Studies on the Ammonium Form of Crystalline Zirconium Phosphate. III.[1,2) Ammonium-Hydrogen Ion-exchange on α-Zirconium Phosphate Prepared by the Direct Precipitation Method

Yoshitsugu Hasegawa* and Motomasa Kuwayama**

Department of Industrial Chemistry, Faculty of Technology,
Tokyo University of Agriculture and Technology, Nakamachi, Koganei, Tokyo 184

(Received November 7, 1977)

The ammonium-hydrogen ion-exchange on α-zirconium phosphate prepared by the direct precipitation method has been investigated by means of pH titration and X-ray diffractometry. In the forward process (α-zirconium phosphate to the ammonium form) the ion-exchange reaction took place in one stage at the equilibrium pH of 5.9—6.0 and the α-zirconium phosphate exchanger was directly converted into the ammonium form. In the reverse process (the ammonium form to α-zirconium phosphate) the reaction proceeded in three stages, that is, the ammonium form→ a half-exchanged form→ an intermediate form→ α-zirconium phosphate. The chemical composition of the half-exchanged form has been represented as $Zr(NH_4PO_4)(HPO_4)\cdot nH_2O$ ($n > 0.5$). A small amount of ammonium ions in the exchanger could not be easily replaced with protons in the solution.

The properties of α-zirconium phosphate as an ion-exchanger have been studied by several workers in recent years. It is well known that the ion-exchange reaction on α-zirconium phosphate is strongly affected by its crystal structure, since the largest opening into the crystal would allow a spherical cation with a diameter of 2.63 Å to diffuse into the crystal. Experimentally, Li^+, Na^+, and K^+ exchanged in acidic solution.[3) Although the ionic radius of the ammonium ion is larger than 1.32 Å, the ammonium-hydrogen ion-exchange took place on α-zirconium phosphate.[4,5) In the hydrogen-lithium ion-exchange system the titration curve exhibited two clear inflections at 50 and 66% exchange on α-zirconium phosphate prepared by the direct precipitation (d.p.) and the long refluxing,[6,7) while only one inflection was observed at 66% exchange on α-zirconium phosphate prepared by the ordinary reflux method.[8) Thus the ammonium-hydrogen ion-exchange on α-zirconium phosphate depends on the degree of crystallinity.

To date the ordinary reflux method has been employed in the course of a survey of ammonium form exchangers, but α-zirconium phosphate of high crystallinity could not be obtained by this method.[9) The present investigation has been undertaken using α-zirconium phosphate prepared by the d.p. method in order to avoid the gelatinous characteristics of the compound.

While the manuscript of this paper was in preparation, Alberti *et al.*[10) have reported the ammonium ion and ammonia uptake on α-zirconium phosphate prepared by the d.p. method.

Experimental

Preparation of the α-Zirconium Phosphate Ion-exchanger. α-Zirconium phosphate, $Zr(HPO_4)_2\cdot H_2O$, was prepared by a modification of Horsley and Nowell's method.[11) Zirconium dichloride oxide octahydrate (32 g) was dissolved in water (1050 ml), and hydrofluoric acid (40%, 22 ml) added slowly followed by orthophosphoric acid (about 85%, 77 ml) under continuous stirring. When gelatinous zirconium phosphate precipitated, a small amount of hydrofluoric acid was added until the precipitate was redissolved. The mixture was placed in a water bath (50 °C) and prehumidified air passed through it for 24—30 h. The precipitated α-zirconium phosphate was decantated with distilled water and separated by centrifugation.

pH *Titrations.* The titrations were carried out in batch. A weighed amount of α-zirconium phosphate (100 mg) was placed in contact with the solution of ammonium chloride–aqueous ammonia (10.0 ml) in a thermostat regulated at 25 °C in the forward titration. The composition of the solution was adjusted so that the total ammonium ion was equal to 0.1 M with a varying ratio of NH_4Cl to aqueous NH_3 in the range from 1 to 0. After the mixture was shaken continuously for a specified period of time, the value of the supernatant solution was measured using a pH meter with a glass electrode. Since the chemical composition of the ammonium form is represented as $Zr(NH_4PO_4)_2\cdot H_2O$, the ammonium form (112 mg) was placed in contact with NH_4Cl–HCl solution (10.0 ml) in the reverse titration. The concentration of ammonium chloride was kept constant (3.36×10^{-2} M) and the amount of hydrochloric acid varied.

