Electrometric Investigations on Vanadates of Mercury(II)

Study of Hg(II) Meta-Vanadate

By R. S. Saxena, C. P. Sharma and M. L. Mittal

With 3 Figures

Abstract

Potentiometric, pH-metric and Conductometric titrations between Mercury (II) Nitrate and Sodium Meta-vanadate have revealed the formation of $(HgO \cdot Na_2O) 2V_2O_5$ and $HgO \cdot V_2O_5$ at pH ranges 6.4—6.9 and 4.5—5.5 respectively.

The formation and composition of mercury(II) meta-vanadates obtained by the interaction of mercuric nitrate and sodium meta-vanadate solutions have been studied by employing electrometric techniques involving pH-metric, potentiometric and conductometric titrations between the reactants in presence of 20% ethanolic medium. The well defined breaks and inflections in titration curves provide cogent evidence for the formation of $(HgO \cdot Na_2O) \cdot 2V_2O_5$ and $HgO \cdot V_2O_5$ in the pH ranges 6.4—6.9 and 4.5—5.5 respectively.

There are very few references in the literature on the study of Hg(II) meta-vanadate and most of the workers had based their conclusions on the analytical studies of the products formed by double decomposition. M. B. Rane and K. Kondiah[1] have reported the formation of $2HgO \cdot V_2O_5$ by adding NH_4-vanadate to an alcoholic $HgCl_2$ or $Hg(NO_3)_2$ solution. E. Montignie[2] suggested the formation of basic salts. J. J. Berzelius[3] obtained by double decomposition mercuric meta-vanadate as a lemon yellow coloured ppt. and also mercuric tetra-vanadate. However, no reference could be traced out concerning with the electrometric study of this reaction. In view of the conflicting details of the reports of previous workers on analytical studies and in the absence of any available electro-analytical data on the subject, it was considered worthwhile to investigate the reac-

[1]) M. B. Rane and K. Kondiah, J. Indian Chem. Soc. 8, 289 (1931).
[2]) E. Montignie, Bull. Soc. Chim. Ind. (5) 3, 2322 (1936).
[3]) J. J. Berzelius, Acad. Handl. Stockholm 1, (1832); Pogg. Ann. 22, 1 (1831).

tion between Hg(II) and alkali meta-vanadate by recent electrometric techniques which have provided more conclusive results on the compositions of such and allied compounds[4]).

Experimental

Reagents, mercuric nitrate, vanadium pentoxide and NaOH (E. Mercks G. R.) were used. Air-free conductivity water was used in the preparation of solutions. Hg(II) content in mercuric nitrate solution was checked by KCNS method.

A standard solution of sodium meta-vanadate was prepared by adding four moles of HCl to a solution containing one mole of alkali ortho-vanadate at 100 °C, which 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 e.m.f. and pH values were measured on a Cambridge null deflection type pH-meter. — Using a glass electrode of the range $0-14$ pH and a platinum indicator electrode in conjunction with saturated calomel electrode. Twenty ml of the titre solution was taken in the cell each time. The observed values of e.m.f. and pH were plotted against the volume of titrant added and from the sharp inflections in titration curves and from maximum values of dE/dV and dpH/dV, the end-points were determined. Conductance measurements were performed on LBR type conductometer (WTW Germany) taking 20 ml of the titre in the cell, which was thermostated at 25 ± 0.1 °C. The end-points were located graphically.
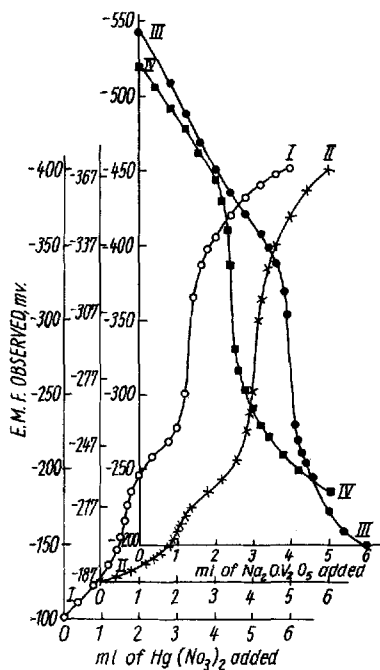

Fig. 1
Direct (I & II) and Reverse (III & IV) Potentiometric titrations between $Hg(NO_3)_2$ and $Na_2O \cdot V_2O_5$
Curve I ml of M/10 $Hg(NO_3)_2$ added to 20 ml of M/60 $Na_2O \cdot V_2O_5$
Curve II ml of M/30 $Hg(NO_3)_2$ added to 20 ml of M/150 $Na_2O \cdot V_2O_5$
Curve III ml of M/10 $Na_2O \cdot V_2O$ added to 20 ml of M/50 $Hg(NO_3)_2$
Curve IV ml of M/25 $Na_2O \cdot V_2O_5$ added to 20 ml of M/200 $Hg(NO_3)_2$

[4]) R. S. SAXENA and M. L. MITTAL, J. Inorg. Nucl. Chem. **27**, 2553 (1965); Experientia **21**, 481 (1965); J. Indian Chem. Soc. **41**, 2 (1964); J. Electroanal. Chem. **5**, 287 (1963); Acta Chim. Acad. Sci. Hung. **34**, 193 (1962).

