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The stoichiometry of the various polyanions formed during the reaction between hydrochloric acid and sodium tungstate has been investigated by means of electrometric techniques involving glass electrode and conductometric titrations as well as by Job's method of continuous variation. The breaks, inflections and maxima in the curves provide cogent evidence for the existence of aggregated tungstate polyanions, para- $W_{12}O_{41}^{10-}$ and meta- $W_{12}O_{39}^{6-}$ corresponding to the ratio of $H^+ : WO_4^{2-}$ as 7 : 6 and 9 : 6 in the pH ranges 5.7-6.0 and 3.6-4.1, respectively. The formation of other polyanions, reported in the literature, such as $W_{12}O_{46}^{20-}$, $H_5W_4O_{16}^{3-}$, $W_3O_{11}^{4-}$ and $W_2O_7^{2-}$ could not be supported by the study.

Keywords: tungstates; isopolyanions; electrometric study.

INTRODUCTION

In aqueous solution, molybdates, tungstates, vanadates, and, to a smaller extent, niobates, tantalates, and cromates, undergo complex hydrolysis-polymerisation reactions upon acidification. The major solute species generated by such reactions are isopoly-anions, of which dichromate $Cr_2O_7^{2-}$, and heptamolybdate, $Mo_7O_{24}^{6-}$, are well-characterised examples.¹ There is no doubt that the formation of isopolytungstates on acidification of the solutions of normal tungstate, WO_4^{2-} , is the most complex and the least understood system.² The difficulties are the least three fold. Firstly there is the inability to obtain well-defined crystalline salts with many of the isopolytungstate anions, and hence the structural basis remains somewhat speculative. Secondly many workers have used solutions containing buffers, many of which contain anions that preferentially form complexes with the tetrahedrally coordinated normal tungstate rather than the octahedrally coordinated polytungstates. Thirdly the rates of formation of some isopolytungstates are very slow.³

Tungstate solutions can absorb considerable quantities of strong acid by mechanism leading to formation of isopolytungstates⁴. Despite extensive investigations the problem of number and composition of the polymeric species has not been completely solved. It is reported^{5,6} that even in a solution initially containing only orthotungstate and acid, may exist eight types of species with $H^+ : WO_4^{2-}$ ratio as 1:3, 2:3, 7:6, 3:2 and 2:1. The degree of aggregation in solutions increases as the pH is lowered, and numerous tungstates $M_2^1O_nWO_3.mH_2O$, differing in the value of n, have been reported from the solutions at different pH's.⁷

The existence of so many isopolyanions 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.

On account of the complexity of the equilibria between the polyanions or due to experimental difficulties associated with the analytical work, the conclusions of earlier workers seems to be overstrained and hence it is considered worthwhile to make a careful and precise study of the acid-tungstate system

by electrometric techniques, which have provided more conclusive evidences on the condensation processes of oxyanions of vanadium (V), arsenic (III), antimony (III), and thioanions of tungsten (VI), molybdenum (VI) and arsenic (III).⁸⁻¹⁵

EXPERIMENTAL

Merck's guaranteed extrapure reagents, sodium tungstate and hydrochloric acid, were used for the preparation of solutions. The concentration of the sodium tungstate solution was further estimated by tannin-antipyrine method¹⁶ and also by precipitation as barium tungstate¹⁶.

pH measurements were carried out on Metrohm Herisau (Switzerland) pH-meter using a Scott Gerate glass combination electrode. Conductance values were recorded by employing a Metrohm conductometer. The sodium tungstate solution (25ml) was placed in the cell each time and thermostated at $25 \pm 0.1^\circ C$. Using different concentrations of HCl and Na_2WO_4 , a series of glass electrode and conductometric titrations have been carried out. The same strengths of reactants were employed in conductometric and glass electrode titrations for the sake of comparison. The curves were plotted between pH and corrected conductance and volume of HCl added. As the inflections in pH titration curves were not strongly defined, differential graphs in dpH/dV were also drawn and end-points were marked by pronounced maxima in dpH/dV . The results obtained by dpH/dV curves were further confirmed by graphs of d^2pH/dV^2 and dV/dpH vs. V.

