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Electrometric studies on the system acid-vanadate and the formation of heavy metal vanadates

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Abstract

The stoichiometry of the polyanions formed by the action of nitric acid on sodium *ortho*-vanadate solution has been studied by means of electrometric techniques involving glass electrode and conductometric titrations as well as Job's method of continuous variation. The well defined inflections and breaks in the titration curves and maxima from continuous variation study provide cogent evidence for the existence of the anions, *pyro*-$V_2O_7^{4-}$, *meta*-VO_3^- and poly-$H_2V_{10}O_{28}^{4-}$ corresponding to the ratios of VO_4^{3-}:H^+ as 1:1, 1:2 and 1:2.6 in the pH ranges (10.1–10.7), (7.0–7.5) and (3.4–3.8), respectively. Similar titrations between alkali and V_2O_5 solutions also confirm the existence of the same anions. The interaction of lead nitrate with sodium vanadate solutions, at specific pH levels 12.4, 10.5, 7.4 and 3.6 was also studied by pH and conductometric titrations. The end-points obtained from the sharp inflections in the titration curves provide definite evidence for the formation of lead *ortho*-$3PbO{\cdot}V_2O_5$, *pyro*-$2PbO{\cdot}V_2O_5$ and *meta*-$PbO{\cdot}V_2O_5$ vanadates in the vicinity of pH 8.2, 6.5 and 5.6, respectively.

Keywords: Electrometric studies; Acid-vanadate; Heavy metal vanadates

1. Introduction

Recently a new interest in the chemistry of vanadium has developed [1,2]. This has arisen in part from antiviral, including anti-AIDS activity of vanadates and their interaction with biological molecules like proteins [3,4]. Vanadium also exhibits catalytic properties in an extensive variety of chemical reactions. These include the use of vanadium oxide as catalyst in the following: sulfur dioxide to the trioxide, the sulfonation of aromatic hydrocarbons or of pyridine, the reduction of olefines; the oxidation of hydroiodic acid by hydrogen peroxide, of sugar by nitric acid, of alcohol by air, of stannous salts by nitric acid, of cyclic organic compounds by hydrogen peroxide, of naphthalene by air, and the reduction of aromatic hydrocarbons by hydrogen [5]. A number of recent studies have shown that vanadium oxide catalyst is very promising in oxidative dehydrogenation of alkanes but its activity and selectivity depends on the manner in which the catalyst is pretreated [6–10]. The structure of the vanadia is a very important factor [9,10]. Khodakov et al. [11] have recently determined that the oxidative dehydrogenation rates of propane increase as the size of poly-vanadate domain increases. Efforts aimed at relating the structures of the vanadium species to its catalytic activity and selectivity suggest that the catalytic performance depends on the type of structure, bond length and distance between active and selective sites [6–15].

In highly alkaline solution, pH>14, vanadium(V) exists as a tetrahedral VO_4^{3-} anion [16]. On acidification the aqueous solutions turn from colorless to orange-yellow polymeric species. A survey of liter-

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ature suggests the occurrence of a series of alkali metal vanadates having the ratio of Na_2O:V_2O_5 as 3:1, 2:1, 1:1, 1:2, 1:2.5, 1:3, 2:3, etc. in solution under different conditions. The existence of so many polymeric species seems to be doubtful; moreover, there is a great variance in the results published by earlier workers which allows no satisfactory interpretation of the mechanism of the condensation process. A further verification of the vanadate system seems very desirable with a view to rationalizing the conflicting details of the previous workers by employing electrometric techniques, which have provided more conclusive evidences on such systems [17–19]. The knowledge on the formation of different species under different conditions will help in the explanation of the catalytic performance of vanadium and may be a key to understanding the catalytic mechanism.

