Vanadates of Lead (II): An Electrometric Study

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The formation and compositions of lead vanadates formed by the interaction of lead nitrate and different alkali vanadates (ortho, pyro, meta and poly) have been investigated by means of pH, e.m.f. and conductometric titrations between the reactants at several concentrations in the presence of 20% alcoholic media. The well defined breaks and inflections in titration curves provide definite evidence for the formation and precipitation of ortho-3PbO·V₂O₅, pyro-2PbO·V₂O₅ and meta-PbO·V₂O₅ vanadates of lead at pH ranges 7.5—9.0, 5.75—7.25 and 4.25—5.25 respectively.

The literature on the study of vanadates of lead (II) is scanty and most of the earlier workers had confined themselves to the preparative and analytical study of these compounds. Roscoe prepared sparingly soluble lead ortho-vanadate Pb₃(VO₄)₂ by adding lead acetate to sodium orthovanadate solution. Ephraim and Beck reported the formation of lead ortho-hexavanadate 3PbO·2V₂O₅·2H₂O by treating manganese hexavanadate with lead nitrate. Berzelius obtained the yellow precipitate of lead due-ter-o-tetra-vanadate PbV₂O₁₁. Ditte prepared lead pyrovanadate Pb₂V₂O₇ by pouring ammonium meta vanadate solution into an acetic acid solution of lead nitrate. Roscoe (Loccit) on mixing sodium pyro-vanadate and lead acetate solutions, obtained lead oxy-pyro-vanadate PbO·2Pb₂V₂O₇; possibly a mixture of Pb₃(VO₄)₂ and Pb₂V₂O₇. Carnot, Zolotavin and Guiter reported the formation of lead meta vanadate under different conditions. In view of the insufficient and conflicting details of the reports of earlier workers on the composition of lead vanadates, and in the absence of any electrometric data on the subject, it was considered worthwhile to study the formation and compositions of lead vanadates, obtained by the interaction of lead nitrate and alkali vanadates at different pH levels, by means of electrometric techniques which have provided more conclusive evidences on the composition of metal vanadates. Hence the present investigation has been undertaken.

Experimental

Anal R. (B.D.H.) reagents NaOH, V₂O₅, Pb(NO₃)₂ and reagent grade HNO₃ were used and their solutions prepared in air-free conductivity water.

A standard solution of sodium ortho-vanadate was prepared by digesting one mole of V₂O₅ in boiling solution of NaOH containing six moles of it. The alkali pyro and meta vanadate solutions were prepared by adding two and four moles of HNO₃ to a solution containing one mole of ortho-vanadate at 100 °C.

pH and e.m.f. measurements were carried out on Cambridge null-deflection type pH-meter using a wide range glass electrode and a bright platinum foil as an indicator electrode in conjunction with S.C.E. The e.m.f. and pH were noted after each addition of the titrant in small increments which were further decreased in the region of the end point and plotted against the volume of the titrant added. The end points were determined from the slope inflection in titration curves and the maximum values of dpH/dV and dE/dV.

The conductance measurements were carried out on an electronic eye indicator type conductometer. Twenty ml of the solution was taken in the conductivity cell each time. The corrected conductances were plotted as a function of the ml of the titrant added and the end points were judged from the breaks in titration curves.

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Results and Discussion

SAXENA and Co-workers have shown that the addition of acid to alkali ortho-vanadate and NaOH to V₂O₅ solutions at room temperature causes the formation of various poly-anions of uncertain composition, but when the solutions were heated after each addition of the titrant, three different iso-

poly-anions viz. (V₂O₅)₄⁰⁻, (VO₃)⁻¹ and (V₁₀O₂₇)₄⁶⁻ are formed in the vicinity of pH 10, 7 and 4.5 respectively. Hence it was considered of interest to ascertain whether similar salts of heavy metals may be precipitated as a result of decomposition. The reaction between Pb(II) and alkali vanadates has therefore, been studied by means of pH, e.m.f. and conductometric titrations with regard to the changes occurring in H⁺ ion concentrations and the compositions of precipitates formed.

Ortho-vanadate titrations: The pH of lead nitrate and alkali ortho-vanadate solutions were measured by a wide range glass electrode and found to be in the vicinity of 4.5 and 12.0 respectively. Fig. 1 illustrates the changes occurring in the pH values during the reaction between Pb(NO₃)₂ and VO₃⁻ ions. In the case of direct titrations (fig.1, Curve1), when lead-nitrate solution from the microburette is

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Fig. 1. Direct and Reverse pH titrations between Pb(NO₃)₂ and alkali vanadates. Curve I. ml of m/5 Pb(NO₃)₂ added to 20 ml of m/100 3 Na₂O·V₂O₅. Curve II. ml of m/5 3 Na₂O·V₂O₅ added to 20 ml of m/10 Pb(NO₃)₂. Curve III. ml of m/10 Pb(NO₃)₂ added to 20 ml of m/125 2 Na₂O·V₂O₅. Curve IV. ml of m/5 2 Na₂O·V₂O₅ added to 20 ml of m/20 Pb(NO₃)₂. Curve V. ml of m/10 Pb(NO₃)₂ added to 20 ml of m/60 Na₂O·V₂O₅. Curve VI. ml of m/25 Na₂O·V₂O₅ added to 20 ml of m/200 Pb(NO₃)₂.

