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Ion-Exchange Properties of Alkali-Metal Redox-Intercalated Vanadyl Phosphate

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Ion exchange of alkali metals in $M_x\mathrm{VOPO_4}\cdot y\mathrm{H_2O}$ (M = H, Na, K, Rb, Cs) is reported. The role of valence, size, and affinity of the cations in the exchange process is discussed. The interlayer distance in the $\mathrm{H_{1-x}K_xVOPO_4}\cdot y\mathrm{H_2O}$ system is discussed in terms of finite layer rigidity theory. Different behavior is observed for $\mathrm{K_xNa_{1-x}VOPO_4}\cdot y\mathrm{H_2O}$ dependening on the starting compound used. When potassium in $\mathrm{KVOPO_4\cdot H_2O}$ is exchanged for $\mathrm{Na^+}$, one phase compound is formed. In contrast, $\mathrm{K_xNa_{1-x}VOPO_4}\cdot y\mathrm{H_2O}$ formed from $\mathrm{NaVOPO_4\cdot H_2O}$ and $\mathrm{K^+}$ is a multiphase system. Ion exchange does not proceed when exchanging ions differ distinctly from each other in size, e.g., sodium and cesium. © 2002 Elsevier Science

Key Words: **alkali metals; vanadyl phosphate; ion exchange.**

INTRODUCTION

Vanadyl phosphate dihydrate is a layered compound that undergoes redox intercalation reactions with alkali metals, alkaline earth metals, and other cations (1, 2) in the presence of a mild reducing agent according to the reaction

$$\mathrm{VOPO_4\cdot 2H_2O} + (x/z)\mathrm{MI}_z + y\mathrm{H_2O} \rightarrow \mathrm{M}_{x/z}\mathrm{VOPO_4}\cdot(2+y)\mathrm{H_2O} + (x/2)\mathrm{I_2}, \qquad [1]$$

where x is the amount of intercalated cation, z is the charge or valence of the cation, and y is the change of the water content in the product. As a reducing agent, iodide of the corresponding metal is used. Besides, hydronium ion can be intercalated in $\mathrm{VOPO_4.2H_2O}$ using a hydrogen transfer agent such as hydroquinone (3). In all cases, the structure of the host layer (i.e., the structure of the alpha form of vanadium phosphate (4)-α_I-$\mathrm{VOPO_4}$) is retained after the intercalation. The host layers containing reduced V(IV) possess a negative charge.

Such intercalates can serve as ion exchangers, as proposed by Jacobson and Johnson (5). As an example, an ion exchange of sodium in $\mathrm{Na_xVOPO_4}\cdot y\mathrm{H_2O}$ for $\mathrm{Ca^{2+}}$ in aqueous solution is described and a full exchange of the ions after 4.5 h is reported. In this paper, we report ion exchange reactions of alkali metals with redox intercalated $\mathrm{VOPO_4}$ according to the reaction

$$\mathrm{M}_{x/z}\mathrm{VOPO_4}\cdot(2+y)\mathrm{H_2O} + x/n\mathrm{A}^{n+} \rightarrow \mathrm{A}_{x/n}\mathrm{VOPO_4}\cdot(2+y)\mathrm{H_2O} + x/z\mathrm{M}^{z+}, \qquad [2]$$

and we discuss the role of valence, size, and affinity of the ions to the $\mathrm{VOPO_4}$ layers in the ion-exchange process.

EXPERIMENTAL

Vanadyl phosphate dihydrate was prepared by refluxing a mixture of vanadium pentoxide with phosphoric acid in water (6). Alkali metal and hydronium intercalated vanadyl phosphate was prepared from $\mathrm{VOPO_4\cdot 2H_2O}$ as described in (7, 8) and dried in air at ambient temperature. All the intercalates were green.

In a typical ion-exchange reaction, 0.5 g of the starting intercalate was shaken with a 1/1 (v/v) acetone/water solution of a salt of the desired cation at 40°C for several days. The products were dried in air at ambient temperature.

