BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 377—380 (1968)

Electrometric Studies on the Reaction between Pb(II) and Alkali Meta-Vanadate

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The reaction between Pb^{2+} and VO_3^- was investigated by means of electrometric techniques involving potentiometric, pH-metric and conductometric titrations between $Pb(NO_3)_2$ and $NaVO_3$ at several concentrations, with each of the reagents alternately used as titrant. The sharp breaks and inflections obtained in titration curves evidenced the formation of lead meta-vanadate having the molecular composition $PbO \cdot V_2O_5$ at pH range 4.25—5.25. The precipitation of the compound has been found to be almost quantitative and the titration results are very accurate and reproducible.

Meagre references are available in the literature on the study of lead vanadates and most of the workers have based their conclusions on the analytical studies of the products formed by double decomposition. Berzelius, Roscoe and Carnot[1] obtained lead meta-vanadate by treating ammonium or alkali meta-vanadate with lead salts. Zolotavin[2] made a study of sparingly soluble vanadates of some metals including lead from the point of law of series by analysis and reported that precipitation of lead meta-vanadate was complete and instantaneous. The lowest pH at which such precipitation took place was determined. Henriguiter[3] reported the formation of lead meta-vanadate as a function of the pH and obtained $PbO \cdot V_2O_5$ by double decomposition and recommended it as a gravimetric method for determination of lead. In view of the insufficient details of the reports of earlier workers on analytical studies and in the absence of any available electrometric data on the subject it was considered desirable and necessary to investigate precisely the reaction between lead salts and alkali meta-vanadate, employing recent electrometric techniques which

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[1] J. J. Berzelius, H. E. Roscoe and A. Carnot, *Proc. Roy. Soc.*, **16**, 220 (1868); *Phil. Trans.*, **158**, 1 (1868).

[2] V. L. Zolotavin, *Zhur. Annal. Khim.*, **2**, 364 (1947).

[3] Henri Guiter, *Ann. Chim.*, **15**, 5 (1941).

TABLE 1. SUMMARY OF THE RESULTS OF E. M. F., pH AND CONDUCTOMETRIC TITRATIONS

Clarity of solutions $Pb(NO_3)_2$	 $Na_2O\cdot V_2O_5$	Calcd	Equivalence points, ml Obs. E. M. F.	 pH	 Condc.	Formula suggested
		Direct titrations: Figs. 1, 2 and 3; Curves I and II				
M/10	M/60	3.33	3.25	3.25	3.20	
M/30	M/150	4.00	3.95	3.95	3.80	$PbO\cdot V_2O_5$
M/60	M/350	3.42	3.35	3.35	3.30	
		Reverse titrations: Figs. 1, 2 and 3; Curves III and IV				
M/30	M/5	3.33	3.45	3.35	3.30	
M/200	M/25	2.50	2.55	2.55	2.50	$PbO\cdot V_2O_5$
M/400	M/60	3.00	3.00	3.00	2.95	

have provided more conclusive information on the formation and composition of such compounds.[4-8]

Experimental

Merck's guaranteed extra pure reagents, V_2O_5, NaOH and lead nitrate were used and their solutions prepared in air free conductivity water. The standard solution of sodium meta-vanadate was prepared by adding four moles of HNO_3 to a solution containing one mole of ortho-vanadate at 100°C. The latter was prepared by dissolving one mole of V_2O_5 in boiling solution of NaOH containing six moles of it.

E. M. F., pH and Conductometric Titrations. The pH and E. M. F. of the solutions were measured on a Cambridge (null-deflection type) pH-meter by means of a glass electrode and a bright platinum foil as an indicator electrode respectively, in conjunction with saturated calomel electrode. The observed values of e.m.f. and pH during the course of titrations were plotted as a function of milliliter of titrant added. The end points were located graphically and checked further by calculating maximum values of dE/dV and dpH/dV. Twenty ml of the titre was taken in the cell each time thermostated at 25 ± 0.1°C. Conductance measurements were carried out by a LBR type conductometer (W. T. W. Germany) taking 20 ml of solution in the cell.

Using different concentrations of the reactants, a series of direct and reverse e.m.f., glass electrode and conductometric titrations were performed in aqueous and aqueous-alcoholic media. Similar strengths of solutions were employed in these titrations for the sake of comparison of results. Only three diagrams illustrating direct and reverse e.m.f. (Fig. 1), pH (Fig. 2) and conductometric (Fig. 3) titrations have been given. The results have been summarised in Table 1.