For the forward process, the titration was also carried out with ammonium acetate–aqueous ammonia solution.

Analytical Procedure. The structural change of the exchanger during the ion-exchange process was measured by X-ray diffractometry. The powder patterns of the exchangers were obtained with a Geigerflex X-ray diffractometer with nickel filtered copper radiation. To avoid obscurity due to overlap and instability of peaks the powder pattern of one sample was recorded under wet and dry conditions. The wet sample was covered with a Mylar film to prevent evaporation after mounting on a glass holder. The dried sample was prepared over a saturated sodium chloride solution (relative humidity about 75% at room temperature). Thermogravimetric and differential scanning calorimetric data were obtained on a Rigaku scanning calorimetric balance TG-DSC standard unit. The chemical analysis of the exchanger was carried out according to the methods described previously.[4)

Results and Discussion

Characterization of the α-zirconium phosphate ion-exchanger was made by X-ray diffraction pattern, TG, DSC data, pH titration with LiCl-LiOH solution, and chemical analysis. The interplanar spacings (*d*-values)

** Present address: New Japan Surveyors and Sworn Measurers Association, 541 Chitose, Takatsu-ku, Kawasaki 211.

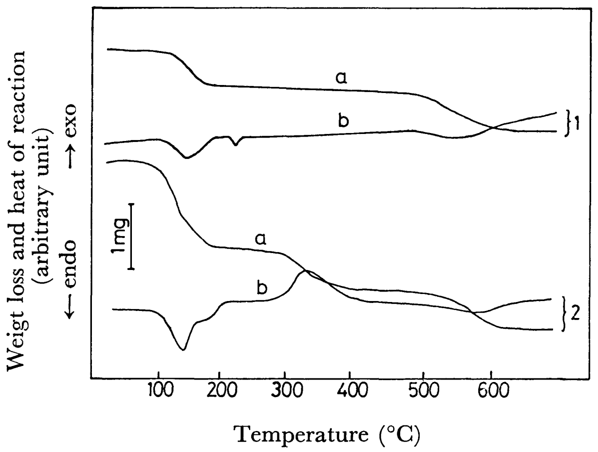

Fig. 1. Thermoanalytical curves. 1: α-Zirconium phosphate in H^+ form, 2: the ammonium form, (a) thermogravimetric and (b) scanning calorimetric curve.

agreed with those given in the literature.[11] The results of thermal analysis are shown in Fig. 1(1). The titration curve for the lithium ion agreed with those reported previously.[6,7] The chemical composition was as follows; Found: Zr, 30.2; PO_4, 63.7; ignition loss, 12.0%. Calcd for $Zr(HPO_4)_2 \cdot H_2O$: Zr, 30.0; PO_4, 63.0; ignition loss, 12.0%. The above results show that the α-zirconium phosphate ion-exchanger used was highly crystalline and essentially identical to that prepared by long refluxing.[5]

The chemical composition of the ammonium form was as follows: Found: Zr, 27.2; PO_4, 57.6; NH_4, 10.8; ignition loss, 20.9%. Calcd for $Zr(NH_4PO_4)_2 \cdot H_2O$: Zr, 27.2; PO_4, 56.7; NH_4, 10.8; ignition loss, 20.9%. The results of thermal analysis for the ammonium form are shown in Fig. 1(2). The curves agreed with those reported for the reflux method.[12] The exothermic peak at about 400 °C might be caused by the oxidation of the evolved ammonia on platinum surface of a crucible.[13]

