

Short Communication

Preparation of insoluble titanium(IV) phosphate possessing ion-exchange character from ilmenite

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An amorphous compound having composition $\text{TiOHPO}_4 \cdot 2.11\text{H}_2\text{O}$ has been prepared by the addition of H_3PO_4 solution to the iron free titanium(IV) solution made from ilmenite. The product shows ion-exchange property towards alkali (Na^+) and alkaline earth (Ba^{++}) metal ions to a limited extent. The product cannot be crystallized by the conventional method.

The crystalline tetravalent metal phosphates, particularly those of Zr^{4+} and Ti^{4+} having α - and γ -layered structures have become an interesting group of compounds for their ion-exchange, intercalation, ion-conduction and catalytic properties¹⁻⁷. Starting materials (ZrOCl_2 and TiCl_4) are rather expensive and the yields are usually very low. So an attempt has been undertaken to prepare insoluble titanium(IV) phosphate (amorphous or crystalline) starting from a cheap source, viz., ilmenite which is abundantly available in the sea-shore of Bangladesh.

Experimental procedure—Ilmenite was collected from the pilot plant to BAEC at Cox's Bazar. It contained 27.7% titanium and 32.5% iron in both ferrous and ferric states. All the chemicals used were of reagent grade. Following up the procedure given by Biswas *et al.*⁸ 800 cm^3 iron free titanyl chloride solution containing 16.1 g dm^{-3} Ti^{4+} , 9 mol dm^{-3} HCl and only 0.0037 g dm^{-3} Fe^{3+} (solution-A) was prepared from ilmenite using 6 mol dm^{-3} HF as leachant.

Precipitation of phosphate was carried out in two different ways: (i) Solution-A was diluted to 1.1 times to decrease the concentrations to 14.65 g dm^{-3} Ti^{4+} and 8.2 mol dm^{-3} HCl and the slow addition of 0.62 cm^3 mol dm^{-3} volume-strength product (VS) of ortho- H_3PO_4 to each cm^3 of this solution; and (b) after decreasing the acidity of solution-A to 2 mol dm^{-3} in HCl using NaOH pellets and Ti^{4+} concentration to 14.3 g dm^{-3} , the slow addition of 1.25 cm^3 mol dm^{-3} VS of ortho- H_3PO_4 to each cm^3 of this solution, resulted in the

complete precipitations under constant stirring over-night. The precipitates were centrifuged, washed several times with dist. water until the pH of the washed solution became 3 and dried over P_2O_5 in a desiccator under vacuum for three months.

The Na^+ and Ba^{2+} ion-exchange curves were obtained both by continuous and batch-wise titration methods as given elsewhere^{9,10}. The supernatant liquids from batch-wise titrations were analysed for PO_4^{3-} contents and acidities. Blank titrations were also carried out to calculate the actual uptake values. To determine the $\text{PO}_4^{3-}/\text{Ti}^{4+}$ ratio, 25 mg sample (3 sets) was dissolved in 4 drops of conc. HF , diluted to 50 cm^3 and analysed for Ti^{4+} by H_2SO_4 - H_2O_2 method¹¹ and PO_4^{3-} by $(\text{NH}_4)_2\text{MoO}_7$ -acetone method¹². The weight losses of the product were determined at 120 and 900°C.

Results and discussion—Products obtained in two different ways are found to be identical. The $\text{PO}_4^{3-}/\text{Ti}^{4+}$ ratio of 0.996 (24.48% Ti^{4+} and 48.2% PO_4^{3-}) and 19.28 wt% loss at 120°C suggest the composition $\text{TiOHPO}_4 \cdot 2.11\text{H}_2\text{O}$ for the product. This composition has been confirmed from the wt % loss of the products at 900°C (23.45%). Considering pyrophosphate as the final pyrolysed product¹³ ($2 \text{ TiOHPO}_4 \cdot 2.11\text{H}_2\text{O} \xrightarrow{900^\circ\text{C}} (\text{TiO})_2\text{P}_2\text{O}_7 + 5.22 \text{ H}_2\text{O}$), the theoretical wt% loss is 23.74%. Since the molecular weight of the compound is 196, the ion-exchange capacity of the compound should be 5.1 meq g^{-1} compared to 7.74 and 9.5 meq g^{-1} for α -layered and amorphous $\text{Ti}(\text{HPO}_4)_2$ respectively⁹.

The pH vs actual Na^+ uptake curve obtained by batch-wise titration is shown as curve A in Fig. 1. It is observed during Na^+ -exchange batch-wise studies that phosphate and titanium ions are released (0.63, 0.64, 0.69, 2.77, 3.56, 6.36 and 9.12% PO_4^{3-} —hydrolysis and 0.30, 0.26, 0.21, 0.18, 0.09, 0.06 and 0.04% Ti^{4+} in solution at eq. pH 3.72, 5.45, 6.95, 8.30, 8.53, 9.38 and 9.90 respectively). Considering the hydrolysis reaction as: $\text{TiOHPO}_4 + 2\text{NaOH} \rightarrow \text{TiO}(\text{OH})_2$ or $\text{TiO}_2 \cdot \text{H}_2\text{O} + \text{Na}_2\text{HPO}_4$, the actual uptake of Na^+ at different eq. pH values in batch-wise titration can be obtained by subtracting the amount of OH^- used to release PO_4^{3-} in solution from the total amount of NaOH consumed. It is noticed from the above data on hydrolysis that the concentration of Ti^{4+} in

