Studies on the Ammonium Form of Crystalline Zirconium Phosphate. II.[1,2] Ammonium-Lithium Ion-exchange Isotherms

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The ion-exchange isotherms for the NH_4^+–Li^+ system on crystalline zirconium phosphate have been determined at 25 °C, and the structural change and water content of the exchanger have also been investigated by means of X-ray diffraction and thermal analysis. The isotherms showed that the ion-exchange reaction took place in one stage, that is, the ammonium-form was converted into the lithium-form in the forward process, and *vice versa* in the reverse process. However, the results of X-ray diffractometry indicated that the ion-exchange reactions proceeded in three stages in each direction. The isotherms also showed a hysteresis loop. This phenomenon can be ascribed to the difference in the water content of the exchangers, because the X-ray powder patterns of the exchanger phases were essentially identical at similar ionic mole fraction of lithium ion in the exchangers of the two processes.

Many inorganic ion-exchangers have been extensively investigated in the field of nuclear energy, water desalination, analytical chemistry, *etc.* Crystalline zirconium bis(monohydrogen orthophosphate) monohydrate, $Zr(HPO_4)_2 \cdot H_2O$, generally called α-zirconium phosphate, is one of the most studied materials. α-Zirconium phosphate as well as its cation-exchanged form has a layered structure, and the ion-exchange reaction is strongly influenced by the interlayer distance of the exchanger and by the ionic radius of an exchanging cation.[3] Also, the hydration and dehydration of cations affect the ion-exchange. Of alkali metal cations, lithium ion has the largest standard free energy for hydration and dehydration,[4,5] and its ionic radius is the smallest. When lithium ion exchanges on a cation-exchanged form with a cation having a larger ionic radius, not all the water molecules bound to the lithium ion are dehydrated.

During an investigation of the ammonium–hydrogen ion-exchange on α-zirconium phosphate prepared by the reflux method, the pH titration curves indicate that the solid phase of $Zr(NH_4PO_4)_{4/3} \cdot (HPO_4)_{2/3} \cdot nH_2O$ is present instead of $Zr(NH_4PO_4)(HPO_4) \cdot n'H_2O$.[6] The interlayer distance of the ammonium-form is shorter than that to be expected from the ionic radius of ammonium ion.[7,8] The behavior of the ammonium–hydrogen ion-exchange is similar to that observed in the hydrogen–lithium ion-exchange.[9]

Thus, it is of interest to study how the relatively short interlayer distance of the ammonium-form exchanger affects its selectivity from the points of view of the mechanism of the ion-exchange and the application to the recovery of metals, and how the ionic hydration and the similar behavior of the ion-exchange reactions affect the ammonium–lithium ion-exchange.

In the present work, the ammonium–lithium ion-exchange isotherms at 25 °C, the structural change, and the water content per mole of the exchanger will be reported.

Experimental

Reagents and Preparation of Exchangers. All the chemicals were of reagent grade and were used without purification.

The ammonium-form exchanger, $Zr(NH_4PO_4)_2 \cdot H_2O$, was prepared according to Hasegawa and Aoki.[6] The lithium-form exchanger, $Zr(LiPO_4)_2 \cdot 4H_2O$, was prepared by the continuous percolation of a 0.1 mol dm^{-3} lithium chloride solution through a column filled with the ammonium-form exchanger. Both the exchangers were dried over a saturated sodium chloride solution (with a relative humidity of about 75% at room temperature). The identification of the exchanger was made by means of the X-ray diffraction pattern and the loss of ignition.

Analytical Procedure. The concentration of ammonium ions in the solution was determined gravimetrically.[10] The concentration of lithium ions was determined by atomic absorption spectrophotometry with a Hitachi atomic absorption spectrophotometer 208. In order to determine the structural change in the exchanger phase during the ion-exchange, X-ray powder patterns were obtained with nickel-filtered Cu *K*α radiation with a Geigerflex (Rigaku Denki Co., Ltd.). The exchanger was conditioned before measurement over a saturated sodium chloride solution at room temperature.

