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The Ion-exchange Behavior of the Ammonium Ion on Crystalline Zirconium Phosphate

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The ion-exchange behavior of the ammonium ion on crystalline zirconium phosphate (c-ZrP) was studied by pH titration and X-ray powder diffraction. The ion-exchange capacity of c-ZrP was 4.4 meq/g in an acidic solution and 6.6 meq/g in an alkaline solution. At an exchange of 66% the $Zr(NH_4PO_4)_{1.33}(HPO_4)_{0.67}\cdot H_2O$ phase was present and at an exchange of 100% $Zr(NH_4PO_4)_2\cdot H_2O$ phase was present. The forward and backward titration curves exhibited a hysteresis loop. This results from the presence of the different phases in the titration of each direction. Through the ion-exchange cycle, the crystallinity of c-ZrP was maintained.

Since the crystalline zirconium phosphate ion-exchanger (referred to as c–ZrP hereafter) was prepared by Clearfield and Stynes,[1] the ion-exchange behavior of the compound has been investigated extensively. Especially for alkali-metal cations, the distribution coefficients, (K_d), the dependence of K_d on pH, and the pH titrations have been studied.[2,3] Clearfield and Smith prepared a single crystal of zirconium bis(monohydrogen orthophosphate) monohydrate, $Zr(HPO_4)_2\cdot H_2O$, and suggested a crystal structure for it.[4–6]

However, the ion-exchange behavior of the ammonium ion on c–ZrP has scarcely been studied at all. Only the composition of the ammonium form of c–ZrP, its interplanar spacing, and a simple thermal analysis have been reported.[1,7]

In the present study, the capacity and reversibility of the ion exchange were measured by pH titrations, and the structural change of c–ZrP was examined by means of the X-ray powder diffraction. A chemical analysis of the ammonium forms of c–ZrP was also carried out.

Experimental

Reagents. All the reagents were of a reagent grade and were used without further purification. The c-ZrP was prepared by refluxing a gelatinous zirconium phosphate in 6.7M phosphoric acid for 120 hr.[3]

pH-Titrations. The titrations were carried out by batch as follows: 250 mg of c-ZrP was placed in contact with 25 ml of an NH_4OH+NH_4Cl solution in a thermostat regulated at 25°C. The composition of the solution was chosen so that the total ammonium concentration was equal to 0.1N, and the ratio of OH^-/Cl^- was varied from 0/0.1 to 0.1/0N. The mixtures were shaken continuously until equilibration. After equilibration, the pH values of the supernatants were measured on a Model MG-1 pH meter (Denki Kagaku Keiki Co., Ltd.) with a glass electrode. The equilibrated pH was attained about 2 hr after the start of shaking. Usually the pH's were determined after the reaction mixtures had been shaken for 12—24 hr.

The analysis of the exchanger obtained at the end-point of the pH titration showed that the composition of the compound was $Zr(NH_4PO_4)_2\cdot H_2O$. Taking the difference in molecular weight from c-ZrP into consideration, in the backward titration 278 mg of the ammonium-form exchanger was placed in contact with the solution of $HCl+NH_4OH$. The ammonium hydroxide added was adjusted to 3.29 meq/g c-ZrP, since 6.6 meq NH_4^+/g c-ZrP was already included in the exchanger, and the amount of added hydrochloric acid was varied.

In confirmation of the ion-exchange capacity, the titrations were carried out with NH_4OH alone and with HCl alone in separate runs.

Analytical Procedure. The ammonium forms of the exchanger were analysed as follows. Zr; A weighed sample (*ca.* 100 mg) and 1.5—2.0 g of sodium peroxide powder were mixed. To the mixture 25 ml of water was added in an ice bath. After a few minutes, the slurry was placed on a water bath and the precipitated zirconium hydroxide was aged for 2—3 hr. After filtration, the precipitate was dissolved in 3N HCl. Then the zirconium was re-precipitated as cupferronate and ignited to ZrO_2. PO_4; The phosphorus was determined gravimetrically by the method described by Kolthoff and Sandell.[8] NH_4^+; The ammonium ion was determined gravimetrically to be tetraphenyl borate.[9]

X-Ray Powder Diffraction. X-Ray powder patterns were obtained with Ni filtered copper X-rays using a Geigerflex (Rigaku Denki Co., Ltd.).