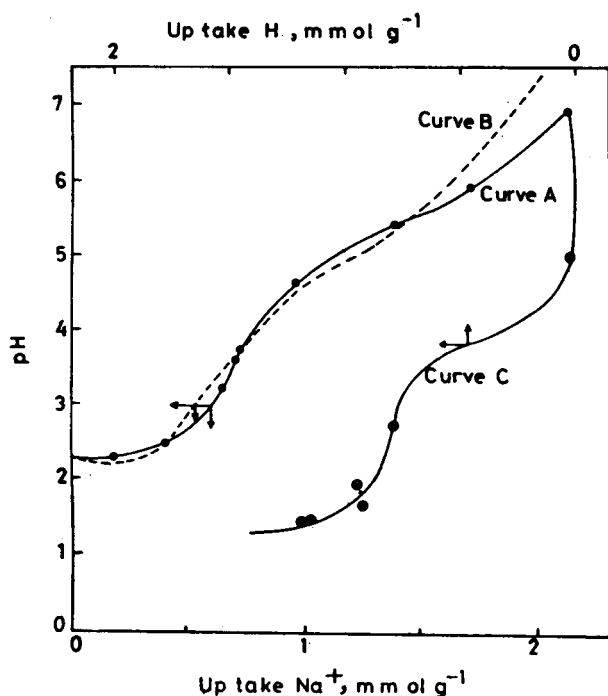


Fig. 1—Na⁺-exchange and regeneration [Curve A—actual Na⁺-uptake obtained by batch-wise titration (calculated by deducting the amounts of NaOH consumed in hydrolysis from total NaOH consumed in each batch); Curve B—Na⁺-uptake obtained by continuous titration by 0.1 mol dm⁻³ (NaCl + NaOH); Curve C—H⁺-uptake obtained by batch-wise titrations. Time in batch titration: 24 h and in continuous titration: 4h]

solution is decreased with increasing PO₄³⁻ concentration at increasing pH values. It is due to the insolubility of TiO(OH)₂¹⁴. The actual uptake curve A in Fig. 1 obtained from batch-wise titration overlaps almost with that in continuous titration, curve B in Fig. 1. This suggests that the H⁺-Na⁺ exchange on the material is faster than the phosphate hydrolysis. Only about 40 and 60% exchanges take place at pH 7 and 10 respectively. The complete exchange is not possible to obtain for increasing hydrolysis at higher pH. The 50% exchange occurs at pH 9. The comparison of this result with that reported by Alberti *et al.*⁹ for amorphous Ti(HPO₄)₂ indicates that the product under investigation is a better exchanger from the points of its less susceptibility towards hydrolysis and greater uptake values.

To investigate on the selectivity of alkali metal ions over alkaline earth metal ions to exchange H⁺ of the product, the ion-exchange study with Ba²⁺ has been performed both by continuous and batch-wise titrations. The uptake curves obtained from two different titration techniques are well separated. Unlike in the case of Na⁺-exchange

study, here the amount of PO₄³⁻-hydrolysed into the solution cannot be estimated for experimental limitations (SO₄²⁻ in (NH₄)₂Mo₂O₇ solution gives a heavy precipitation of Ba²⁺ existing in solution). The amount of Ti⁴⁺-hydrolysed into the solution cannot also be estimated for the same reason (colorimetric estimation of Ti⁴⁺ uses H₂SO₄-H₂O₂ as coloring agent). Attempts to estimate the amount of PO₄³⁻ hydrolysed by other techniques involving colorimetry have not given fruitful results. For Ba²⁺, the theoretical ion-exchange capacity of the product should be 2.55 mmol g⁻¹. An uptake of only 0.8 mmol Ba²⁺ g⁻¹ has been obtained at pH 12 by direct titration, whereas by batch-wise titration, an uptake of 1.1 mmol Ba²⁺ g⁻¹ (including the amount Ba(OH)₂ used up in hydrolysis if at all) has been obtained at the same pH. Around pH 7, the uptake of Ba²⁺ is relatively small (0.5 mmol g⁻¹). It is, therefore, concluded that the exchanger can preferentially adsorb Na⁺ than Ba²⁺.

The batch-wise regeneration of Na⁺-exchanged material is given as curve C in Fig. 1; as pH vs H⁺-uptake curve in mmol g⁻¹. Comparison of two curves (A&C) in Fig. 1 indicates that the elution is not completed even by the use of 0.1 mol dm⁻³ HCl (without any NaCl solution). Under this condition the eq. pH becomes 1.4 and H⁺-uptake of 1.2 mmol g⁻¹ is obtained. Therefore, hysteresis is encountered here as expected for most of the inorganic exchangers. From the nature of the curves, it is expected that the complete elution can be obtained only by the use of conc. HCl to decrease the pH of the equilibrated solutions.

Following the procedure given by Alberti *et al.*⁹ for crystallizing amorphous Ti(HPO₄)₂, an attempt has been made to crystallize the amorphous product under investigation but without any success. It is believed¹⁵ that in forming the crystalline α- or γ-layered titanium phosphate, Ti⁴⁺ must have six co-ordinating positions as present in amorphous Ti(HPO₄)₂. In this case, since titanium exists as TiO²⁺, two co-ordinating positions are occupied by oxygen; so that there are only for available co-ordination positions of TiO²⁺ which cannot satisfy the condition for the formation of layered tetravalent metal phosphates.

Conclusions—The following conclusions can be drawn: By addition of H₃PO₄ to the iron free titanyle chloride solution made from ilmenite through HF-leaching route, an amorphous product is obtained. The product on conditioning over P₂O₅ for 3 months is shown to have a composition TiOH-PO₄·2.11H₂O. The product shows ion-exchange properties towards Na⁺ and Ba²⁺. It is found as a better exchanger than amorphous Ti(HPO₄)₂. Both

for Na^+ and Ba^{2+} , 100% exchange is not obtained even at pH 10. The exchanger undergoes severe hydrolysis above pH 8. Hysteresis is encountered during elution, and crystallization of amorphous TiOHPO_4 is not possible.

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