Table 1. Dependence of X_{Li} on the time

Time (day)	0.25	0.5	1	2	3
X_{Li}[a]	0.93	0.94	0.93	0.94	0.93

a) X_{Li} = the mole fraction of lithium ion in the solution of F8 in Fig. 1.

Ion-exchange Isotherms. A weighed amount of the exchanger (100 mg) was shaken continuously with 10.0 cm^3 of a solution containing a total of 0.100 M of ammonium and lithium chlorides at 25 °C. In order to select the reaction time, the concentration of lithium ions in the solution was determined after a given period of time for the F8 sample in Fig. 1. The concentration of lithium ions varied within the limits of experimental error (Table 1). A reaction of at least 48 h was thus chosen. Near the end point (the mole fraction of lithium or ammonium ion, X_{Li} or X_{NH_4} = 1.0) the volume of the solution was increased and/or the amount of the exchanger was decreased to prompt the reaction, and also a shaking period longer than 48 h was taken.

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Results and Discussion

In order to investigate the effect of the pH's of solutions on the ion-exchange isotherms and to calculate the ionic fraction of exchanging cations in the exchanger phase, the concentrations of ammonium and lithium ions and pH values in the solution phase were determined separately. As is shown in Table 2, the sum of the ionic fraction of the solution phase for ammonium and lithium ions was equal to unity in all cases, within the limits of experimental error. The pH values were slightly higher than the pH's which were determined for the solutions containing the same ionic fraction of ammonium and lithium ions and no exchanger. The difference in the hydrogen-ion concentration was very small, and it is possible to neglect the effect of the pH value of the solution on the ion-exchange reaction.

Table 2. Mass balance data for NH_4^+/Li^+ exchange

	X_{Li}	X_{NH4}	Total ionic fraction	pH	
				Initial	Final
F1	0.78	0.19	0.97	5.78	5.75
F2	0.81	0.19	1.00	5.80	6.05
F3	0.84	0.18	1.02	5.80	6.18
F4	0.85	0.16	1.01	5.80	6.25
F5	0.90	0.13	1.03	5.80	6.20
F6	0.91	0.11	1.02	5.80	6.58
F7	0.95	0.06	1.01	5.80	6.80
F8	0.97	0.03	1.00	5.80	6.90
R1	0.98	0.33	1.01	5.78	6.50
R2	0.94	0.08	1.02	5.71	6.35
R3	0.86	0.14	1.00	5.65	6.20
R4	0.79	0.22	1.01	5.60	6.45
R5	0.72	0.32	1.04	5.50	6.20
R6	0.66	0.36	1.02	5.52	5.95
R7	0.59	0.42	1.01	5.52	6.00
R8	0.51	0.49	1.00	5.48	5.95
R9	0.44	0.59	1.03	5.50	5.35
R10	0.23	0.75	0.98	5.50	5.40

F and R denote the forward and reverse processes respectively. F1 ...R10 correspond to those in Fig. 1. X_{Li} and X_{NH4} represent the mole fractions of the respective ions.

Forward Process (The Ammonium-form→the Lithium-form). The ion-exchange isotherm is shown in Fig. 1(a). It was found that the isotherm showed a steep sloping when the mole fraction of lithium ion in the solution, X_{Li}, was larger than 0.7. No clear plateaus or vertical portions were observed in the isotherm. These facts indicate that the ammonium-form was converted into the lithium-form without the formation of an intermediate, half-exchanged form, $Zr(NH_4PO_4)(LiPO_4)\cdot mH_2O$. Since it took a long time to prepare the lithium-form, perfect conversion seems to be difficult.