When the original solution was added to ortho-vanadate solution a gradual decrease in pH was observed till the stochiometric end-point is reached and after which the smallest addition of the titrant causes a sharp fall in pH, indicating the completion of reaction and suggesting the formation of lead ortho-vanadate at the pH range (7.5–9.0). In the case of reverse titrations (fig. 1, Curve II), when ortho-vanadate solution was used as the titrant, the pH first increases slowly and at the end point a marked jump in pH was observed, corresponding to the molar ratio of PbO : V₂O₅ as 3 : 1, confirming the formation of the same compound (3 PbO·V₂O₅) according to the equation.

3 Na₂O·V₂O₅ + 3 Pb(NO₃)₂ = 3 PbO·V₂O₅ + 6 NaNO₃.

Employing similar concentrations of reactants, both the direct and reverse e.m.f. (Fig. 2, Curves I and II)
II) and conductometric (fig. 3, Curves I and II) titrations were also carried out. The titration curves yield well defined breaks and inflections at the stoichiometric end point corresponding to the reacting ratio of PbO : V$_2$O$_5$ as 3 : 1 and confirm the formation of the identical compound, lead ortho-vanadate, 3 PbO·V$_2$O$_5$.

**Pyro-vanadate titrations:** Alkali pyro-vanadate solutions were prepared as described earlier. The direct titration curves (fig. 1, Curve III) are similar to those of direct ortho-vanadate titration curves, with the inflection corresponding to the molecular ratio of PbO : V$_2$O$_5$ as 2 : 1, suggesting the formation of lead pyro-vanadate, 2 PbO·V$_2$O$_5$ in the pH range (5.75 — 7.25). In the case of inverse titrations (fig. 1, Curve IV), the first addition of alkali pyro-vanadate (pH ≈ 10.0) to lead nitrate solution (pH ≈ 4.5) causes an initial decrease in pH till about half the volume of titrant required for the precipitation of lead pyro-vanadate, is added. This initial lowering in pH value is due to the presence of hydrolysed acid from lead salt. Later on, with the progress of the reaction, pH begins to rise and a pronounced upward inflection is obtained at the stoichiometric end point, corresponding to the formation of lead pyro-vanadate, having the molecular composition 2 PbO·V$_2$O$_5$. The formation of lead pyro-vanadate may be represented as follows:

$$3 \text{ Na}_2\text{O} \cdot \text{V}_2\text{O}_5 + 4 \text{ HNO}_3 = 2 \text{ Na}_2\text{O} \cdot \text{V}_2\text{O}_5 + 2 \text{ NaNO}_3 + 2 \text{ H}_2\text{O}.$$  
$$2 \text{ Na}_2\text{O} \cdot \text{V}_2\text{O}_5 + 2 \text{ Pb(NO}_3)_2 = 2 \text{ PbO} \cdot \text{V}_2\text{O}_5 + 4 \text{ NaNO}_3.$$  

The course of this reaction was also followed by means of potentiometric and conductometric titrations. A sharp break in titration curves (figs. 2—3, Curves III—IV) was obtained at a point corresponding to the formation of lead pyro-vanadate.

**Meta-vanadate titrations:** The solution of sodium meta-vanadate was prepared as described earlier and its reaction with lead salt has been investigated by performing pH, e.m.f. and conductometric titrations. The end-points obtained from the titration curves (figs. 1—3, Curves V and VI) indicate that Pb$^{2+}$ and VO$_3^{-}$ ions combine in the ratio of 1 : 2 and suggest the formation of lead meta-vanadate PbO·V$_2$O$_5$ at the pH range 4.25 — 5.25. The reaction can be represented as follows:

$$3 \text{ Na}_2\text{O} \cdot \text{V}_2\text{O}_5 + 4 \text{ HNO}_3 = \text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5 + 4 \text{ NaNO}_3 + 2 \text{ H}_2\text{O}.$$  
$$\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5 + \text{Pb(NO}_3)_2 = \text{PbO} \cdot \text{V}_2\text{O}_5 + 2 \text{ NaNO}_3.$$  

The feeble breaks obtained in reverse conductometric titrations curves (fig. 3, Curve VI) as a consequence of the appreciable increase in conductance values in initial stages of titration indicate clearly the liberation of highly mobile H$^+$ ions and provide strong support to the observations noted in reverse pH and e.m.f. titrations.

The reaction between lead nitrate and alkali poly-vanadate has also been studied, but the curves do not exhibit any appreciable break or inflection at the stoichiometric end point. This may be ascribed to (I) small difference in the pH values of reactants (II) the presence of NaNO$_3$ in appreciable amount in poly-vanadate solution, preventing the occurrence of breaks in the conductometric titration curves.

It is observed that after each addition of the titrant, it takes a little time for the pH, e.m.f. and conductance values to become steady. Thorough stirring in the vicinity of the end point has a favourable effect. Each titration takes half an hour for completion.

It is apparent from the present study that the lead salt with different alkali vanadates yields corresponding salts by metathesis, namely lead ortho-3PbO·V$_2$O$_5$, pyro-2PbO·V$_2$O$_5$ and meta-PbO·V$_2$O$_5$ vanadate at pH ranges 7.5 — 9.0, 5.75 — 7.25, 4.25 — 5.25 respectively.

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