2. Experimental

Merck's extra-pure reagents V_2O_5, NaOH, KOH, $Pb(NO_3)_2$, $Nd(NO_3)_3$, HNO_3, ethanol and hydrochloric acid were used. The solution of sodium *ortho*-vanadate Na_3VO_4 was prepared by digesting 1 mol of V_2O_5 in boiling solution of NaOH containing 6 mol of it.

pH measurements were carried out on Metrohm Herisau pH-meter using Scott Gerate glass combination electrode. Conductance values were recorded by employing a Metrohm conductometer. A series of pH and conductometric titrations was carried out between sodium *ortho*-vanadate in concentrations $\geq 10^{-4}$ M and acid (HNO_3 and HCl) using same strength of the reactants in each technique. All observations were taken at the state of chemical equilibrium. For attaining the equilibrium state the titrations were performed by heating the solution after each addition of titrant and cooling to 25°C before taking observations. The achievement of constant values of pH and conductance required about 40 s boiling after each addition of the titrant for the formation of *pyro*-vanadate, whereas the time needed for attaining the state of chemical equilibrium for the formation of *meta*- and poly-vanadate was 1 and 2.5 min, respectively. The curves were plotted between pH and corrected conductance vs. volume of acid used. As the inflections of pH curves were not strongly defined, pronounced maxima in dpH/dV were used to locate the end-points.

Job's method of continuous variation was also employed using electrical conductance measurements for establishing the composition of the polyanions formed by the interaction of equimolar nitric acid and sodium *ortho*-vanadate. The differences in specific conductivities (sum of the conductivity of the constituent solutions minus the observed specific conductivity of the mixtures) were plotted against composition of mixtures.

The results of the above study were further confirmed by titrating V_2O_5 solution with KOH utilizing the same techniques. The pH and conductance values were measured at the state of chemical equilibrium, which was achieved by heating the titre solution after each addition of KOH and then cooling to 25°C.

The formation of lead vanadates was investigated by the action of lead nitrate with different vanadate anions at specific pH levels 12.4, 10.5, 7.4 and 3.6 using different concentrations of the reactants. A series of pH and conductometric titrations was performed by direct and reverse methods, i.e. when lead nitrate solution from the microburette was added to sodium vanadate solution and vice versa. Twenty-five milliliter of ethanolic solution (20%) was taken in the cell, which was thermostated at 25±0.1°C.

The precipitates obtained at the end-points of titrations between lead nitrate and sodium vanadates were also analyzed to substantiate the electrometric results. The different lead vanadates were prepared by mixing stoichiometric amounts of lead nitrate solution with the respective sodium vanadate solutions. The precipitates obtained were washed several times with 20% ethanolic solution and dried in a vacuum desiccator for 40 h. A known amount (ca. 2 g) of each of the above precipitates was dissolved in a minimum quantity of nitric acid and then analyzed quantitatively for lead as sulfate [20] and vanadium spectrophotometrically by *pyro*-tungstate method [21]. From the proportions of lead and vanadium in the compounds thus obtained their composition was established.

3. Results

The results of the electrometric titrations of HNO_3 with Na_3VO_4 are summarized in Table 1. A typical

Table 1
Summary of results of electrometric titrations of HNO_3 with Na_3VO_4[a]

Molarity of solutions		Equivalence points (ml) for the formation of								
HNO_3 (Mλ)	Na_3VO_4 (Mλ)	*Pyro*-vanadate			*Meta*-vanadate			Poly-vanadate		
		Calculated	A[b]	B[b]	Calculated	A	B	Calculated	A	B
4	50	2.00	2.00	2.00	4.00	4.00	4.00	5.20	5.21	5.22
80	900	2.22	2.22	2.20	4.44	4.45	4.45	5.78	5.80	5.80
200	2000	2.50	2.50	2.48	5.00	5.00	5.98	6.50	6.52	6.50
900	10000	2.25	2.25	2.22	4.50	4.48	4.48	5.85	5.88	5.88

[a] Volume of Na_3VO_4 solution taken in the cell=25 ml.

[b] A and B represent results obtained from pH and conductometric titrations, respectively.

titration curve between pH observed and volume of the acid added is demonstrated in Fig. 1 (curve 1). The three inflections in the titration curve corresponding to $H^+:VO_4^{3-}$ as 1:1, 2:1 and 2.6:1 indicate the formation of three vanadate species. The conductometric titrations between the acid and Na_3VO_4 also confirm the formation of the same species (Fig. 1, curve 2).

The curve obtained by Job's method of continuous variation gave a sharp maximum demonstrating the formation of a vanadate species at $H^+:VO_4^{3-}$ as 2.6:1 (Fig. 2).