For the kinetics measurement, 0.3 g of $\mathrm{HVOPO_4\cdot 3.6H_2O}$ was stirred in a vessel thermostated at 40°C with 40 ml of the 0.01 M solution of KCl. The change of pH was monitored with a combined silver-chloride glass electrode. The dependence of the concentration of protons released by the ion exchange as a function of time was determined.

The ion exchange of protons in $\mathrm{HVOPO_4\cdot 3.6H_2O}$ for $\mathrm{K^+}$ was carried out by shaking 0.4 g of $\mathrm{HVOPO_4\cdot 3.6H_2O}$ with various volumes (from 12.5 to 400 ml) of 0.01 M KCl in 50 vol% acetone/water mixture at 40°C for 9 days.

The ion exchange of sodium in $\mathrm{NaVOPO_4\cdot H_2O}$ for $\mathrm{K^+}$ was carried out in the same way with 0.41 g (2×10^{-3} mol) of $\mathrm{NaVOPO_4\cdot H_2O}$ at 40°C by shaking the solid with 0.01 M KCl (25–400 ml) for 9 days. The exchange of $\mathrm{K^+}$ in $\mathrm{KVOPO_4\cdot H_2O}$ for $\mathrm{Na^+}$ was done by shaking 0.45 g

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(2×10^{-3} mol) of the solid with 0.01 M NaCl (25 to 400 ml) at 40°C for 9 days.

Molar fraction x'_A of ion A in the starting mixture is then given by

$$x'_A = \frac{n(A^+)}{n(A^+) + xn(B_x\mathrm{VOPO_4} \cdot y\mathrm{H_2O})}, \qquad [3]$$

where $n(A^+)$ is the amount (in moles) of A^+ salt in the starting mixture and $xn(B_x\mathrm{VOPO_4} \cdot y\mathrm{H_2O})$ corresponds to the amount of B^+ in the solid. Molar fraction x''_A of an ion A^+ in the solid product containing two ions ($A_{x(A)}B_{x(B)}\mathrm{VOPO_4} \cdot y\mathrm{H_2O}$) is given as

$$x''_A = \frac{x(A)}{x(A) + x(B)}. \qquad [4]$$

The compositions of the products were determined by energy-dispersive X-ray spectrometry (EDX) microanalyses of vanadium, phosphorus, and the intercalated cations using an electron-dispersive X-ray analyzer KEVEX Delta V coupled with an electron scanning microscope Tesla BS-340. The accelerating voltage of the primary electron beam was 15 kV. The powder diffraction data were obtained with an X-ray difractometer (HZG-4, Germany) using Ni-filtered Cu$K\alpha$ radiation. Diffraction angles from 5 to 90° (2θ) were considered. Silicon (a = 5.43055 Å) was used as an external standard. Thermogravimetric analysis was performed with a Derivatograph MOM (Hungary) in the 30–450°C temperature range at the heating rate of 5°C/min in air.

RESULTS AND DISCUSSION

$HVOPO_4 \cdot 3.6H_2O + K^+$

Time dependence of the exchange of protons in $\mathrm{HVOPO_4 \cdot 3.6H_2O}$ for K^+ has an exponential shape as shown in Fig. 1. The reaction is almost completed after 200 h at 40°C. The basal spacing of the compounds with partially exchanged proton for potassium depends on the amount of the exchanged potassium cations (Fig. 2).

