Electrometric Studies on the Reaction between Silver and Alkali Metavanadate

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In earlier publications[1-4] the authors have studied the reaction between Ag^+ and VO_4^{3-}, $V_2O_7^{4-}$ ions and some of their analytical applications by electrometric methods. In continuation of previous investigations, the present work has been undertaken with a view to study the formation and composition of silver metavanadate by the interaction of silver nitrate and alkali metavanadate solutions, and to examine the possibility of developing this as an analytical method for the determination of vanadium as silver metavanadate.

Experimental

Anal. R. (BDH) reagents, vanadium(V) oxide, sodium hydroxide, silver nitrate, and reagent grade nitric acid were used and their solutions prepared in air-free conductivity water. Furthermore a standard solution of sodium orthovanadate was prepared by dissolving the requisite amount of vanadium(V) oxide in a boiling solution of sodium hydroxide of the required strength. Orthovanadate solution thus prepared was treated with a calculated quantity of nitric acid at 100°C to yield standard sodium metavanadate solution.

Amperometric Titrations.—A manual polarograph with scalamp galvanometer as a current recorder was used for the amperometric titrations. A dropping mercury electrode having the following characteristics: $m=2.416$ mg./sec., $t=3.58$ sec., and $m^{2/3}t^{1/6}=2.226$ mg$^{2/3}$ sec$^{-1/2}$ at $E_{d.e.}=-1.0$ V. (vs. SCE) was used in conjunction with a SCE connected to the cell by an agar - potassium nitrate bridge. All amperometric titrations were performed in the presence of the base electrolyte sodium nitrate, 0.005% thymol as maximum supressor, and 40% alcoholic media, at $E_{d.e.}=-0.3$ V. (vs. SCE). At this potential under the above conditions, VO_3^- ion does not produce any measurable diffusion current, whereas Ag^+ ion yields a diffusion current almost proportional to its concentration. Twenty milliliters of the titer solution was taken in the cell each time and deaerated and stirred by bubbling hydrogen. The diffusion current obtained after each addition of titrant was corrected for the dilution effect and plotted against the volume of titrant in millilitre. The end-point was located graphically. The results of amperometric titrations are summarised in Table I.

TABLE I. SUMMARY OF THE RESULTS OF AMPEROMETRIC TITRATIONS

Molarity of solutions		Equivalence points, ml.	
$AgNO_3$	$Na_2O\cdot V_2O_5$	Calcd.	Obs.
Direct titrations Fig. 1 curve I(D)			
M/25	M/250	4.00	4.00
M/40	M/500	3.20	3.20
M/100	M/1200	3.33	3.30
M/150	M/2000	3.00	3.05
Reverse titrations Fig. 1 curve II(R)			
M/250	M/100	4.00	4.00
M/750	M/250	3.33	3.40
M/1500	M/450	3.00	3.10

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[1] R. S. Saxena and O. P. Sharma, *Talanta*, **11**, 863 (1964).

[2] R. S. Saxena and O. P. Sharma, *Naturwissenschaften*, **51**, 433 (1964).

[3] R. S. Saxena and O. P. Sharma, *Indian J. Chem.*. **2**, 502 (1964).

[4] R. S. Saxena and O. P. Sharma, *Z. anal. Chem.* (1964) (in press).

TABLE II. RESULTS OF E. M. F. AND GLASS ELECTRODE TITRATIONS

Molarity of solutions		Equivalence points, ml.		
		Calculated for the formation of $Ag_2O \cdot V_2O_5$	Observed from	
$AgNO_3$	$Na_2O \cdot V_2O_5$		Max. dE/dV	Max. dpH/dV
Direct titrations Fig. 2 curve I(D)				
M/10	M/100	4.00	3.98	
M/20	M/250	3.20	3.20	
M/50	M/600	3.33	3.30	
M/75	M/1000	3.00	2.95	
Reverse titrations Fig. 2 curve II(R) and Fig. 3 curves I and II				
M/50	M/20	4.00	4.02	4.00
M/200	M/75	3.75	3.74	3.78
M/500	M/150	3.00	3.00	3.02
M/750	M/250	3.33	3.30	3.30

Potentiometric and Glass Electrode Titrations.—The E. M. F. and pH of the solutions were measured on a Cambridge (null deflection type) pH meter by means of a bright silver electrode and a glass electrode of the range 0—9 respectively, in conjunction with a saturated calomel electrode connected to the cell by a low resistance salt bridge. After each addition of the titrant, the E. M. F. and pH were measured and plotted against the volume of titrant added, the end point was obtained from the sharp inflection in the titration curves and also from the pronounced maxima in dE/dV and dpH/dV respectively. A series of E. M. F. and pH titrations was performed, using the same concentrations of the reactants for the sake of comparison, both by the direct and inverse methods. Only reverse glass electrode titrations yielded dependable results. The results or the investigations carried out are tabulated below. Only two representative graphs are given for the sake of brevity.

Discussion

The pH of silver nitrate and $Na_2O \cdot V_2O_5$ was measured with a glass electrode and found to be 6.30 and 7.50 respectively. The titration curves (Fig. 3, curves I and II) illustrate the changes occurring in H^+ ion concentration when $Na_2O \cdot V_2O_5$ is added to silver nitrate solution. A sharp change in pH was observed at the stoichiometric end point where the molecular ratio of Ag^+ and VO_3^- ions is 1:1 corresponding to the formation of silver metavanadate $Ag_2O \cdot V_2O_5$ in the pH-range 6.25—7.0.