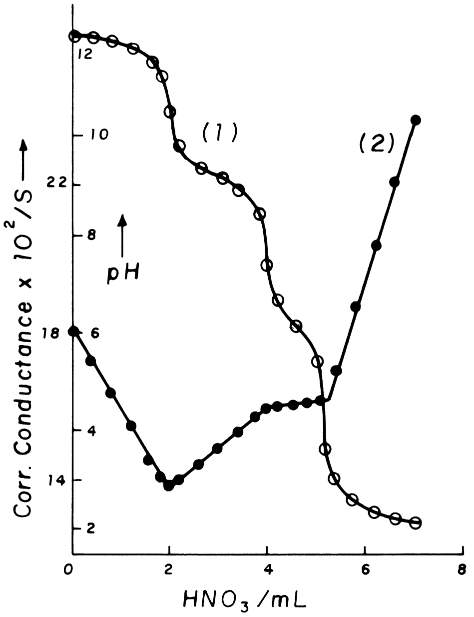

Fig. 1. pH (1) and conductometric (2) titrations. Twenty-five milliliter of M/50 Na_3VO_4 titrated with M/5 HNO_3.

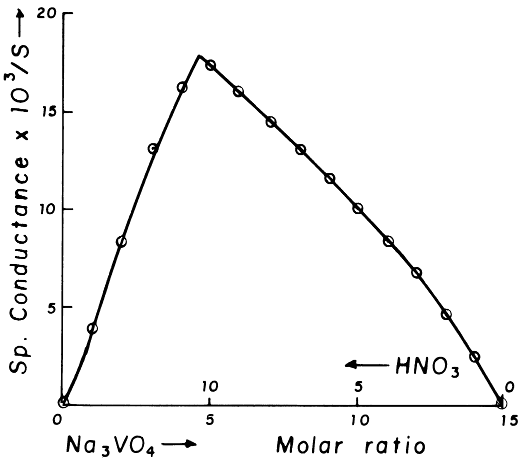

Fig. 2. Continuous variation study by Job's method using equimolar (0.02 M) solutions of HNO_3 and Na_3VO_4.

Fig. 3 demonstrates the variation of pH and conductance during the titrations of V_2O_5 solution with KOH. The inflections and breaks in the titration curves correspond to $H^+:VO_4^{3-}$ as 1:1, 2:1 and 2.6:1 confirming the formation of the same three species as shown by the acid-vanadate system (Table 2).

The results of the electrometric study on the formation of lead vanadates are summarized in Table 3. Three Figures illustrating the formation of *ortho*-vanadate (Fig. 4), *pyro*-vanadate (Fig. 5) and *meta*-vanadate (Fig. 6) of lead have been given. The precipitates obtained at the end-points of the electrometric titrations between lead nitrate and sodium vanadates were also analyzed to substantiate the electrometric results. The analytical results (see Table 4) confirm those obtained by the electrometric study.

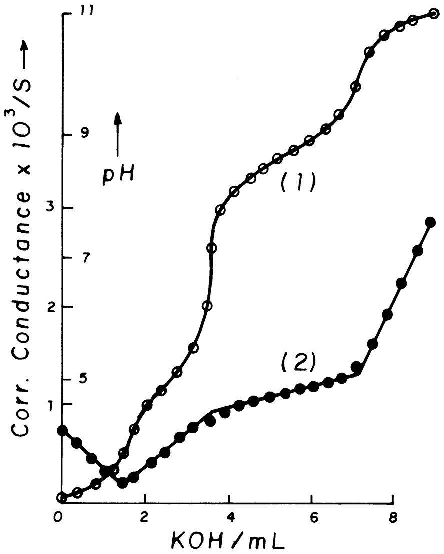

Fig. 3. pH (1) and conductometric (2) titrations. Twenty-five milliliter of M/1400 V_2O_5 titrated with M/100 KOH.

4. Discussion

Vanadium pentoxide dissolves slowly in cold sodium hydroxide solution giving clear yellow solution whose color disappears on standing for some time. If however, vanadium pentoxide is dissolved in boiling NaOH solution a clear and colorless solution is immediately obtained. Moreover, the addition of even the slightest amount of acid to the colorless solution of sodium *ortho*-vanadate produces yellow coloration, which also disappears on boiling. The observations suggest that boiling the solution during the reaction have an appreciable effect on the composition of the compounds formed and on the completion of the reaction. Hence the titrations of alkali *ortho*-vanadate with acids have been carried out by heating after each addition of the titrant and cooling the solution to 25°C before pH and conductance measurements. Similar procedure was also adopted during the studies of KOH with V_2O_5 solutions.