Using different concentrations of reactants, a series of direct and reverse pH, e.m.f. and conductometric titrations were carried out. Similar strengths of solutions were employed in these titrations for the sake of comparision of results. Three diagrams, illustrating direct and reverse e.m.f. (fig. 1), pH (fig. 2) and conductometric (fig. 3) titration curves have been given for the sake of brevity.
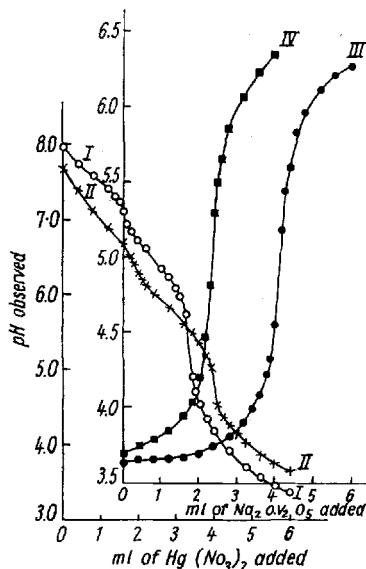
Fig. 2

Direct (I & II) and Reverse (III & IV) pH-metric titrations between $Hg(NO_3)_2$ and $Na_2O \cdot V_2O_5$.

Curve I ml of M/10 $Hg(NO_3)_2$ added to 20 ml of M/60 $Na_2O \cdot V_2O_5$

Curve II ml of M/30 $Hg(NO_3)_2$ added to 20 ml of M/150 $Na_2O \cdot V_2O_5$

Curve III ml of M/10 $Na_2O \cdot V_2O$ added to 20 ml of M/50 $Hg(NO_3)_2$

Curve IV ml of M/25 $Na_2O \cdot V_2O_5$ added to 20 ml of M/200 $Hg(NO_3)_2$
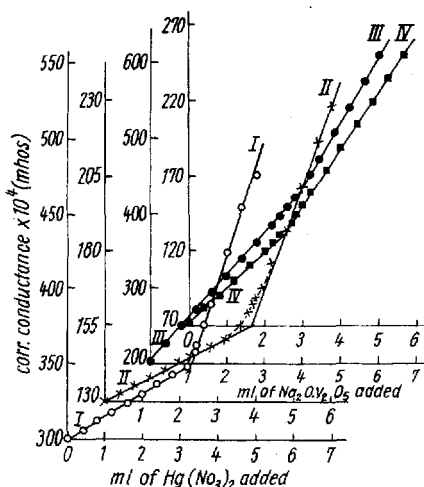
Fig. 3

Direct (I & II) and Reverse (III & IV) Conductometric titrations between $Hg(NO_3)_2$ and $Na_2O \cdot V_2O_5$.

Curve I ml of M/10 $Hg(NO_3)_2$ added to 20 ml of M/60 $Na_2O \cdot V_2O_5$

Curve II ml of M/30 $Hg(NO_3)_2$ added to 20 ml of M/150 $Na_2O \cdot V_2O_5$

Curve III ml of M/10 $Na_2O \cdot V_2O$ added to 20 ml of M/50 $Hg(NO_3)_2$

Curve IV ml of M/25 $Na_2O \cdot V_2O_5$ added to 20 ml of M/200 $Hg(No_3)_2$

Discussion

Saxena and Co-workers[5][6][7] have shown that the addition of acid to sodium ortho-vanadate and NaOH to vanadium pentoxide solutions at

[5] R. S. Saxena and M. L. Mittal, Acta Chim. Acad. Sci. Hung. 40, 109 (1964).

[6] R. S. Saxena and M. L. Mittal, Naturwiss. 51 (1964).

[7] R. S. Saxena and O. P. Sharma, J. Inorg. and Nucl. Chem. 28, 1881 (1966).

Table 1
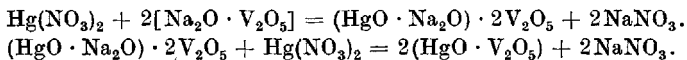Summary of the results of e.m.f., pH and conductometric titrations

Molarity of Solutions $Hg(NO_3)_2 : Na_2O \cdot V_2O_5$		Equivalance points (ml)					Formula Supported.
		Calc.		Observed		Condc.	
				E.M.F.	pH		
Direct Titrations. Figs. 1, 2 and 3, Curves I and II							
M/10	M/60	1.66	3.33	1.65 3.35	1.65 3.30	3.30	(HgO · Na₂O)
M/30	M/150	2.00	4.00	2.05 4.05	1.95 4.00	3.90	· 2V₂O₅ and
M/60	M/350	1.70	3.40	1.65 3.35	1.65 3.45	3.35	HgO · V₂O₅
M/100	M/525	1.90	3.81	1.80 3.70	1.85 3.75	3.75	
Reverse Titrations. Figs. 1, 2 and 3, Curves III and IV							
M/50	M/10	4.00		4.00	4.05	4.00	
M/200	M/25	2.50		2.45	2.40	2.55	HgO · V₂O₅
M/400	M/60	3.00		3.05	2.95	3.05	
M/800	M/150	3.75		3.80	3.80	3.85	