The compound with the lowest content of potassium ($\mathrm{H_{0.96}K_{0.04}VOPO_4 \cdot 2.6H_2O}$) consists of two phases with d = 6.417 and 6.466 Å and contains one molecule of water less than pristine $\mathrm{HVOPO_4 \cdot 3.6H_2O}$. The phase with higher basal spacing disappears when the content of potassium is increased. The basal spacing of the phase with lower d decreases with increasing content of potassium up to a compound with composition $\mathrm{H_{0.6}K_{0.4}VOPO_4 \cdot 2.2H_2O}$; then the basal spacing remains constant with increasing amount of potassium ions. From this behavior it is obvious that even a very small amount of K^+ ($x = 0.04$) initiates redistribution of the water molecules so that two new phases are formed and a dramatic decrease of water content is observed (from $y = 3.6$ to 2.6). This is most probably given by the fact that the hydration ring of the water molecules around H^+ ions is broken by the presence of K^+. With increasing content of K^+ the amount of water further slightly decreases, from $y = 2.6$ to 2.2. At $x = 0.4$, when almost every second site on the host layer is occupied by K^+, the decrease of d is finished. Potassium ions are fully exchanged for H^+ up to x = 0.4, then the further exchange becomes difficult as documented by Fig. 3. Only one phase is present in compounds with $x > 0.04$. Experiments with an excess of potassium chloride in the starting mixture proved that K^+ ions are able to exchange only about one half of H^+ in $\mathrm{HVOPO_4 \cdot 3.6H_2O}$; the compound with the maximum content of potassium is $\mathrm{H_{0.47}K_{0.53}VOPO_4 \cdot 2.2H_2O}$. The basal spacing of this compound (d = 6.33 Å) is lower than that

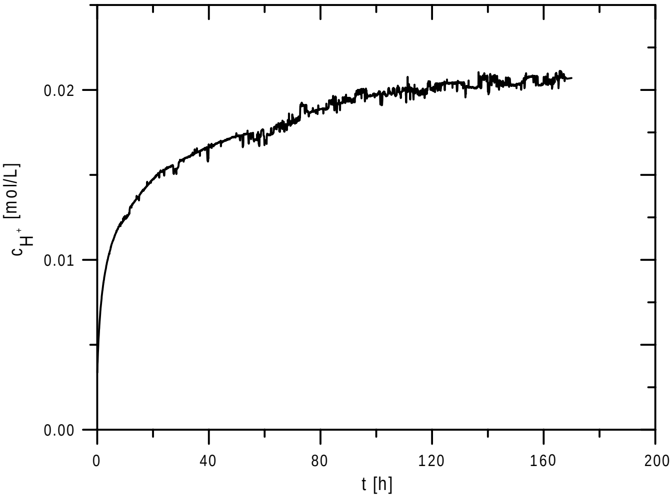

FIG. 1. Concentration of protons released during the reaction of $\mathrm{HVOPO_4 \cdot 3.6H_2O}$ with K^+ ions as a function of time.

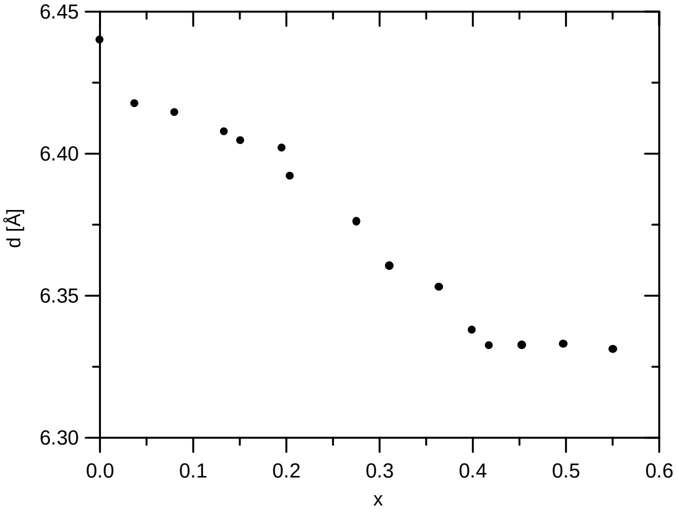

FIG. 2. The change of the interlayer distance d in $\mathrm{H_{1-x}K_xVOPO_4 \cdot}$ $y\mathrm{H_2O}$ with x.