4.1. Acid-vanadate system

It was noted that during the course of titrations between acid and alkali *ortho*-vanadate at room temperature the first addition of the acid produced a transient brown-red color, which changed to yellow orange and the intensity of color increased with the progressive addition of the acid. The pH of such acidified solutions took time to become steady, showing that the reaction proceeded by way of some unstable intermediate compounds. The titration curves without prior heating did not yield sharp inflections which could throw any light on the composition of various polyanions formed in the solution, but when these solutions were boiled after each addition of the titrant, the nature of the curves changed and three prominent inflections (Fig. 1, curve 1) were obtained at the molar ratios of H^+:VO_4^{3-} as 1, 2 and 2.6 corresponding to the stoichiometry for the formation of *pyro*-$V_2O_7^{4-}$, *meta*-VO_3^- and poly-$H_2V_{10}O_{28}^{4-}$ vanadate anions, in the pH ranges (10.1–10.7), (7.0–7.5) and 3.4–3.8), respectively.

Conductometric titrations between the acid and alkali *ortho*-vanadate were also carried out using the same concentrations of the reactants for the sake of comparison of results. The observed breaks confirm

Table 2
Summary of results of electrometric titrations of KOH with V_2O_5[a]

Molarity of solutions		Equivalence points (ml) for the formation of								
KOH (Mλ)	V_2O_5 (Mλ)	Poly-vanadate			*Meta*-vanadate			*Pyro*-vanadate		
		Calculated	A[b]	B[b]	Calculated	A	B	Calculated	A	B
100	1400	1.43	1.43	1.45	3.57	3.55	3.55	7.14	7.15	7.15
200	2500	1.60	1.60	1.60	4.00	4.00	4.00	8.00	8.00	8.02
300	4300	1.40	1.42	1.40	3.49	3.50	3.48	6.98	7.00	7.00
500	7500	1.33	1.35	1.35	3.33	3.35	3.30	6.67	6.65	6.70

[a] Volume of V_2O_5 solution taken in the cell=25 ml.

[b] A and B represent results obtained from pH and conductometric titrations, respectively.

Table 3
Summary of results of electrometric study on formation of lead vanadates. Volume of titre solution taken in the cell=25 ml

Molarity of solutions		Equivalence points (ml)			Formula supported
		Calculated	Observed from		
			pH	Conductance	
$Pb(NO_3)_2$	Na_3VO_4				
Direct ortho-vanadate titrations					Fig. 4, curves 1 and 3, $3PbO{\cdot}V_2O_5$
M/10	M/150	2.50	2.50	2.50	
M/40	M/750	2.00	2.00	2.00	
M/100	M/1750	2.14	2.12	2.15	
Reverse ortho-vanadate titrations					Fig. 4, curves 2 and 4, $3PbO{\cdot}V_2O_5$
M/75	M/10	2.22	2.20	2.22	
M/275	M/40	2.42	2.42	2.45	
M/800	M/100	2.08	2.08	2.10	
$Pb(NO_3)_2$	$Na_4V_2O_7$				
Direct pyro-vanadate titrations					Fig. 5, curves 1 and 3, $2PbO{\cdot}V_2O_5$
M/10	M/250	2.00	2.00	2.00	
M/30	M/700	2.14	2.15	2.12	
M/80	M/1750	2.29	2.28	2.28	
Reverse pyro-vanadate titrations					Fig. 5, curves 2 and 4, $2PbO{\cdot}V_2O_5$
M/50	M/10	2.50	2.50	2.50	
M/300	M/50	2.08	2.08	2.05	
M/1400	M/250	2.23	2.22	2.22	
$Pb(NO_3)_2$	$NaVO_3$				
Direct meta-vanadate titrations					Fig. 6, curves 1 and 3, $PbO{\cdot}V_2O_5$
M/10	M/60	2.08	2.08	2.10	
M/50	M/250	2.50	2.50	2.50	
M/120	M/650	2.31	2.32	2.32	
Reverse meta-vanadate titrations					Fig. 6, curves 2 and 4, $PbO{\cdot}V_2O_5$
M/200	M/10	2.50	2.50	2.50	
M/1000	M/40	2.00	2.00	2.02	
M/1500	M/70	2.33	2.35	2.35	

the formation of *pyro*-, *meta*- and poly-vanadates in the solution (Fig. 1, curve 2). The titration curves show that a rapid diminution in conductance values occurred during the reaction up to the first equivalence point, which corresponds to the formation of *pyro*-vanadate, revealing that the vanadate must be considerably hydrolyzed. This is in agreement with the glass electrode titration curves of *ortho*-vanadate, which shows high value during this part of the curve. From these observations it is inferred that *ortho*-vanadate is not very stable and hydrolyzes giving hydroxyl and $V_2O_7^{4-}$ ions.