Results and Discussion

pH *Titration Curves.* The titration curves obtained for NH_4OH–NH_4Cl solution media are shown in Fig. 1. The forward titration curve can apparently be divided into two regions. The first region of the ion exchange extends from zero exchange to 4.4meq/g c–ZrP ammonium ion uptake. In the second region, the ion-exchange reaction proceeds slowly and the end-point of neutralization is not observed claerly. The titration curve in Fig. 2(a) also shows that the ion-exchange capacity of c–ZrP for the ammonium ion in

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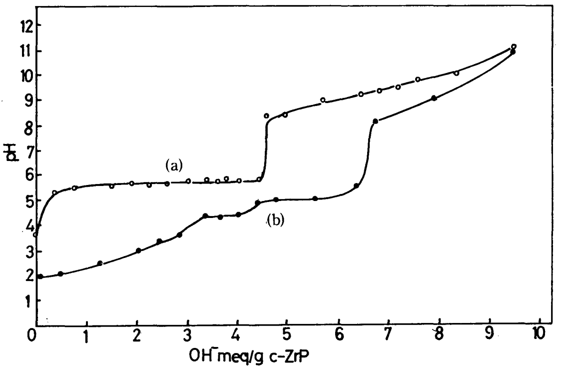

Fig. 1. pH titration curves for c–ZrP. Titrant: forward direction (—○—), 0.1N NH_4OH+0.1N NH_4Cl, backward direction (—●—), 0.1N HCl+NH_4Cl.

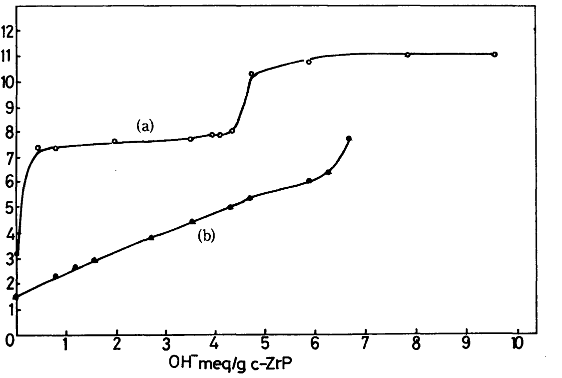

Fig. 2. pH titration curves for c–ZrP. Titrant: forward direction (—○—), 0.1N NH_4OH only, backward direction (—●—), 0.1N HCl only.

an acidic solution is equal to about 4.4 meq/g. As the theoretical ion-exchange capacity of c–ZrP is 6.6 meq/g, the value of 4.4 meq corresponds to a 66% exchange.

In the backward titration (Fig. 1(b)), it was found that the ion-exchange reaction took place in two stages. The first stage extended from an exchange of 100% to 67%, and the second stage, from 66 to 0%. That is, 0—33% of the ammonium ion in the exchanger was re-exchanged with the hydrogen ion at pH 5.5—5.0 and 34—100% over the pH range from 5.0 to 2.0. The second stage might be further divided into two steps if one takes account of the plateau found at an exchange of around 34—50% at pH 4.5. From Figs. 1(b) and 2(b) it turns out that the total ion-exchange capacity for the ammonium ion is equal to 6.6 meq/g c–ZrP experimentally.

The titration curves in Fig. 1 show the irreversibility of the ammonium-hydrogen ion exchange on c–ZrP; it results in a hysteresis loop of the curves. These may be due to the presence of different phases in the forward and backward titrations (the details will be presented later).

The ion exchange of the ammonium ion on c–ZrP resembles that of the lithium ion in some respects. Clearfield and Troup, and Nancollas and Harvie, have reported, respectively, that lithium-ion exchange takes place in two stages and that the ion-exchange capacity of c–ZrP for the lithium ion is 4.4 in an acidic solution and 6.6 meq/g in an alkaline solution.[10,11] This is what was observed for the ammonium ion.

It has already been established that c–ZrP works as a dibasic exchanger to the sodium ion and that the two groups of phosphate protons exist in the ratio of 1 to 1.[12] This can reasonably be expected from the $Zr(HPO_4)_2\cdot H_2O$ formula. For ammonium exchange, this is not the case; *i.e.*, the two groups of phosphate protons seems to exist in the ratio of 2 to 1. This phenomenon was also observed in the lithium-ion exchange.[10,11]

The compositions of the 66%-exchange phase (Phase I) and 100%-exchange phase (Phase II) are as follows. Phase I, Found: Zr; 28.3, PO_4; 57.6, NH_4; 7.2, ignition loss; 18.0%. Calcd for $Zr(NH_4PO_4)_{1.33}(HPO_4)_{0.67}\cdot H_2O$, Zr; 28.2, PO_4; 58.6, NH_4; 7.43, ignition loss; 18.1%. Phase II, Found: Zr; 27.4, PO_4; 54.9, NH_4; 10.8, ignition loss; 21.1%. This corresponds to $Zr(NH_4PO_4)_2\cdot H_2O$ (Calcd for Zr; 27.2, PO_4; 56.7, NH_4; 10.8, ignition loss: 20.9%).