It is known that α-zirconium phosphate and its sodium-form have a layered structure and that the first reflection in the X-ray powder pattern corresponds to the interlayer spacing.[3] This means that when two solid phases coexist, two reflections are observed at lower diffraction angles. As the ammonium-form has a layered structure,[8] similar phenomena can be expected. Based on this hypothesis, it has been possible to deduce the structural change of the exchanger phase during the ion-exchange. The precise estimation of the intensity of two peaks is difficult in this case, however, because two peaks overlapped at lower diffraction angles. Hence, the intensity ratio in Table 3 is only approximate.

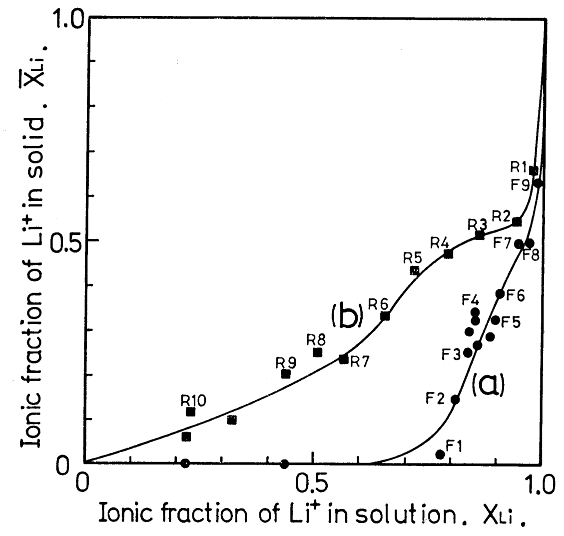

Fig. 1. Ion-exchange isotherms, (a) forward and (b) reverse process. X_{Li}: the mole fraction of lithium ion in the solution phase. $\bar{X}_{Li}$: the mole fraction of lithium ion in the solid phase.

Table 3. Relative intensities of the interlayer distances in the forward process

Symbol[a)]	Interlayer distances		
$\bar{X}_{(Li)}$	9.4 Å	10.0 Å	10.5 Å
F1 (0.03)	10	—	—
F2 (0.15)	10	1.1	—
F3 (0.25)	3.0	10	—
F4 (0.35)	—	10	3.5
F5 (0.33)	—	10	5.1
F6 (0.38)	—	10	7.2
F7 and F8 (0.50)	—	—	10
F9 (0.63)	—	3.0	10
Li form (1.0)	—	10	—

a) Symbols correspond to those in Fig. 1(a).

In the region of the mole fraction of lithium ion in the exchanger phase $\bar{X}_{Li}=0-0.03$, the interlayer distance remained constant (9.4 Å), corresponding to that of the ammonium-form. When $\bar{X}_{Li}$ was above 0.15, a peak appeared at 10.0 Å, and its intensity increased with an increase in $\bar{X}_{Li}$. Between F3 and F4 ($\bar{X}_{Li}\doteqdot 0.3$), the peak at 9.4 Å diminished and another peak appeared at 10.5 Å. This change in the exchanger phase indicates that a new phase with an interlayer distance of 10.0 Å was present in the very narrow region of X_{Li}.

Two peaks, at 10.0 and 10.5 Å, were observed in the region of $\bar{X}_{Li}=0.3$—0.4. The intensity of the former decreased with an increase in $\bar{X}_{Li}$, and only the peak at 10.5 Å was present at F7 and F8 ($\bar{X}_{Li}\fallingdotseq 0.5$).

Above $\bar{X}_{Li}=0.5$ the peak at 10.5 Å disappeared gradually, and the intensity of the peak at 10.0 Å increased again. This peak at 10.0 Å should be considered as a different one from that observed in the region of $\bar{X}_{Li}=0.15$—0.4, because it is not probable that the same phase exists in another region of $\bar{X}_{Li}$. The interlayer distance of 10.0 Å was identical to that of the lithium-form reported by Alberti *et al.*[11] It can thus be inferred from the X-ray studies that the ion-exchange reaction took place in three stages, while the isotherm showed no clear stages.