In all these titrations an abnormal inflection occurred at the stage of formation of $H_2V_{10}O_{28}^{4-}$, thereafter the solution became strongly acidic; this was marked by a sharp increase in conductivity values and pronounced decrease in pH.

When the solutions of alkali *ortho*-vanadate were boiled after each addition of the acid, the decomposition seems to proceed as follows: the *ortho*-vanadate was hydrolyzed almost completely and at one-third decomposition, the solution consisted, therefore, of *pyro*-vanadate anions which also hydrolyzed to some extent. The next stage between the one-third and two-third decomposition consisted in the formation of *meta*-vanadate anion. Further addition of the acid resulted in the formation of the poly-vanadate anion, at which the species became sufficiently stable and practically no change was caused by further addition

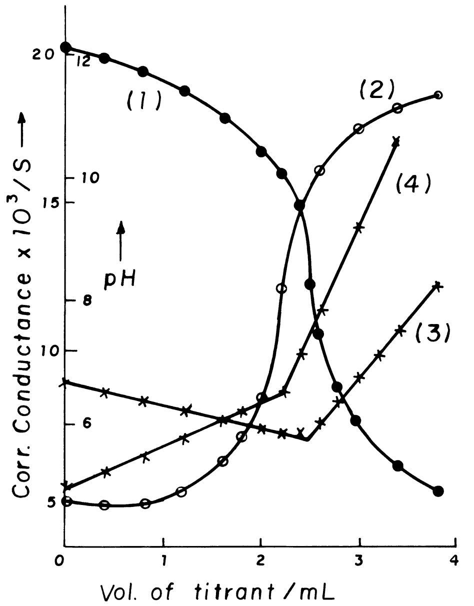

Fig. 4. Direct and reverse pH and conductometric titrations between $Pb(NO_3)_2$ and Na_3VO_4. (1) and (3): M/10 $Pb(NO_3)_2$ added to 25 ml of M/150 Na_3VO_4. (2) and (4): M/10 Na_3VO_4 added to 25 ml of M/75 $Pb(NO_3)_2$.

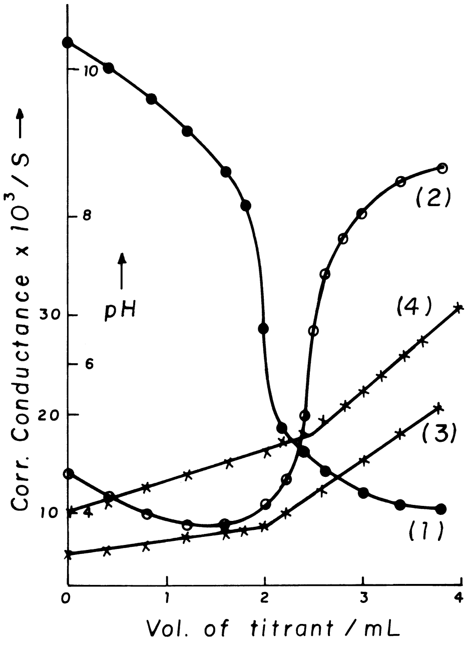

Fig. 5. Direct and reverse pH and conductometric titrations between $Pb(NO_3)_2$ and $Na_4V_2O_7$. (1) and (3): M/10 $Pb(NO_3)_2$ added to 25 ml of M/250 $Na_4V_2O_7$. (2) and (4): M/10$Na_4V_2O_7$ added to 25 ml of M/50 $Pb(NO_3)_2$.