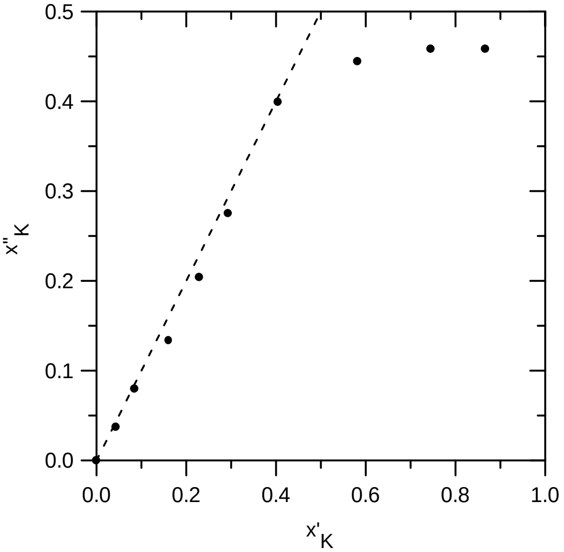

FIG. 3. Molar fraction of K^+ ions (x''_K) in solid $H_{1-x}K_xVOPO_4 \cdot yH_2O$ vs molar fraction of K^+ in the starting mixture (x'_K).

found for pure $KVOPO_4 \cdot yH_2O$ ($d = 6.38$ Å) prepared by the redox intercalation (8).

The nonlinear dependence of d on the amount of exchanged potassium in the range $x = 0.0$–0.4 (Fig. 2) can be explained by using a finite layer rigidity model (9). In this model, two different ions, A and B, are present in the interlayer space (gallery). The fraction of ion A is given by the value of z. When only ion B is present in the gallery, then the basal spacing is $d(0)$ and $z = 0$. When all intercalated ions are A, then the basal spacing is $d(1)$ and $z = 1$. For a compound with the both ions in the gallery, basal spacing is $d(z)$ with $d(0) < d(z) < d(1)$ and $0 < z < 1$. The relationship between normalized basal spacing $d_n(z)$ given by

$$d_n(z) = \frac{d(z) - d(0)}{d(1) - d(0)} \qquad [5]$$

and fraction z is

$$d_n(z) = 1 - (1 - z)^p, \qquad [6]$$

where p is a parameter describing rigidity of the host layer or an area which is influenced by the intercalation of ion A in a gallery which is otherwise filled with ions B. The higher the parameter p, the more rigid is the host layer. For instance, for $V_{1-x}Li_xC_6$ (where V represents a vacancy), a compound with flexible monoatomic graphite layers, is $p = 2$, whereas for $Rb_{1-x}Cs_xVm$ (Vm = vermiculite), with more rigid polyatomic host layers, is $p = 7$ (10).

In our case, we used as $d(0)$ the value of the basal spacing for $K_{0.4}H_{0.6}VOPO_4 \cdot 2.2H_2O$ and consequently $z = 0$ stands for compound with the index $x = 0.4$ for potassium. As $d(1)$, the basal spacing of $H_{0.96}K_{0.04}VOPO_4 \cdot 2.6H_2O$, $d = 6.417$ Å, was chosen. This is because the compound with zero content of potassium ($x = 0.0$, i.e., $z = 1.0$), which is $HVOPO_4 \cdot 3.6H_2O$, differs in the content of water from its closest potassium exchanged substance, $H_{0.96}K_{0.04}VOPO_4 \cdot 2.6H_2O$, and consequently the basal spacing is much more different (see above). The normalized basal spacing $d_n(z)$ as a function of z is given in Fig. 4. These data fit well by function (5) when the parameter p is set to 2.0 as shown by the solid line in the figure. This value indicates that vanadyl phosphate belongs to the most flexible host layers used in intercalation chemistry, which is in agreement with the conclusions made previously (11).

$NaVOPO_4 \cdot H_2O + K^+$

In this case, the starting compound is $NaVOPO_4 \cdot H_2O$ with a basal spacing of 5.64 Å. When treated with 0.01 M–KCl solution, $NaVOPO_4 \cdot H_2O$ easily replaces Na^+ by K^+ and a multiphase system is formed. By aging the product for about three months, this system changes to a two-phase substance. The phase with lower basal spacing has the d value close to that of $NaVOPO_4 \cdot H_2O$ (5.67 Å), the phase with higher basal spacing has d close to that found for $KVOPO_4 \cdot H_2O$ (6.38 Å). The basal spacing of these phases changes with the amount of KCl solution in the starting mixture as shown in Fig. 5. The amount of water y has a maximum at $x'_{Na} = 0.7$ and decreases with higher amount of K^+ in the starting mixture.