With a view to bring out the breaks more prominently, conductance was also plotted as a function of the pH. To show the dilution effect on formation of the polyanions the curves on two dilutions are presented. The results of the electrometric titrations are shown in Table 1.

Job's method of continuous variation was employed using electrical conductance measurements for determining the composition of the polyanions formed by the interaction of Na_2WO_4 with hydrochloric acid. This consists of plotting the differences in specific conductivities (the sum of observed specific conductivities of the constituent solutions minus the observed specific conductivities of the mixture) against the composition of the mixtures.

Table 1. Summary of the results of the electrometric titration. Volume of sodium tungstate solution taken in the titration cell = 25ml.

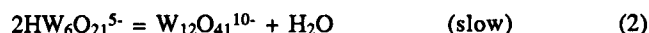
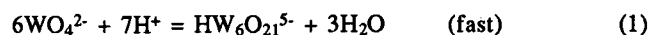
Molarity of solutions		Equivalence points (ml) for the formation of					
HCl	Na ₂ WO ₄	Paratungstate			Metatungstate		
		Calc.	A	B*	Calc.	A.	B*
1.5	0.125	2.43	2.45	2.45	3.13	3.15	3.15
0.5	0.040	2.33	2.30	2.35	3.00	3.00	3.00
0.2	0.018	2.63	2.65	2.65	3.38	3.40	3.40
0.1	0.010	2.92	2.90	2.90	3.75	3.80	3.75

* A and B represent the end-points observed from pH and conductometric titrations respectively.

RESULTS AND DISCUSSION

The pH titrations of the acid against sodium tungstate are shown in Fig. 1. Two points of inflection are obtained; the first at H⁺:WO₄²⁻ as 7:6 corresponding to the formation of paratungstate and the second at H⁺:WO₄²⁻ as 9:6 due to the formation of metatungstate anions. In the first stage of the titration, when H⁺:WO₄²⁻ is less than 7:6, the addition of the acid brings about a gradual change in pH with a rapid attainment of its equilibrium value. When the ratio of the acid to normal tungstate passed 7:6, the initial pH dropped sharply leading to the observed inflection due to the formation of paratungstate anion in the pH range 5.7-6.0. But in contrast to the earlier part of the titration, the pH value showed an increasing tendency on waiting after each addition of the

titrant and took a long time for attaining the equilibrium value, leading to a partial disappearance of the paratungstate A (HW₆O₂₁⁵⁻) to a more stable ion, paratungstate Z (W₁₂O₄₁¹⁰⁻). The increase in pH value observed on standing should be the result of an increase in negative charge (from -5 on HW₆O₂₁⁵⁻ to -10 on W₁₂O₄₁¹⁰⁻) on the formation of higher polymer of a weaker acid. The existence of these two species is in agreement with the ultracentrifuge results.¹⁷⁻²⁰ The paratungstate formation may be represented in a simplified way as follows:



During the region of the second inflection in the titration

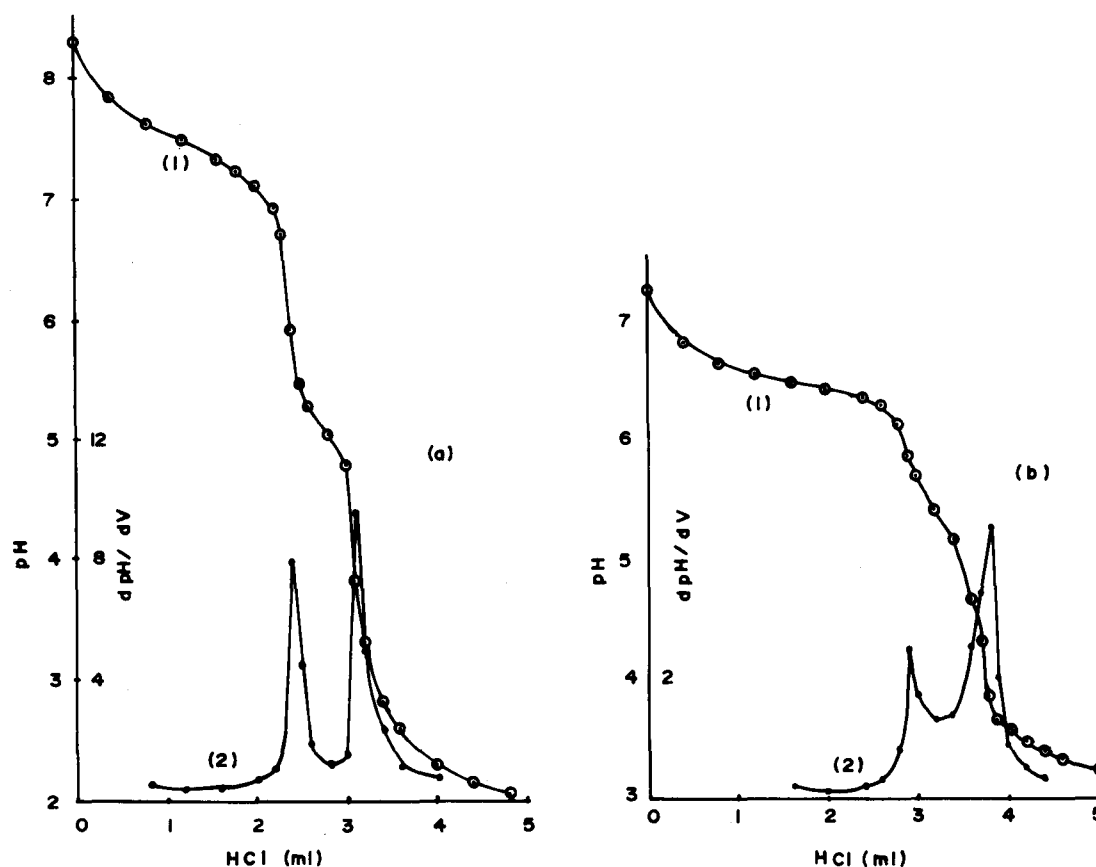
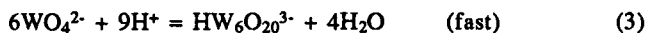


Figure 1. pH titrations of Na₂WO₄ with HCl. (a) 1.5M HCl to 25 ml of 0.125M Na₂WO₄; (b) 0.1M HCl to 25 ml of 0.01M Na₂WO₄. Curve (1) pH and (2) dpH/dV.

curves, corresponding to the formation of metatungstate isopolyanion, the tendency to increase the pH value on waiting was again observed, leading to a conclusion that the formation of the final metatungstate species, $W_{12}O_{39}^{6-}$, is also a slow process and should be preceded by the information of an unstable species $HW_6O_{20}^{3-}$, pseudo-metatungstate.^{4,7} The two stage reaction may be represented as follows:



A comparison of Fig. 1 (a) with Fig. 1 (b) shows that in the case of higher concentration of the solutions the pH curves are steeper and dpH/dV is more pronounced than for dilute solutions. The decrease in sharpness of the inflection corresponding to the formation of paratungstate, with dilution of

the solutions may probably be attributed to the formation of metatungstate along with paratungstate under such conditions, as also reported by Kepert.^{2b} Out the two inflections shown in the curves, the one corresponding to aggregation process of tungstate to metatungstate is most marked.

It was observed that after passing the second inflection the pH values got stabilized and did not give any more inflection even with an addition of a lot excess of the acid ($H^+ : WO_4^{2-} :: >10:1$) and hence not confirming the formation of the tungstic acid.^{2c}

Conductometric titrations between HCl and Na_2WO_4 were also carried out employing the same concentrations of the reactants as in pH titrations for the sake of comparison of the results. The plots (Fig. 2) of corrected conductance as a function of volume of titrant yielded two well-defined breaks at the ratio $H^+ : WO_4^{2-}$ as 7:6 and 9:6 corresponding to the formation of paratungstate and metatungstate, respectively, as