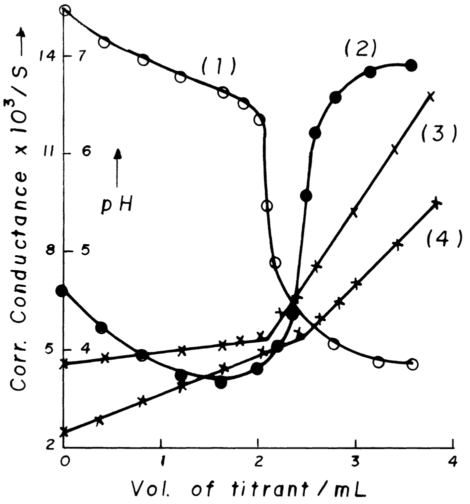

Fig. 6. Direct and reverse pH and conductometric titrations between $Pb(NO_3)_2$ and $NaVO_3$. (1) and (3): M/10 $Pb(NO_3)_2$ added to 25 ml of M/60 $NaVO_3$. (2) and (4): M/10 $NaVO_3$ added to 25 ml of M/200 $Pb(NO_3)_2$.

of the acid. The formation of the poly-vanadate was characterized by a yellow coloration, which did not disappear even after boiling.

The formation of polyanions was also followed by Job's method of continuous variation using electrical conductance measurements. One sharp maximum obtained at H^+:VO_3^- as 2.6:1 confirm the formation of poly-vanadate anion (Fig. 2).

The stepwise condensation of *ortho*-vanadate to poly-vanadate can be represented by the following set of equations:

$$2VO_4^{3-} + 2H^+ = V_2O_7^{4-} + H_2O$$

$$V_2O_7^{4-} + 2H^+ = 2VO_3^- + H_2O$$

$$10VO_3^- + 6H^+ = H_2V_{10}O_{28}^{4+} + 2H_2O$$

The glass electrode and conductometric studies on the system acid-vanadate clearly suggest the formation of vanadate anions, *pyro*-$V_2O_7^{4-}$, *meta*-VO_3^- and poly-$H_2V_{10}O_{28}^{4-}$ corresponding to the ratio of VO_4^{3-}:H^+ as 1:1, 1:2 and 1:2.6 in the pH ranges (10.1–10.7), (7.0–7.5) and (3.4–3.8), respectively; and confirm the existence of these anions as reported in the literature [22,23]. The *meta*-vanadate anion VO_3^- may also be present as trimer $V_3O_9^{3-}$

Table 4
Summary of analytical results of the precipitates of lead vanadates

Proposed formula of the compound	Mode of analysis	Analysis %: Found (Calculated)	
		Pb	V
Analysis of lead ortho-vanadate precipitates			
$3PbO\cdot V_2O_5$	Direct[a]	72.91(73.00)	11.99(11.97)
	Reverse[b]	73.11	11.93
Analysis of lead pyro-vanadate precipitates			
$2PbO\cdot V_2O_5$	Direct	65.89(65.96)	16.28(16.22)
	Reverse	66.02	16.17
Analysis of lead meta-vanadate precipitates			
$PbO\cdot V_2O_5$	Direct	51.08(51.14)	25.20(25.15)
	Reverse	51.21	25.11

[a] Lead nitrate solution added to sodium *ortho*-vanadate solution.
[b] Sodiun *ortho*-vanadate solution added to lead nitrate solution.

and tetramer $V_4O_{12}^{4-}$ as suggested by Pope and Dale [22] and confirmed by Andersson et al. [24]; and as dimer $V_2O_6^{2-}$ and pentamer $V_5O_{15}^{5-}$ as reported by Crans [25]. The existence of $V_6O_{16}^{2-}$ as reported by Sen Gupta [26] and Russel and Salmon [27], and of $V_3O_8^-$, $V_5O_{14}^{3-}$, $V_{10}O_{28}^{6-}$ and $HV_{10}O_{28}^{5-}$ as reported by Bystrom and Evans [28] and Naumann and Hallada [29] could not be confirmed by this study.

4.2. Alkali-vanadium pentoxide system

A series of glass electrode and conductometric titrations was carried out between KOH and V_2O_5 solutions to find out if similar species as formed in the acid-vanadate system could also be obtained in reverse case.