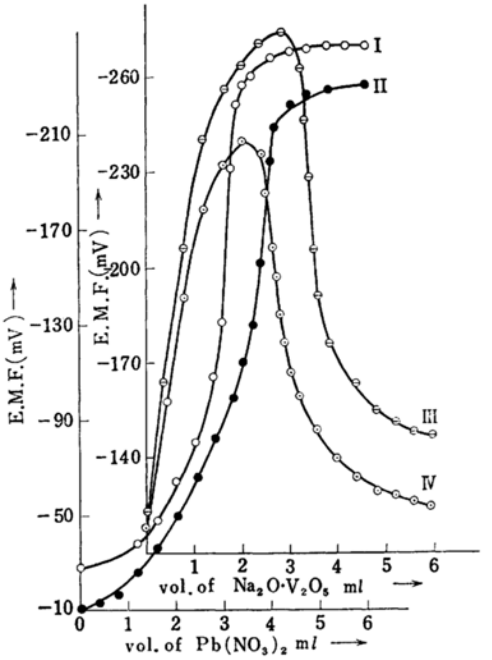

Fig. 1. Direct (I and II) and reverse (III and IV) potentiometric titrations between $Pb(NO_3)_2$ and $Na_2O\cdot V_2O_5$.
Curve I: ml of M/10 $Pb(NO_3)_2$ added to 20 ml of M/60 $Na_2O\cdot V_2O_5$
Curve II: ml of M/30 $Pb(NO_3)_2$ added to 20 ml of M/150 $Na_2O\cdot V_2O_5$
Curve III: ml of M/5 $Na_2O\cdot V_2O_5$ added to 20 ml of M/30 $Pb(NO_3)_2$
Curve IV: ml of M/25 $Na_2O\cdot V_2O_5$ added to 20 ml of M/200 $Pb(NO_3)_2$

Discussion

The vanadate anion (VO_4^{3-}) in acid medium shows anomalous behaviour and forms different isopoly anions of varying compositions through a series of intermediate steps. The systematic electrometric investigations carried out by the authors[9-11] on such systems have shown the formation of three different poly anions *viz.* pyro$(V_2O_7)^{4-}$,

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4) R. S. Saxena, C. P. Sharma and M. L. Mittal, *J. Praktische. Chem.* (1967), in press.

5) R. S. Saxena and O. P. Sharma, *Z. anorg. u. allgem. Chem.*, **333**, 1 (1964).

6) R. S. Saxena and M. L. Mittal, *J. Nucl. & Inorg. Chem.*, **27**, 2553 (1965).

7) R. S. Saxena and M. L. Mittal, *Z. anorg. u. allegem. Chem.*, **324**, 208 (1963).

8) R. S. Saxena and O. P. Sharma, *Talanta*, **2**, 863 (1964).

9) R. S. Saxena and O. P. Sharma, *J. Inorg. Nucl. Chem.*, **28**, 1881 (1966).

10) R. S. Saxena and M. L. Mittal, *Acta Chim. Acad. Sci. Hung.*, **40**, 109 (1964).

11) R. S. Saxena and M. L. Mittal, *Naturwissenschaften*, **51**, 1 (1964).

meta (VO_3^-) and $(V_{10}O_{27})^{4-}$ in the vicinity of pH 10, 7 and 4.5 respectively. With a view to ascertaining whether these polyanions form the corresponding heavy metal derivatives, the reaction between VO_3^- and Pb(II) has been investigated electrometrically.

Figure 1 illustrates the direct and reverse e.m.f. titrations between $Pb(NO_3)_2$ and $Na_2O{\cdot}V_2O_5$ using a bright platinum foil as an indicator electrode. In direct titrations (Fig. 1, curves I—II) when $Pb(NO_3)_2$ solution was added from a micro-burette to sodium meta-vanadate solution, a gradual rise in e.m.f. was observed from the start of the reaction with a sharp jump in potential obtained at the end point corresponding to the formation and precipitation of lead meta-vanadate $PbO{\cdot}V_2O_5$. Beyond the stoichiometric end-point the e.m.f. attains almost a constant value. In the case of reverse titration (Fig. 1, curves III and IV), when sodium meta-vanadate was used as titrant, the first addition of the latter causes a sharp rise in e.m.f. which continues upto the addition of about 0.5 mol of $Na_2O{\cdot}V_2O_5$ per mole of $Pb(NO_3)_2$ but on further addition, the e.m.f. value starts decreasing, resulting in the occurrence of sharp inflection or maxima in dE/dV at the endpoint indicating the precipitation of the same compound $PbO{\cdot}V_2O_5$. The inverse titration curves are peculiar in form but provide accurate and reproducible results.

The pH of the $Pb(NO_3)_2$ and $Na_2O{\cdot}V_2O_5$ was measured by means of glass electrode and found to be about 4.60 and 7.40 respectively. The titration curves (Fig. 2, curves I and II) represent the changes occurring in H^+ ion concentrations when $Pb(NO_3)_2$ solution was treated with alkali-vanadate solution.