In order to determine the water content per mole of the exchanger, the solid obtained during the ion-exchange process was heated to 420 °C and the weight loss was measured. The molecular formula of the exchanger can be assumed to be $Zr(NH_4PO_4)_a\cdot(LiPO_4)_{2-a}\cdot nH_2O$. Since the exchanger loses its water of hydration and ammonia in the temperature range of 100—420 °C, the water content is calculated by means of the following equation:

$$n=[295.0p+(11.0p-17.0)a]/18.0(1-p), \qquad (1)$$

where a and n are moles of NH_4^+ and H_2O per formula weight of the exchanger, as shown above, and p is the portion of weight loss to the molecular weight.

The relationship between the water content per mole of the exchanger (n) and $\bar{X}_{Li}$ is shown in Fig. 2(a). The value of n increased linearly with $\bar{X}_{Li}$. The change in n can be represented as follows;

$$\begin{aligned} n &= 3(\bar{X}_{Li})+1 \\ &= (3/2)(2-a)+1. \qquad (2) \end{aligned}$$

Equation 2 shows that the net water molecules diffusing with a lithium ion into the crystal lattice of the exchanger were equal to 1.5. The water content of the ion-exchanger of the lithium-form was equal to $3.9H_2O$/mol, less than that previously reported.[11,12] This is due to the tendency of the lithium-form to lose the water of hydration.[11]

Reverse Process (the Lithium-form→the Ammonium-form). The ion-exchange isotherm of the reverse process is shown in Fig. 1(b). In contrast with the forward process, this ion-exchange reaction took place at $X_{NH_4}<0.03$. The isotherm showed an almost vertical sloping in the region of $\bar{X}_{Li}=1.0$—0.5. Near R2 and R3 ($X_{Li}\fallingdotseq 0.5$) the curve tended to have a plateau, and then it again sloped below $\bar{X}_{Li}=0.5$.

Table 4 shows the change in the peaks in the powder patterns at lower diffraction angles. Even at the beginning of the reaction the peak at 10.5 Å appeared and two phases coexisted. The peak at 10.5 Å showed its maximum intensity at R2, while the peak at 10.0 Å was present as a shoulder. The intensity of the peak at 10.0 Å increased again at R3. This peak after R3 should be regarded as another, separate one, as has been stated above. The findings indicate that the phase with the interlayer distance of 10.5 Å was formed at the narrow region of X_{Li} between R2 and R3. In the region of $\bar{X}_{Li}=0.5$—0.3, two peaks at 10.0 and 10.5 Å were observed. The intensity of the 10.0 Å peak increased with a decrease in $\bar{X}_{Li}$ and showed its maximum at R6. The peaks at 10.0 and 9.4 Å coexisted below $\bar{X}_{Li}=0.3$. The latter corresponds to the interlayer distance of the ammonium-form. Near the end point (X_{Li} and $\bar{X}_{Li}=0$), only the ammonium-form was present. The results showed that the ion-exchange reaction proceeded in three stages.

TABLE 4. RELATIVE INTENSITIES OF THE INTERLAYER DISTANCES IN THE REVERSE PROCESS

Symbol[a)]	Interlayer distances		
($\bar{X}_{Li}$)	9.4 Å	10.0 Å	10.5 Å
R1 (0.67)	—	8	10
R2 (0.54)	—	s	10
R3 (0.52)	—	5.2	10
R5 (0.44)	—	8.2	10
R6 (0.34)	—	10	8.0
R7 (0.22)	10	8.1	—
R9 (0.20)	10	8.6	—
R10 (0.12)	10	s	—

a) Symbols correspond to those in Fig. 1(b).
s: Shoulder.