Fig. 3 illustrates the changes occurring in conductance and H^+ ion concentration during the addition of KOH to V_2O_5 solutions. The initial low pH and high conductance values of V_2O_5 solution indicate the formation of strong acid in solution. During the addition of KOH, a rapid diminution in conductance and H^+ ion concentration (Fig. 3) indicate that this acid is neutralized when 0.8 mol of KOH per mole of V_2O_5 has been added forming poly-vanadate $H_2V_{10}O_{28}^{4-}$ in the range of pH (3.6–3.9). On further addition of the titrant, it was noted that if the solutions were not heated after each addition of KOH, they readily acquired high pH and conductance values; but on heating, a sharp inflection occurred at a stage corresponding to the addition of 2 mol of KOH per mole of V_2O_5 in pH range (6.9–7.4) suggesting the formation of *meta*-vanadate VO_3^- (or in its polymeric forms as pointed out in the acid study). Its formation was further marked by the fact that the yellow color of the solution disappeared at this point of neutralization. After the addition of 4 mol of KOH per mol of V_2O_5 a third sharp break was obtained which corresponds to the formation of *pyro*-vanadate $V_2O_7^{4-}$ in the range of pH (10.1–10.6). The stepwise action of KOH on V_2O_5 solution can be represented by the following set of equations:

$$5V_2O_5 + 4OH^- = H_2V_{10}O_{28}^{4-} + H_2O$$

$$H_2V_{10}O_{28}^{4-} + 6OH^- = 10VO_3^- + 4H_2O$$

$$2VO_3^- + 2OH^- = V_2O_7^{4-} + H_2O$$

The results of KOH–V_2O_5 titrations substantiate those obtained by the acid-vanadate system.

4.3. Formation of lead vanadates

The above studies show that the addition of acid to *ortho*-vanadate and alkali to vanadium pentoxide causes the formation of three different vanadate anions viz. *pyro*-$V_2O_7^{4-}$, *meta*-VO_3^- and poly-$H_2V_{10}O_{28}^{4-}$. Hence it was considered of interest to ascertain whether similar salts of heavy metals may be precipitated as a result of double decomposition. The reaction between Pb(II) and alkali vanadates has therefore been studied by means of pH and conductometric titrations. A solution of sodium *ortho*-vanadate was prepared by digesting 1 mol of V_2O_5 in boiling solution of NaOH containing 6 mol of it. The solutions of sodium *pyro*-, *meta*- and poly-vanadates were prepared by adding 1, 2, and 2.6 mol of HNO_3 to 1 mol of Na_3VO_4 at 100°C.

$$6NaOH + V_2O_5 = 2Na_3VO_4 + 3H_2O$$

$$2HNO_3 + 2Na_3VO_4 = Na_4V_2O_7 + 2NaNO_3 + H_2O$$

$$2HNO_3 + Na_3VO_4 = NaVO_3 + 2NaNO_3 + H_2O$$

$$26HNO_3 + 10Na_3VO_4 = Na_4H_2V_{10}O_{28} + 26NaNO_3 + 12H_2O$$

4.3.1. *Lead ortho-vanadate*

Fig. 4 (curves 1 and 2) illustrates the changes occurring in H^+ concentration when lead nitrate solution is treated with Na_3VO_4 solution. In direct titrations (curve 1), when lead nitrate solution (pH 4.4) was added from the microburette to Na_3VO_4 solution (pH 12.4) a gradual decrease in pH was observed till at the stoichiometric end-point was reached and after which the smallest addition of the titrant caused a sharp fall in pH, indicating the completion of reaction and suggesting the formation of lead *ortho*-vanadate around pH 8.2. In the case of reverse titrations (curve 2), when *ortho*-vanadate solution was used as titrant, the pH first changed slowly, but at the equivalence point a marked upward jump in pH corresponding to molar ratio Pb^{2-}: VO_4^{3-} as 3:2, confirmed the formation of the same compound according to the following equation:

$$3Pb^{2+} + 2VO_4^{3-} = (3PbO \cdot V_2O_5)$$

Employing similar concentrations of the reactants, both direct (Fig. 4, curve 3) and reverse (Fig. 4, curve 4) conductometric titrations between the solutions of lead nitrate and sodium *ortho*-vanadate were also carried out. Well defined breaks in the titration curves were obtained at a 3:2 molar ratio of Pb^{2+}:VO_4^{3-}, which confirm the formation of the identical compound, lead *ortho*-vanadate $3PbO \cdot V_2O_5$. In the direct titrations (curve 3), when lead nitrate solution was added from the microburette to the *ortho*-vanadate solution in the titration cell, a gradual decrease in conductance values was observed (due to removal of VO_4^{3-} ions in the form of precipitate) until the stoichiometric end-point, after which the conductance increased with the increase in ionic concentration. In the case of reverse titrations (curve 4), as the lead ions are removed in the form of precipitate and more mobile sodium ions are introduced in the solution, the conductance value starts increasing from the very beginning.