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 vanadates, pyro-($2\,Na_2O \cdot V_2O_5$), meta-($Na_2O \cdot V_2O_5$) and poly-($Na_2O \cdot 2\,V_2O_5$) are formed. Hence it was considered of importance to ascertain whether similar salts of heavy metals may be precipitated as a result of double decomposition. The reaction between alkali meta-vanadate and mercuric nitrate has, therefore, been studied by electrometric techniques.

Fig. 1 illustrates direct and reverse potentiometric titrations between alkali meta-vanadate and mercuric nitrate solutions. In direct titrations (curves-I and II), when $Hg(NO_3)_2$ solution was added to the meta-vanadate solution, a gradual increase in e.m.f. was observed upto the addition of about one half mole of $Hg(NO_3)_2$ per mole of $Na_2O \cdot V_2O_5$, after which a steeper rise in potential was obtained. When the observed values of e.m.f. were plotted as a function of the volume of titrant added, the curves were found to indicate two inflections; first, which was found to be less pronounced, at the molecular ratio of $HgO:V_2O_5$ as $1:2$ suggesting the formation of an intermediate product $(HgO \cdot Na_2O) \cdot 2V_2O_5$ and the second well defined occurred at the molecular ratio $HgO:V_2O_5 :: 1:1$ corresponding to the formation of $HgO \cdot V_2O_5$. When alkali meta-vanadate was used as titrant (reverse titrations, Fig. 1, Curves-III and IV), only one inflection was obtained at a point confirming the formation of mercuric meta-vanadate $HgO \cdot V_2O_5$. It is observed that beyond this break the e.m.f. changes assume almost a constant rate which continues even upto the addition of more than two moles of meta-vanadate per mole of $Hg(NO_3)_2$.

Both direct and reverse potentiometric titration curves are regular in form and provide sharp jumps. Direct titrations indicated the formation of two compounds, $(HgO \cdot Na_2O.) \cdot 2V_2O_5$ which on addition of mercuric nitrate beyond its half mole per mole of alkali meta-vanadate changes to mercuric meta-vanadate $HgO \cdot V_2O_5$. The reaction equilibria can be represented as follows:

$$Hg(NO_3)_2 + 2[Na_2O \cdot V_2O_5] = (HgO \cdot Na_2O) \cdot 2V_2O_5 + 2NaNO_3.$$
$$(HgO \cdot Na_2O) \cdot 2V_2O_5 + Hg(NO_3)_2 = 2(HgO \cdot V_2O_5) + 2NaNO_3.$$

The glass electrode titration curves (Fig. 2) represent the changes occuring in H^+ ion concentration when mercuric salt solution was treated with sodium meta-vanadate. The plots of pH changes vs. the volume of titrant added yield sharp inflections at the points corresponding to the molecular ratio of $HgO:V_2O_5$ as 1:2 and 1:1 confirming the formation of identical compounds as suggested by e.m.f. study viz. $(HgO \cdot Na_2O.) \cdot 2V_2O_5$ at pH range $6.4-6.9$ and mercuric meta-vanadate $HgO \cdot V_2O_5$ at pH range $4.5-5.5$. In this case also, reverse titrations yield only one break indicating the formation of mercuric meta-vanadate.

The course of the reaction was also followed by means of conductometric titrations between the reactants. The titration curves have been found to yield strongly defined breaks at the stoichiometric end-points suggesting the formation of mercuric meta-vanadate $HgO \cdot V_2O_5$ in accordance with the e.m.f. and pH study. Conductometric titrations do not throw any light on the formation of intermediate product.

It is noted that after each addition of the reagent, it takes a little time for the pH e.m.f. and conductance values to become steady. A thorough stirring in the vicinity of the end-point has a favourable effect. In these titrations the presence of ethanol has been found to give accurate results, as it decreases the solubility of the compounds formed. 20% ethanolic medium has, therefore, been employed for the entire course of study.

The present electrometric investigations on the reaction between mercuric nitrate and sodium meta-vanadate confirm the formation of $(HgO \cdot Na_2O.) \cdot 2V_2O_5$ and $HgO \cdot V_2O_5$ at pH levels $6.4-6.9$ and $4.5-5.5$ respectively. The formation of the compound $(HgO \cdot Na_2O) \cdot 2V_2O_5$ takes place only in presence of excess of alkali meta-vanadate, it exists as an intermediate product with little stability and changes into mercuric meta-vanadate with increase in the concentration of Hg(II).