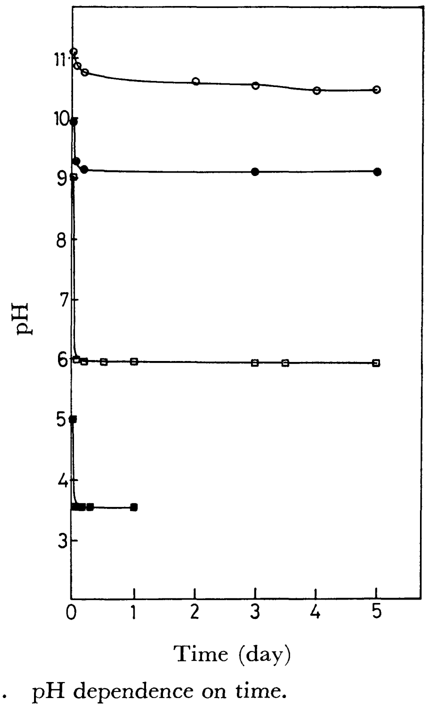

Fig. 2. pH dependence on time.
OH^- meq/g α-zirconium phosphate; ■ 0, □ 3, ● 7, ○ 10.

pH *Titrations*. To determine the equilibration time the pH values of the solutions were measured at specific intervals of time. Figure 2 shows that the ion-exchange reaction proceeded rapidly initially and then the pH value gradually fell to an equilibrium value. It took about 5 days to attain equilibrium for 0.1 M aqueous ammonia, compared to 6 h for 0.1 M ammonium chloride solution. In the reverse titration the pH values were measured at 6.00 and 3.00 meq H^+/g α-zirconium phosphate. The observed equilibrium was attained within one day for both solutions. Thus, a reaction time of 2—5 days was chosen in the forward process and 2 days in the reverse one.

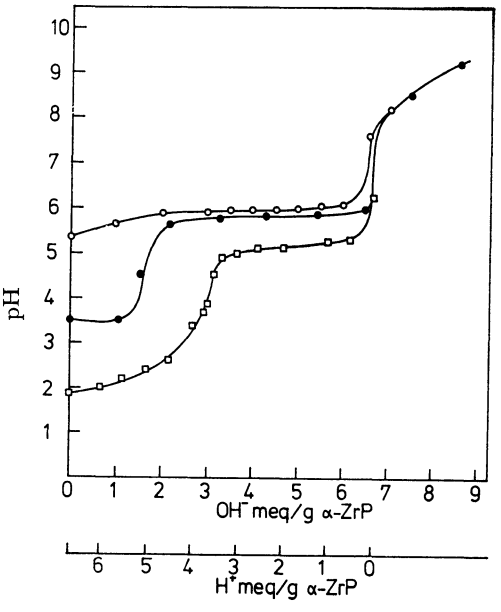

Fig. 3. pH titration curves.
(a) ● Forward titration NH_4Cl-NH_3(aq), (b) ○ forward titration NH_4CH_3COO-NH_3(aq), (c) □ reverse titration NH_4Cl-HCl.

The pH titration curves obtained are shown in Fig. 3. The curve (a) shows that in the forward process the ammonium-hydrogen ion-exchange reaction took place at a pH of about 3.5 until approximately $OH^- = 1.0$ meq, whereupon the pH rose sharply to the equilibrium pH of 5.9. The lowering of the pH in the initial stage may be ascribed to the selective uptake of the ammonium ion on α-zirconium phosphate. Figure 3(b) demonstrates that in ammonium acetate–aqueous ammonia solution the equilibrium pH and the ion-exchange capacity were almost equal to those observed for the chloride solution. In the initial stage of curve (b) compared with the curve (a) higher pH values are due to the bufferring action of the ammonium acetate solution. The α-zirconium phosphate ion-exchanger behaved as a monobasic exchanger with a capacity of 6.64 meq/g. The equilibrium pH was found to be approximately 5.9—6.0.

The titration curve of the reverse process is shown in

Fig. 3(c). It appears that the ion-exchange reaction took place in two stage, that is, in the first stage 50% of the ammonium ions in the exchanger were replaced with hydrogen ions and in the second stage the remaining ammonium ions were involved in the reaction. The reaction proceeded in a more acidic solution than for the forward titration, especially in the second stage. At the hydrogen ion addition of 6.0 and 6.6 meq the pH values of the solutions were found to be 2.03 and 1.88. The low pH value indicates that some hydrogen ions remained in the solution phase and the ionic mole fraction of the ammonium ion in the exchanger, $\bar{X}_{\mathrm{NH_4}^+}$, was higher than expected from the forward process. Assuming that the apparent value of pH on a pH meter is equal to $-\log [\mathrm{H}^+]$, the hydrogen ion concentration can be calculated to be 9.3×10^{-3} and 1.3×10^{-2} mol/l and this corresponds to the fact that hydrogen ions of 5.2 and 5.4 mmol/g α-zirconium phosphate exchanged with the ammonium ions in the exchanger. Consequently, $\bar{X}_{\mathrm{NH_4}^+}$ is estimated to be 0.22 and 0.19. This demonstrates that the α-zirconium phosphate exchanger has a strong affinity for the ammonium ion especially when the exchanger is loaded by a small amount of ammonium ion. A similar behavior has been observed in another system.[14)]