$KVOPO_4 \cdot H_2O + Na^+$

In contrast to the exchange of Na^+ in $NaVOPO_4 \cdot H_2O$ for K^+, $KVOPO_4 \cdot H_2O$ treated with Na^+ solution forms

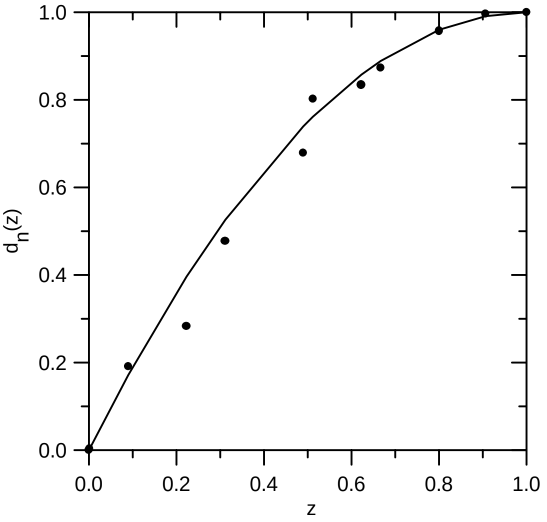

FIG. 4. Normalized basal spacing $d_n(z)$ as a function of normalized content of potassium z in $H_{1-x}K_xVOPO_4 \cdot yH_2O$. (solid line) Data calculated using finite layer rigidity model.

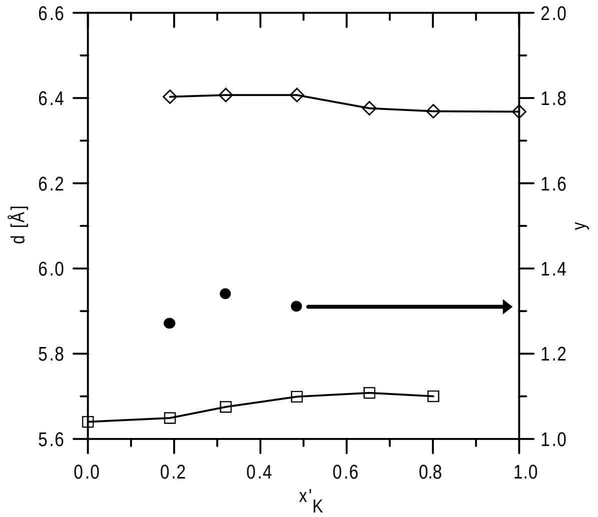

FIG. 5. Interlayer distances *d* (diamonds, first phase, squares, second phase) and content of water *y* (circles) for $NaVOPO_4 \cdot H_2O$ treated with K^+ salt as a function of molar fraction of K^+ in the starting mixture.

only one phase. This exchange does not proceed up to $x'_{Na} = 0.45$, as follows from EDX and powder XRD data. At higher amounts of sodium cation in the starting mixture, one-phase substance containing both ions is formed with higher basal spacing than that for $KVOPO_4 \cdot H_2O$ (see Fig. 6). The formation of this one-phase substance is accompanied with an increase of water content in the compound, which indicates that the Na^+ ion enters gallery as a hydrated species. This behavior is quite different from the redox intercalation of Na^+, where the increase of Na^+ is connected with the decrease of water content in the intercalate (7).