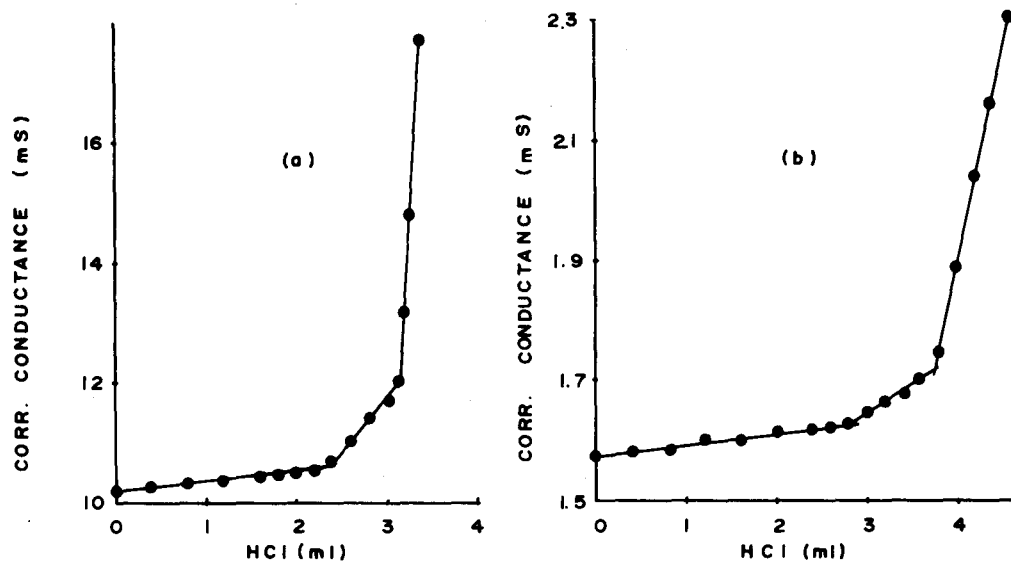


Figure 2. Conductometric titrations of Na_2WO_4 with HCl. (a) 1.5M HCl to 25 ml of 0.125M Na_2WO_4 ; (b) 0.1M HCl to 25 ml of 0.01M Na_2WO_4 .

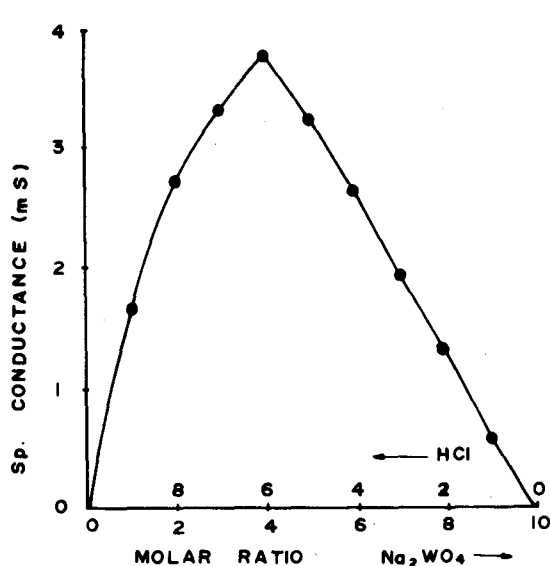


Figure 3. Continuous variation study by Job's method using 0.02M HCl and 0.02M Na_2WO_4 .

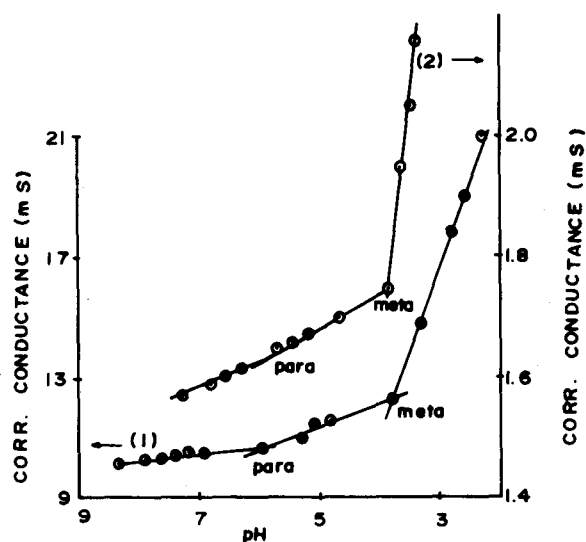


Figure 4. Plot of conductance as a function of pH. Curve (1) Titration of 0.125M Na_2WO_4 with 1.5M HCl. Curve (2) Titration of 0.01M Na_2WO_4 with 0.1M HCl.