The direct glass electrode titration curves are regular in form and yield one break corresponding to the formation of lead meta-vanadate. Reverse titrations, however, are found to yield sharp upward jump at the same stoichiometric end-point but are peculiar in form. Although the pH of the sodium meta-vanadate is about three units higher than that of $Pb(NO_3)_2$, but the first addition of the former causes an appreciable fall in pH and this decrease continues even upto the addition of about half the amount of alkali vanadate per mole of lead nitrate. Beyond this position pH begins to increase and a sharp upward jump is

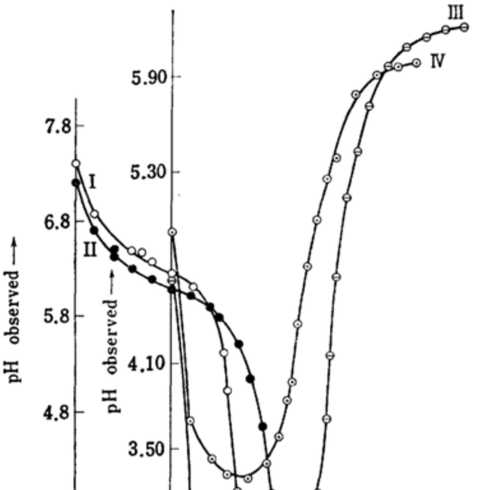

Fig. 2. Direct (I and II) and reverse (III and IV) pH titrations between $Pb(NO_3)_2$ and $Na_2O{\cdot}V_2O_5$.
Curve I: ml of M/10 $Pb(NO_3)_2$ added to 20 ml of M/60 $Na_2O{\cdot}V_2O_5$
Curve II: ml of M/30 $Pb(NO_3)_2$ added to 20 ml of M/150 $Na_2O{\cdot}V_2O_5$
Curve III: ml of M/5 $Na_2O{\cdot}V_2O_5$ added to 20 ml of M/30 $Pb(NO_3)_2$
Curve IV: ml of M/25 $Na_2O{\cdot}V_2O_5$ added to 20 ml of M/200 $Pb(NO_3)_2$

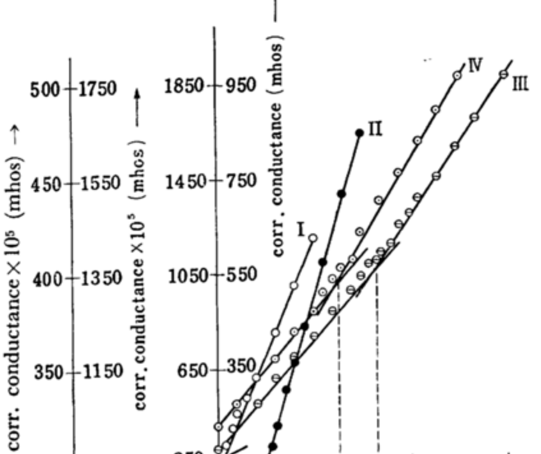

Fig. 3. Direct (I and II) and reverse (III and IV) conductometric titrations between $Pb(NO_3)_2$ and $Na_2O{\cdot}V_2O_5$.
Curve I: ml of M/10 $Pb(NO_3)_2$ added to 20 ml of M/60 $Na_2O{\cdot}V_2O_5$
Curve II: ml of M/30 $Pb(NO_3)_2$ added to 20 ml of M/150 $Na_2O{\cdot}V_2O_5$
Curve III: ml of M/5 $Na_2O{\cdot}V_2O_5$ added to 20 ml of M/30 $Pb(NO_3)_2$
Curve IV: ml of M/25 $Na_2O{\cdot}V_2O_5$ added to 20 ml of M/200 $Pb(NO_3)_2$

obtained at stoichiometric end-point (Fig. 2, curves III and IV).

This initial fall in pH, which continues upto the addition of half mole of alkali meta-vanadate per mole of lead nitrate (Fig. 2, curves III—IV) indicate the liberation of free acid during the course of reaction due to hydrolysis and the formation of basic lead-vanadate which on further addition of alkali vanadate gradually changes into lead meta-vanadate, simultaneously liberating equivalent amount of NaOH, which consequently results in the increase of pH. Finally a sharp upward jump was obtained at the molecular ratio of PbO: V_2O_5 as 1 : 1 confirming the formation of lead meta-vanadate ($PbO{\cdot}V_2O_5$). These observations are clearly borne out by the shape of pH-titration curves. The probable mechanism of the reaction can be stated as follows:

$$Pb(NO_3)_2 + 0.5(Na_2O \cdot V_2O_5) + H_2O \rightarrow Pb(VO_3)OH + HNO_3 + NaNO_3 \quad (1)$$

$$Pb(VO_3)OH + 0.5(Na_2O \cdot V_2O_5) \rightarrow Pb(VO_3)_2 + NaOH \quad (2)$$

The course of this reaction was also followed by means of conductometric titrations between the reactants at different concentrations. The end-points indicate the formation of lead meta-vanadate, $PbO{\cdot}V_2O_5$. The feeble breaks obtained in reverse titration curves as a consequence of appreciable increase in conductance values in initial stages of titration, indicates clearly the liberation of highly mobile H^+ ions and provide strong support to the observation noted in reverse pH titrations.

It was noticed that after each addition of the reagent, it takes a little time for the e.m.f., pH and conductance values to become steady. The presence of ethanol slightly improves the end-point as it decreases the dielectric constant of the medium and consequently the solubility of the precipitated compound. The accuracy and reproducibility of these electrometric titrations have been found to be excellent.