The titration curves, (a) and (c) in Fig. 3, indicate the irreversible ion-exchange reaction for the ammonium–hydrogen ion-exchange system.

Since the α-zirconium phosphate exchanger and its salt form have a layered structure, the structural change of solid phase is revealed in comparison with the reflections of the powder patterns at lower diffraction angles.[15)] A similar phenomena may be expected, because the ammonium form also has a layered structure.[16)]

Table 1. Phases present in the forward titration

OH- meq/gZrP	Medium	
	Cl-	CH_3COO^-
0	H	H
1.0	H	H+A
2.2	H+A	H+A
3.2	H+A	H+A
4.3	A+H	A+H
5.4	A+H	A+H
6.4	A+H	A+H
6.5		A
7.6	A	

H=Hydrogen form $Zr(HPO_4)_2 \cdot H_2O$,
A=Ammonium form $Zr(NH_4PO_4)_2 \cdot H_2O$.

Table 1 shows the structural change in the exchanger in the forward process. At the beginning of the ion-exchange reaction only the α-zirconium phosphate phase was present. Two phases, the α-zirconium phosphate and the ammonium phase, coexisted in the range of $\bar{X}_{\mathrm{NH_4}^+}=0.33$—$0.91$. The intensity of the diffraction peak of α-zirconium phosphate decreased with an increase in $\bar{X}_{\mathrm{NH_4}^+}$. Table 1 also shows that the structural change of the exchanger was similar in the chloride and acetate solution. At the initial stage of the ion-exchange the reaction proceeded further in the acetate solution than in the chloride solution, because the solution phase of acetate had higher pH value. α-Zirconium phosphate was directly converted into the ammonium form. These data support the validity of the interpretation of the titration curves given above.

Table 2. Phases present in the reverse titration

H^+ meq/gZrP	Phase
0	A
0.05	A+A′
2.00	A+A′
2.50	A′+A
3.30	A′+A
3.50	A′

A=Ammonium form, A′=A phase having peaks at 11.5 and 10.5° ($I_{11.5}/I_{10.5}=8/5$).

A complicated change was observed on the X-ray diffraction patterns of the solid phases during the reverse titration. In the first stage, 0—50% of the ion-exchange, four peaks were observed for the wet samples at a range of lower angles. The intensity of the peak at $2\theta=8.6°$ was strongly affected by the water content of the sample. When the same sample was dried over a saturated sodium chloride solution, three peaks were observed on the powder pattern. On the assumption that the number of phases does not change on drying out of the solid sample, assignment of the peaks was conducted. The peak at 9.4° originated from the ammonium form and its intensity decreased with an increase in the mole fraction of hydrogen ion in the exchanger, $\bar{X}_{\mathrm{H}^+}$. This peak was found in both wet and dry samples up to $H^+=3.30$ meq/g α-zirconium phosphate. The intensity of other two peaks at 11.5° and 10.5° increased as the ion-exchange process proceeded. In consideration of the inflection point of the titration curve (Fig. 3(c)) and the phase rule,[9)] only two phases must be present in this region. Hence, the two peaks may be assigned as one phase, namely the half-exchanged form. A similar change was reported for α-zirconium phosphate prepared by long refluxing.[5)] The ammonium ion and water contents of the half-exchanged form were determined by elemental analysis after drying. Found: N, 4.32; H, 1.84; ignition loss at 950 °C (100—ash), 13.4%. Calcd for $Zr(NH_4PO_4)(HPO_4) \cdot 0.5H_2O$: N, 4.53; H, 1.96; ignition loss, 14.3%. The half-exchanged form had more waters of hydration in solution than in the dry condition.