An examination of the results of potentiometric titrations (Fig. 2 curves I(D) and II (R)) reveals that the reaction between silver nitrate and $Na_2O \cdot V_2O_5$ can be suitably followed using a bright silver electrode. As the titration proceeds, the E. M. F remains almost constant until in the vicinity of the end point a marked change in E. M. F. occurs; beyond that it remains practically constant.

Conductometric titrations between silver nitrate and $Na_2O \cdot V_2O_5$ were also tried but they failed to provide any conclusion regarding the composition of silver metavanadate.

The same concentrations of reactants were used in potentiometric and pH titrations for the sake of comparison. After each addition of the titrant, it takes a little time for the E. M. F., and pH values to become steady. The results are accurate and reproducible.

The amperometric titration betweens silver nitrate and $Na_2O \cdot V_2O_5$ were performed at an electric tension of −0.3 V. vs. SCE. In the direct titrations (Fig. 1, curve I(D)), when $Na_2O \cdot V_2O_5$ is used as the titer, VO_3^- ion does not yield any measurable diffusion current and hence no change in current is observed on the addition of silver nitrate solution untill the stoichiometric end point is reached, after which the diffusion current due to Ag^+ ions increases with the addition of silver nitrate. In the case of reverse titrations (Fig. 1, curve II(R)), the diffusion current due to Ag^+ ion

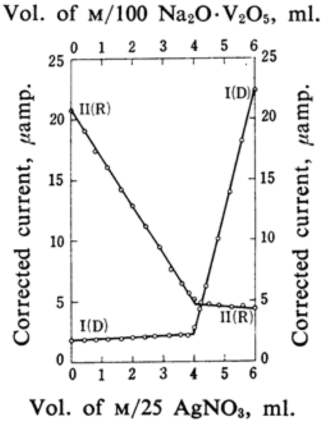

Fig. 1. Direct (I(D)) and reverse (II(R)) amperometric titrations beween $AgNO_3$ and $Na_2O \cdot V_2O_5$.
Curve I(D), M/25 $AgNO_3$ vs. M/250 $Na_2O \cdot V_2O_5$; Curve II(R) M/100 $Na_2O \cdot V_2O_5$ vs. M/250 $AgNO_3$

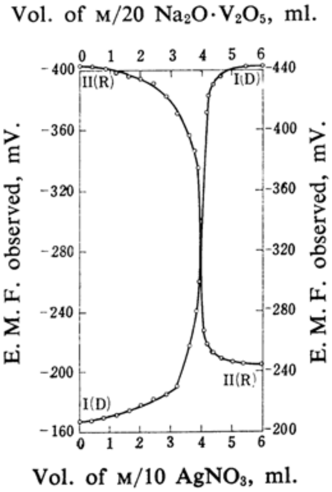

Fig. 2. Direct (I(D)) and reverse (II(R)) potentiometric titrations between $AgNO_3$ and $Na_2O\cdot V_2O_5$.
Curve I(D), M/10 $AgNO_3$ vs. M/100 $Na_2O\cdot V_2O_5$; Curve II(R) M/20 $Na_2O\cdot V_2O_5$ M/50 $AgNO_3$

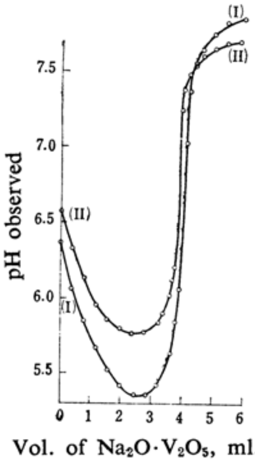

Fig. 3. Reverse pH titrations between $AgNO_3$ and $Na_2O\cdot V_2O_5$.
Curves I M/20 $Na_2O\cdot V_2O_5$ vs. M/50 $AgNO_3$; II M/75 $Na_2O\cdot V_2O_5$ vs. M/200 $AgNO_3$

gradually decreases on the addition of alkali metavanadate solution and reaches a minimum at the end point, beyond which the current almost remains constant. Amperometric titration curves are L shaped; a sharp break is obtained at the end point corresponding to the formation of silver metavanadate $Ag_2O\cdot V_2O_5$ in the pH range 6.25–7.0. The accuracy and reproducibility of these titrations has been found to be excellent even at low concentrations (0.5 mM) [of $Na_2O\cdot V_2O_5$. The presence of 40% ethanol improves the end point as the compound formed is appreciably soluble.

A comparative study of the electrometric experiments clearly suggests that pH and potentiometric titrations yield accurate results only with concentrated solutions of the reactants; at greater dilutions, the breaks and inflections are not strongly defined. Amperometric titrations, however, give very accurate end points even with low concentrations of reactants (Table I). In view of the simplicity, rapidity and accuracy of the titrations, the amperometric method may be recommended for the determination of V^{5+} as silver metavanadate in the pH-range 6.25—7.0.

Summary

The reaction between Ag^+ and VO_3^- ions has been investigated by means of electrometric techniques involving amperometric, potentiometric and glass electrode titrations between silver nitrate and $Na_2O\cdot V_2O_5$ in 40% alcoholic media. The end point obtained from the sharp breaks and inflections in the titration curves, occurs at a stage where the molecular ratio of Ag^+ and VO_3^- ions is 1 : 1 and corresponds to the formation and precipitation of silver metavanadate, $Ag_2O\cdot V_2O_5$, in the pH range 6.25—7.0. Amperometric titrations yield very accurate results and offer a simple and rapid method of determining vanadium(V) as silver metavanadate.

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