The change in the water content per mole of the exchanger, n, calculated by means of Eq. 1 is shown in Fig. 2(b). The value of n was approximately represented as follows above $\bar{X}_{Li}=0.3$:

$$\begin{aligned} n &= 2(\bar{X}_{Li})+2 \\ &= (2-a)+2. \qquad (3) \end{aligned}$$

Below this point the equation changes to approximately:

$$\begin{aligned} n &= 5(\bar{X}_{Li})+1 \\ &= 5/2(2-a)+1 \end{aligned}$$

(the dashed line in Fig. 2). Equation 3 shows that one water molecule migrates with a lithium ion and that the water content of the exchanger phase was higher in the reverse direction than in the forward one.

The X-ray powder patterns of the exchanger phase with a similar $\bar{X}_{Li}$ were essentially identical and made no noticeable difference in the crystal structure. The water content of the exchanger in the forward process was different from that in the reverse one at the same $\bar{X}_{Li}$. Consequently, the hysteresis phenomenon can be ascribed to the difference in the number of water molecules involved in the ion-exchange reactions.

At the first stage in both processes, the interlayer distance of the exchanger expanded, though the change was larger in the forward process than in the reverse one. This indicates that more energy is needed and that

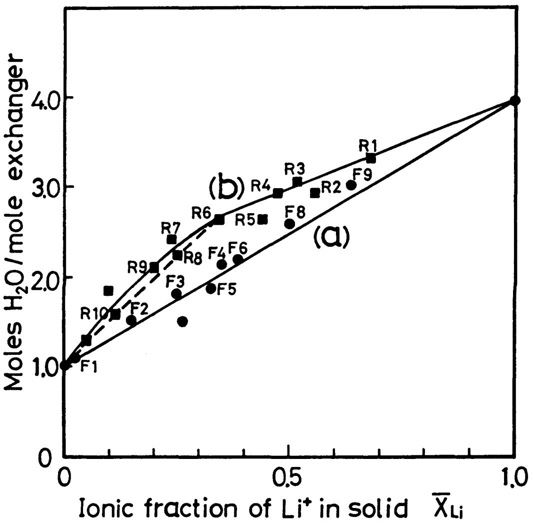

Fig. 2. Change in the water content per one mole of the exchanger phase (*n*). (a) forward and (b) reverse process.

it is more difficult for the ion-exchange reaction to take place in the forward process. In the second stage, the interlayer distance expanded in the forward process, but contracted in the reverse one. Hence, the ion-exchange reaction in the forward process may need a higher X_{Li}.

While hydration in the exchanger phase is an important factor in affecting the ion-exchange reaction,[6,10] ionic hydration in the solution phase must also be taken into account. During the ion-exchange process, bare or partially hydrated cations diffuse into the exchanger because of the steric factor.[3,8] Ions must lose hydrated water molecule(s) in order to exchange. Kim and Rubin calculated the activation energy for dehydration of alkali cations.[5] Though the activation energy for ammonium ion has not been estimated, it can be considered, according to the model employed by them, that the activation energy for dehydration of ammonium ion will be less than that for lithium ion, mainly because of the crystal ionic radius and the mass of ammonium ion. Thus, it is easier for ammonium ion than lithium ion to diffuse into the exchanger. The activation energy for dehydration of primary hydrated lithium ion was estimated to be greater than that of sodium ion if each ion loses the same number of bound water molecules.[5] A comparison with the obtained isotherms for NH_4^+–Li^+ and NH_4^+–Na^+ systems suggests that the lithium ion is partially dehydrated,[10] for the ion-exchange reaction took place at a low ionic fraction of lithium ion in the solution.

The relationship between the formation of a new phase and the absence of the step-by-step change in the isotherm can be explained by the following factors: (1) the two ion-exchange reactions ocurred in a very narrow X_{Li} region, as shown in the NH_4^+–Na^+ systems, and (2) two phases formed the solid solution over a wide range of composition, because the exchanger used showed a good crystallinity but was not fully crystalline, as was pointed out in the case of the Li^+–H^+ exchange.[13]

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