In the second stage of the reverse titration, the dried exchanger had two peaks at 11.5 and 10.5°. The intensity of the peak at 11.5° decreased with increase in $\bar{X}_{\mathrm{H}^+}$ and the peak was observed as a shoulder of the peak at 10.5°. Subsequently the intensity of the peak at 11.5° increased again with the reaction above the hydrogen ion addition of 4.5 meq suggesting that a half-exchanged and an intermediate form were present in the region of $H^+=3.6$—4.5 meq. An intermediate and α-zirconium phosphate coexisted above $H^+=4.5$ meq (Table 3). At the final stage of the reverse titration an intermediate form was still present. This indicates

TABLE 3. CHANGE OF THE INTENSITY RATIO IN THE SECOND STAGE OF THE REVERSE TITRATION

H^+ meq/gZrP	$I_{11.5}/I_{10.5}$	Phase
3.50	8/5	A′
4.00	5/6	A′, A″
4.50	1/20	A′, A″ or A″, H
5.00	4/11	A″, H
6.00	5/3	A″, H
6.60	11/7	A″, H

A″=A phase deduced having a peak only at 10.5°, H=Hydrogen form.

that the ion-exchange reaction does not proceed stoichiometrically and that the ammonium ion was held by the exchanger.

The conclusion drawn are as follows. (1) Highly crystalline zirconium phosphate ion-exchanger was prepared under the mild conditions employed and the exchanger was essentially identical to that prepared by long refluxing. (2) The α-zirconium phosphate ion-exchanger behaved as a monobasic acid to aqueous ammonia and was converted into the ammonium form. In the reverse process the ion-exchange reaction took place in three stages. (3) A small amount of ammonium ion in the exchanger could not be replaced easily with hydrogen ion.

The authors are grateful to Professor Shuji Abe for his continuing interest and encouragement. They also wish to thank Mrs. Michiko Asuke for her assistance in the elemental analysis.

References

1) Part II. Y. Hasegawa and Y. Komiyama, *Bull. Chem. Soc. Jpn.*, **51**, 2302 (1978).

2) A part of this work was presented at the 26th International Congress on Pure and Applied Chemistry, Tokyo, Japan, September, 1977.

3) A. Clearfield, G. H. Nancollas, and R. H. Blessing, "Ion Exchange and Solvent Extraction," ed by J. A. Marinsky and Y. Marcus, Marcel Dekker, New York (1973), Vol. 5, pp. 21—28.

4) Y. Hasegawa and H. Aoki, *Bull. Chem. Soc. Jpn.*, **46**, 836 (1973).

5) A. Clearfield and R. A. Hunter, *J. Inorg. Nucl. Chem.*, **38**, 1085 (1976).

6) G. Alberti, U. Costantino, S. Alluli, M. A. Massucci, and M. Pelliccioni, *J. Inorg. Nucl. Chem.*, **34**, 1347 (1973).

7) A. Clearfield and D. A. Tuhtar, *J. Phys. Chem.*, **80**, 1296 (1976).

8) A. Clearfield and J. Troup, *J. Phys. Chem.*, **74**, 314 (1970).

9) A. Clearfield and A. S. Medina, *J. Phys. Chem.*, **75**, 3750 (1971); A. Clearfield, A. Oskarsson, and C. Oscarsson, *Ion Exchange Membrane*, **1**, 91 (1972).

10) G. Alberti, R. Bertrami, U. Costantino, and J. P. Gupta, *J. Inorg. Nucl Chem.*, **39**, 1057 (1977).

11) S. E. Horsley and D. V. Nowell, *J. Appl. Chem. Biotechnol.*, **23**, 215 (1973).

12) Y. Hasegawa, *Bull. Chem. Soc. Jpn.*, **46**, 3296 (1973).

13) T. Flora, *Acta Chem. Acad. Scientiarum Hungacae, Tomus*, **69**, 1 (1971).

14) Y. Hasegawa, *J. Inorg. Nucl. Chem.*, **38**, 319 (1976).

15) A. Clearfield, W. L. Duax, A. S. Medina, G. D. Smith, and J. R. Thomas, *J. Phys. Chem.*, **73**, 3424 (1969).

16) A. Clearfield and J. M. Troup, *J. Phys. Chem.*, **77**, 243 (1973).