4.3.2. *Lead pyro-vanadate*

The pH (Fig. 5, curves 1 and 2) and conductometric (Fig. 5, curves 3 and 4) titrations provide well defined inflections at molar ratio Pb^{2+}:$V_2O_7^{4-}$ as 2:1, corresponding to the stoichiometry for the formation of lead *pyro*-vanadate $2PbO \cdot V_2O_5$ in the neighborhood of pH 6.5. The precipitation of the compound can be represented as follows:

$$2Pb^{2+} + V_2O_7^{4-} = (2PbO \cdot V_2O_5)$$

In case of inverse titrations (Fig. 5, curve 2), the first addition of alkali *pyro*-vanadate (pH 10.5) to lead nitrate solution (pH 4.4) caused an initial decrease in pH till about half the volume of titrant required for the precipitation of lead *pyro*-vanadate was added. This initial lowering in pH value was due to the presence of hydrolyzed acid from lead salt. Later on, with the progress of the reaction, pH began to rise and a pronounced upward inflection was obtained at the stoichiometric end-point corresponding to the formation of lead *pyro*-vanadate.

4.3.3. *Lead meta-vanadate*

Fig. 6 illustrates the results of pH and conductometric titrations between solutions of lead nitrate and sodium *meta*-vanadate. The end-points obtained from the titration curves indicate that Pb^{2+} and VO_3^- ions combine in the ration 1:2 and suggest the formation of lead *meta*-vanadate $PbO \cdot V_2O_5$ around pH 5.6, according to the reaction,

$$Pb^{2+} + 2VO_3^- = PbO \cdot V_2O_5$$

The feeble breaks obtained in reverse conductometric titration curves (Figs. 5 and 6, curves 4) 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 the reverse pH titrations (Figs. 5 and 6, curves 2).

The reaction between lead nitrate and sodium poly-vanadate was also studied, but the curves did not exhibit any appreciable break or inflection at the stoichiometric end-point. This may be ascribed to small difference in the pH values of reactants and the presence of $NaNO_3$ in appreciable amount in poly-vanadate solution; preventing occurrence of breaks in the conductometric titration curves.

It was noted that the presence of ethanol in lead vanadate titrations slightly improves the end-points and gives better results as it decreases solubility of the precipitates formed and minimizes hydrolysis and adsorption. 20% ethanolic medium was therefore employed for the entire course of the study. A thorough stirring in the vicinity of the end-point had a favorable effect.

The precipitates obtained at the end-points of the titrations of lead nitrate with sodium vanadates were analyzed by classical methods. Lead was determined as sulfate and vanadium by phosphotungstate method, and oxygen was calculated from the difference in the percentage. From the proportions of lead, vanadium and oxygen in the compounds thus obtained, their compositions were established, which were found to be the same as obtained by the electrometric study (Table 4).

Similar investigations on the interaction of neodymium nitrate with sodium vanadate at specific pH levels 12.4, 10.5, 7.4 and 3.6 confirm the formation of neodymium *ortho*-$Nd_2O_3.V_2O_5$, *pyro*-$2Nd_2O_3.3V_2O_5$ and *meta*-$Nd_2O_3.3V_2O_5$ vanadates in the neighborhood of pH 6.9, 6.2 and 5.3, respectively. As the structure of these compounds is not known these are represented as double oxides, the manner, which is usually adopted for such, compounds [30,31].

5. Conclusions

The results of the electrometric investigations on acid-vanadate system, at the specific concentration level of $\geq 10^{-4}$ M, suggest the formation of *para*-V_2O_7, *meta*-VO_3^- and poly-$H_2V_{10}O_{28}^{4-}$ vanadate anions in the pH ranges (10.1–10.7), (7.0–7.5) and (3.4–3.8), respectively. Similar studies on KOH–V_2O_5 system confirm the results obtained by the acid system. The electrometric and analytical investigations on the interaction of lead nitrate with sodium vanadate at specific pH levels 12.4, 10.5 and 7.4 provide definite evidence for the formation of lead *ortho*-$3PbO\cdot V_2O_5$, *pyro*-$2PbO\cdot V_2O_5$ and *meta*-$PbO\cdot V_2O_5$ vanadates in the vicinity of pH 8.2, 6.5 and 5.6, respectively.

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