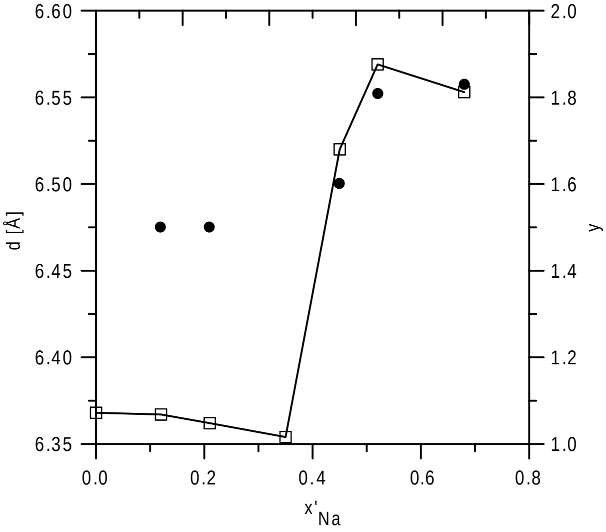

FIG. 6. Interlayer distances *d* (squares) and content of water *y* (circles) for $KVOPO_4 \cdot H_2O$ treated with Na^+ as a function of molar fraction of Na^+ in the starting mixture.

TABLE 1
Alkali Metals Ion Exchange in $HVOPO_4 \cdot 3.6H_2O$

Salt	Product	*d* [Å]
$NaNO_3$	$H_{0.8}Na_{0.2}VOPO_4 \cdot yH_2O$	6.24 (6.52)
KNO_3	$H_{0.5}K_{0.5}VOPO_4 \cdot yH_2O$	6.34
$RbNO_3$	$H_{0.7}Rb_{0.3}VOPO_4 \cdot yH_2O$	6.40

$HVOPO_4 \cdot 3.6H_2O + Na^+$

By shaking equimolar amounts of $HVOPO_4 \cdot 3.6H_2O$ and Na^+ salt in the acetone–water mixture (1/1 vol.) at 40°C, a two-phase system of $H_{0.8}Na_{0.2}VOPO_4 \cdot yH_2O$ is formed (Table 1). The powder X-ray diffractograms show an intensive peak with $d = 6.24$ Å and a very weak peak with $d = 6.52$ Å. There is no influence of a counter-ion in the Na^+ salt used, for instance both NaCl and $NaNO_3$ gave identical products.

In a reverse process, when $NaVOPO_4 \cdot H_2O$ is treated with diluted HCl, a decrease of content of Na^+ in the compound is observed and the basal spacing increases to 6.52 Å. This exchange is complicated by a partial dissolution of the solid in acid medium.

Ion Exchange of Rb^+ and Cs^+

To compare the ability of the exchange of protons for alkali metals, $HVOPO_4 \cdot 3.6H_2O$ was shaken with equimolar amounts of $NaNO_3$, KNO_3, $RbNO_3$, and CsCl. The results are given in Table 1.

The most easily exchanging cation is K^+. For Rb^+, the exchange seems to be hindered by the size of the cation. Tendency of Na^+ ion to exchange H^+ in $HVOPO_4 \cdot 3.6H_2O$ is lower compared with K^+. Cesium cation does not exchange protons at all. As found by EDX, the product of treatment of $HVOPO_4 \cdot 3.6H_2O$ with CsCl solution contained a small amount of intercalated K^+, Na^+, and only traces of Cs^+. Both K^+ and Na^+ were taken up from CsCl, which contains about 1% of potassium and less than one percent of sodium as found by EDX analysis of CsCl. Such a compound can therefore serve as an "ion sieve" which is able to "extract" smaller ions from their mixture in a solution.

Potassium cations in $KVOPO_4 \cdot H_2O$ can be exchanged for Rb^+ and Cs^+. Sodium cations in $NaVOPO_4 \cdot H_2O$ can be exchanged for Rb^+, but not for Cs^+. Also the reverse exchange, i.e., the cesium cation in $Cs_xVOPO_4 \cdot yH_2O$ for Na^+ does not proceed. The results of the ion exchanges studied are summarized in Table 2.

