batch method within fixed times in a shaker with 120 rpm at 25 °C, as described elsewhere.[6] NaH amounts of 0.3 g and NaT and NaTS amounts of 0.1 g were used, because the interlayer Na^+ ions in NaH are one-third as many as those in NaT and NaTS. The rate of cation-exchange reaction on each specimen was measured using 40 cm^3 of 1×10^{-2} N CsCl solution. Each specimen was equilibrated in 40 cm^3 of NaCl + CsCl solution with various ratios of the two salts for 24 h in order to determine the exchange isotherms at a constant total normality of 1×10^{-2} N. The rates of the $(x + y)Na^+ \rightarrow (xK^+ + yCs^+)$ exchange reactions on NaH and NaT were also measured, using 40 cm^3 of KCl + CsCl solution with a K^+/Cs^+ ratio of 1.0 at Cs^+ ion concentration of 1×10^{-2} N in order to further examine Cs^+ ion selectivity on NaH.

After the reaction, the solid and solution phases were separated by filtration and centrifugation, and a part of the supernatant solution was collected for chemical analyses. The solutions were analyzed for Na, K, and Cs by atomic absorption spectroscopy, using a Hitachi 180-30 instrument. The specimens before and after the cation-exchange reactions were characterized by powder X-ray diffraction (XRD), using a Rigaku X-ray diffractometer RINT 1000 with Cu Kα radiation, and by TG-DTA, using a Rigaku PTC 10A instrument with α-Al_2O_3 as reference material. At least two or more replications were carried out in the cation-exchange experiments.

Each sample was identified as a swelling state with a basal spacing of 12.3 Å at room temperature and rh = 70% and confirmed to contain no impurities by XRD. The interlayer Na^+ ion in each sample was estimated to be surrounded by two water molecules from the TG-DTA analysis. The cation-exchange reactions of NaH and NaTS with CsCl solutions attained steady states within 4 h, while that of NaT with CsCl solution attained a steady state within 12 h. The molar ratios of Na^+/Cs^+ during the reactions were found to be close to 1.0.

The interlayer Na^+ ions of ca. 100% in NaH, 50% in NaT, and 46% in NaTS, whose theoretical cation-exchange capacities are 78, 235, and 233 mequiv/100 g, respectively, were exchanged for Cs^+ ions at an equilibrium state. The cation exchange that occurred in NaH was complete, while those in NaT and NaTS were incomplete. XRD revealed that NaH, NaT, and NaTS after Cs^+ uptake maintained the mica structures. Namely, NaH after Cs^+ uptake was identified as CsH with a basal spacing of 10.7 Å, which is nonswellable. The original and Cs phases were observed in NaT and NaTS after Cs^+ uptake.

The exchange isotherms on NaH, NaT, and NaTS at a constant total normality of 1×10^{-2} N are shown in Figure 1. The $Na^+ \rightarrow Cs^+$ exchange process on mica is represented by eq 1. Cs^+ ions are preferable to Na^+ ions

$$Cs^+ + Na{-}mica \rightarrow Na^+ + Cs{-}mica \tag{1}$$

if the exchange isotherm lies above the diagonal line, whereas Na^+ ions are preferable to Cs^+ ions if the exchange isotherm lies below the diagonal line, and the diagonal line represents no preference between these ions.[7]

The $Na^+ \rightarrow Ca^+$ exchange isotherm on NaH rose steeply and attained $\overline{X}_{Cs} = 1.0$ in the initial stage, where $\overline{X}_{Cs}$ is the equivalent Cs^+ fraction in the mica.

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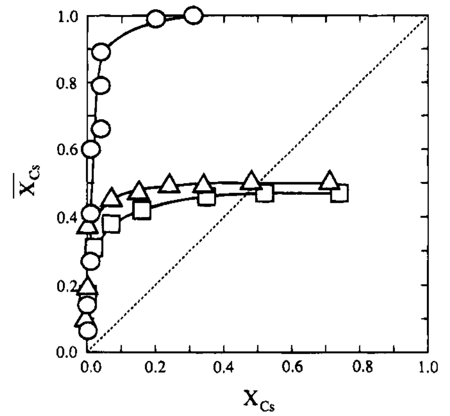

Figure 1. $Na^+ \rightarrow Cs^+$ exchange isotherms on NaH (○), NaT(△), and NaTS(□) at a constant total normality of 1×10^{-2} N.