Table 2

H ⁺ :WO ₄ ²⁻	a	b*	pH range	Polytungstate	Common name	Rate
7:6	7	6	5.5-6.0	HW ₆ O ₂₁ ⁵⁻	Paratungstate A	Fast
7:6	14	12	5.7-6.0	W ₆ O ₄₁ ¹⁰⁻	Paratungstate Z	Slow
9:6	9	6	3.5-4.1	HW ₆ O ₂₀ ³⁻	Pseudo-metatungstate	Fast
9:6	18	12	3.6-4.1	W ₁₂ O ₃₉ ⁶⁻	Metatungstate	Slow

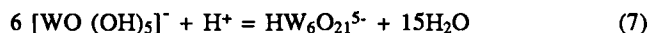
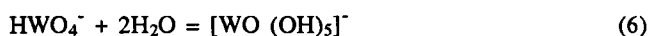
* a and b are as in the Eq. 8.

suggested by the preceding pH study. In all these titrations the break corresponding to the addition of 1.5 equivalents of the acid per Na₂WO₄ is strongly defined, followed by a sharp rise in conductance which was determined to be the same as expected for the addition of free acid to the system.

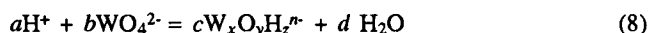
The course of the isopolyanion formation of tungstate by the acid was also followed by employing Job's method of continuous variation using electrical conductance measurements. The plot of difference in specific conductivity values against composition of mixtures indicated a sharp maximum (Fig. 3) corresponding to the molar ratio of HCl:Na₂WO₄ as 9:6; this provides further evidence for the formation of the metatungstate polyanions.

The curves (1) and (2) in Fig.4 where conductance is plotted as a function of pH also bring out these two inflections prominently.

When a basic tungstate solution containing WO₄²⁻ and Na⁺ is acidified, the tungstate ions have been found to condense in definite steps, as evidenced by the foregoing electrometric experiments, to form different isopolytungstate anions. The overall condensation process may be considered formally at least to begin with partial neutralization of the tungstate ions, and then expanding its coordination sphere from four to six by water molecules followed by the formation of a highly aggregated isopolyanion at lower pH value.



The condensation process may be represented by the following general equation, which is almost similar to the one proposed by MacInnis and Kim⁶:



with the values for *a* and *b* as represented in Table 2.

It is quite probable that the highly charged species given in Table 2 may be hydrated; e.g., W₁₂O₃₉⁶⁻ as H₂W₁₂O₄₀⁶⁻, and W₁₂O₄₁¹⁰⁻ as H₁₀W₁₂O₄₆¹⁰⁻ as suggested by Cotton and Wilkinson.¹⁰

The results of a careful pH and conductometric study on the acid tungstate system provides definite evidence for the formation of para -W₁₂O₄₁¹⁰⁻ (via HW₆O₂₁⁵⁻) and meta-W₁₂O₃₉⁶⁻ (via HW₆O₂₀³⁻) in the pH ranges 5.7-6.0 and 3.6-4.1, respectively. Similar study was carried out by using sulphuric acid in place of hydrochloric acid; the existence of the same species was confirmed as indicated by the investigations with HCl. The observation of MacInnis and Kim⁶ about the forma-

tion of W₁₂O₄₆²⁰⁻, W₃O₁₁⁴⁻ and WO₃.H₂O, of Meier and Schwarzenbach²¹ about H₅W₄O₁₆³⁻ and Simons²² about W₂O₇²⁻ could not be confirmed by the study.

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