TABLE 2
Ion Exchange in Alkali Metals Redox Intercalated $VOPO_4$

Starting material	*m* [g]	Salt	*m* [g]	Product	*d* [Å]
$NaVOPO_4 \cdot H_2O$	0.41	KCl	—[a]	$K_xNa_{1-x}VOPO_4 \cdot yH_2O$	2 phases[a]
$Na_{0.48}VOPO_4 \cdot yH_2O$	0.5	$RbNO_3$	3.7	$Na_{0.1}Rb_{0.3}VOPO_4 \cdot 1.5H_2O$	6.52; 6.45
$Na_{0.6}VOPO_4 \cdot yH_2O$	0.5	CsCl	2	—[b]	
$KVOPO_4 \cdot 1H_2O$	0.43	NaCl	—[a]	$K_xNa_{1-x}VOPO_4 \cdot yH_2O$	1 phase[a]
$K_{0.7}VOPO_4 \cdot 1.5H_2O$	0.5	$RbNO_3$	3.7	$K_{0.4}Rb_{0.2}VOPO_4 \cdot 1.34H_2O$	6.39
$K_{0.58}VOPO_4 \cdot yH_2O$	0.3	CsCl	2.5	$Cs_{0.23}K_{0.36}VOPO_4 \cdot 1.4H_2O$	6.58
$Rb_{0.4}VOPO_4 \cdot 1.2H_2O$	0.5	NaCl	2	—[b]	
$Rb_{0.4}VOPO_4 \cdot 1.2H_2O$	0.5	KCl	2	$K_{0.2}Rb_{0.2}VOPO_4 \cdot 1.43H_2O$	6.45
$Rb_{0.4}VOPO_4 \cdot 1.2H_2O$	0.5	CsCl	2.5	$Cs_{0.1}Rb_{0.3}VOPO_4 \cdot 1.5H_2O$	6.48
$Cs_{0.45}VOPO_4 \cdot 1.5H_2O$	0.5	NaCl	1.46	—[b]	
$Cs_{0.4}VOPO_4 \cdot 1.5H_2O$	0.27	KCl	2	$Cs_{0.27}K_{0.24}VOPO_4 \cdot 1.58H_2O$	7.02; 6.40
$Cs_{0.38}VOPO_4 \cdot 1.5H_2O$	0.22	$RbNO_3$	3.7	$Cs_{0.22}Rb_{0.19}VOPO_4 \cdot 1.5H_2O$	7.06; 6.50

[a] See Results and Discussions.
[b] The ion exchange does not proceed.

The ability of a cation A to exchange another cation M in the interlayer space of the host (according to Eq. [2]) is influenced by three phenomena: (i) the electrostatic interaction between negatively charged host layer and the exchanging cations, (ii) the free energy involved in the changes in hydration of M and A during the exchange process (let us suppose that there is no hydration change on the host layers), and (iii) the energy needed for the change in an interlayer geometry, i.e., the change of the basal spacing of the intercalate (12, 13). The electrostatic energy given by the interaction between the host layer and the counterion decreases with the radius of this counterion. This energy arising from the interaction of the host and exchanging cation A is compensated by the energy necessary for the release of an exchanged cation M. The free energy of hydration is connected with the standard free energy of hydration of the corresponding ion. For alkali metal ions, the hydration energy decreases in the sequence Na > K > Rb > Cs. Regarding the electrostatic and hydration energies, it follows from our observation that the hydration energy governs the exchange processes for smaller cations. The exchanging ability of larger cations (Rb and Cs) is influenced by the energy necessary for the change of the basal spacing. Therefore, sodium cannot replace cesium anchored to $VOPO_4$ as hydration energy of Na^+ is too high compared with that of Cs^+. On the other hand, Cs^+ ion is too large to be able to enter the interlayer space of $NaVOPO_4$.

Contrary to the previously described observation (5), we found that only traces of calcium are incorporated in the interlayer space of $Na_{0.5}VOPO_4 \cdot 2H_2O$ treated with aqueous $CaCl_2$ solution at 40°C. In addition, the amount of Na^+ in the product decreases compared to the starting compound, which indicates that the Na^+ is exchanged for H^+ in slightly acid $CaCl_2$ solution. Generally, we observed that an ion exchange of alkali metals for divalent cations was very difficult. On the other hand, such exchange is in most cases easily accomplished when divalent metal intercalated $VOPO_4$ is used as a starting material. The study of these exchange processes is now under way.

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