This means that Cs^+ ions are strongly preferred over Na^+ ions. The $Na^+ \rightarrow Ca^+$ exchange isotherms on NaT and NaTS rose steeply and attained plateaus above the diagonal line in the initial stages, which also suggest that Cs^+ ions are strongly preferred over Na^+ ions in the low-concentration region of Cs^+ ions. They, however, lay below the diagonal line in the ranges $X_{Cs} > 0.50$ for NaT and $X_{Cs} > 0.46$ for NaTS, respectively, where X_{Cs} is the equivalent Cs^+ fraction in solution. These data indicate that Na^+ ions were preferred over Cs^+ ions in the high-concentration region of Cs^+ ions and are due to the incompleteness of the cation-exchange reactions.

The Cs^+ ion selectivity is more clearly depicted with a Kielland plot[2,8] obtained from the cation-exchange isotherm. The Kielland plots for $Na^+ \rightarrow Cs^+$ exchanges on NaH, NaT, and NaTS are shown in Figure 2. The corrected selectivity coefficient, K_{Na}^{Cs}, on NaH is hardly dependent on $\overline{X}_{Cs}$, while those on NaT and NaTS are strongly dependent on $\overline{X}_{Cs}$. It was found that NaH exhibited the superior Cs^+ ion selectivity invariant over the whole $\overline{X}_{Cs}$ range, although NaT exhibited a stronger preference for Cs^+ ions than NaH in the range $\overline{X}_{Cs} < 0.35$. The exchange capacity of NaT for Cs^+ ions is similar to that of K-depleted phlogopite mica.[9] The characteristics for the selective Cs^+ ion uptakes by NaH and NaT were further examined in the presence of K^+ ions, because NaT exhibited a superior K^+ ion selectivity.[1,2] The time dependences of K^+ and Cs^+ uptakes by NaH and NaT from KCl + CsCl solutions are shown in Figure 3. The results revealed that NaH selectively took up Cs^+ ions, while NaT took up equivalent amounts of K^+ and Cs^+ ions.

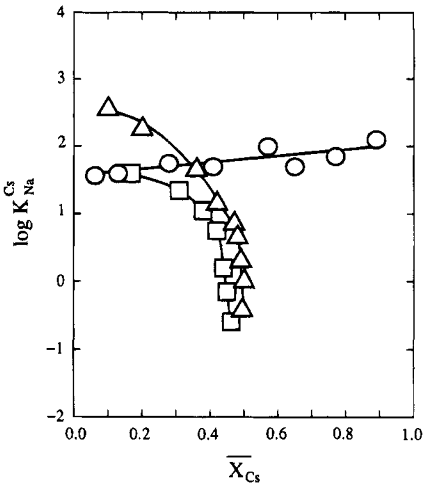

Figure 2. Kielland plots for $Na^+ \rightarrow Cs^+$ exchanges on NaH (○), NaT(△), and NaTS(□).

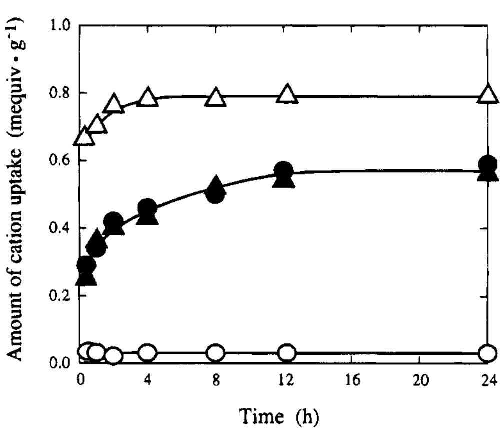

Figure 3. Time dependences of amounts of K^+ (○ and ●) and Cs^+ (△ and ▲) uptakes by NaH (open) and NaT (filled) from KCl + CsCl solution with $K^+/Cs^+ = 1.0$, respectively.

In conclusion, NaH was found to exhibit excellent Cs^+ ion selectivity without depending on the concentration of Cs^+ ions. These basic studies suggest that NaH can be utilized in the separation and immobilization of Cs^+ ions from systems that contain Na^+, K^+, and Cs^+ ions.

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