X-Ray Diffraction. In Figs. 3 and 4, the X-ray diffraction patterns of the samples taken from the titration experiments are shown schematically. In Table 1, the interplanar spacing (*d* values) of c–ZrP, Phase I and Phase II, are shown. The *d* values of Phase II agreed with that reported by Clearfield and Stynes,[1] but did not agree with that reported by Dyer *et al.*[7]

At the initiation of the forward titration, a new reflection at d=9.49 Å was observed. In the ion-exchange process, the relative strength of this reflection increased and the reflection of 7.60 Å, which is the first one in c–ZrP, decreased. Beyond an exchange of

TABLE 1. *d* VALUES OF c-ZrP, PHASE I AND PHASE II

c-ZrP		Phase I		Phase II	
d(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0
		9.49	s	9.49	vs
7.49	vs	7.58	vs		
7.01	vw			4.72	vw
				4.67	w
				4.62	vw
4.47	w	4.48	w	4.46	w
4.42	vw	4.43	w		
		3.97	w	4.00	s
		3.66	w	3.68	m
3.55	s	3.56	s	3.57	vw
3.52	m	3.53	m		
3.21	vw				
		3.12	vw	3.14	m
				2.89	vw
				2.72	vw
2.64	vw	2.64	w	2.66	vw
2.62	vw	2.62	vw		
2.40	vw	2.41	vw		

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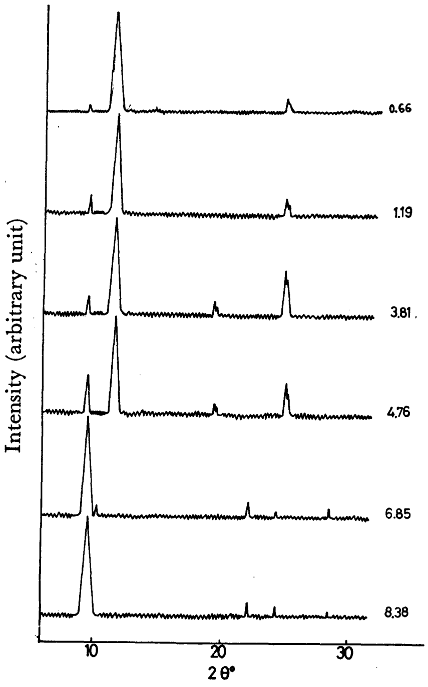

Fig. 3. Schematic diagrams of X-ray diffraction patterns for the ammonium forms of c–ZrP in forward titration. Numerals correspond to that of abscissa in Fig. 1.

66%, these two reflections were both observed. Finally, the latter reflection diminished.

Crystalline zirconium phosphate is known to have a layered structure, the interlayer distance is represented by the first reflection in the X-ray powder pattern. The change in the interplanar distance is found to be shorter than that to be expected from the ionic radius of the ammonium ion. Clearfield and Stynes[1] suggested that the shorter *d* value for the first reflection of the ammonium form might be due to hydrogen-bond formation between the ammonium ion and the phosphate group.

It is not possible to deduce, from the obtained diffractograms alone, whether the phases accompanied by the ion exchange are entirely different from that of c–ZrP or whether they are a mixture of two phases, c–ZrP and the ammonium-form exchanger. By analogy with the lithium-ion exchange, however, the existence of two phases is very likely, Phase I just at an exchange of 66% and Phase II at 100%.

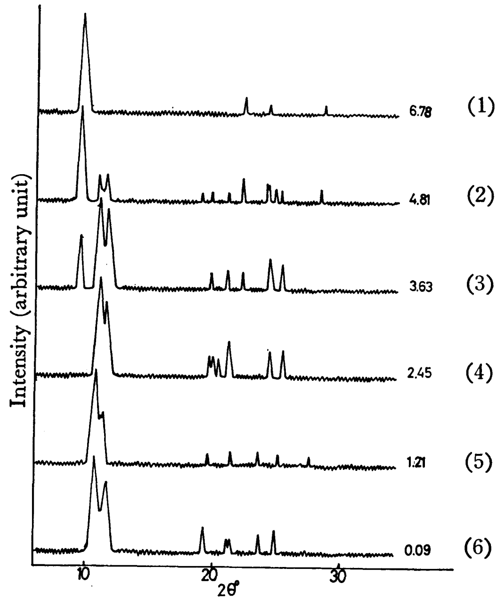

Fig. 4. Schematic diagrams of X-ray diffraction patterns for the ammonium forms of c–ZrP in backward titration. Numerals correspond to that of abscissa in Fig. 1.

The X-ray diffraction patterns of the samples which were taken from the backward titration were different from those of the forward titration. On the re-exchange of the ammonium ion with the hydrogen ion, the first reflection (d=9.50 Å) decreased and the second (d=8.20 Å) and third reflections (d=7.60 Å) appeared. The third reflection is identical with the first one of c–ZrP. The first reflection was not observed in Sample (4). It corresponds to the third reflection at 3.3 meq OH^-/g c–ZrP in the titration curve of Fig. 1(b). At the end of the backward titration, the exchanger was no longer identical with the original one, c–ZrP.

As has been stated above, the structural change in the exchanger is irreversible through the whole range of the ion exchange. This is the cause of the hysteresis loop in the titration curves.

In the ion-exchange cycle for the lithium ion, gelatinous zirconium phosphate was formed.[10] When the ammonium ions in the exchanger were replaced by protons, the crystallinity was maintained.

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