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Potentiometric and conductometric studies on the system acid-isopolytungstate and the formation of lanthanum tungstates

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Abstract: The stoichiometry of the polyanions formed by the action of nitric acid on sodium tungstate (≤ 0.01M) has been studied by means of electrometric techniques involving pH-potentiometric and conductometric titrations. The well defined inflections and breaks in the titration curves provide evidence for the existence of the 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 interaction of lanthanum nitrate with sodium tungstate solutions, at specific pH levels 8.0, 5.9 and 4.0 was also studied by pH and conductometric titrations, in aqueous and alcoholic media, with each of the reagents alternatively used as titrant. The electrometric experiments provide definite evidence of the formation of *normal*-$La_2O_3.3WO_3$, *para*-$5La_2O_3.36WO_3$ and *meta*-$La_2O_3.12WO_3$ tungstates in the vicinity of pH 6.3, 5.0 and 4.2, respectively. Analytical investigations on the precipitates formed confirm the results of the electrometric study.

Keywords: isopolytungstates; lanthanum; electrometry; polyanions.

Introduction

In aqueous solutions molybdates, tungstates, vanadates, and to smaller extent, niobates, tantalates, and chromates, undergo complex hydrolysis-polymerization reactions upon acidification. The major species generated by such reactions are isopolyanions, of which $Cr_2O_7^{2-}$, and heptamolybdate, $Mo_7O_{24}^{6-}$, are well-characterized 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 at least three fold. Firstly, there is the instability 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 [3,4].

Tungstate solutions can absorb considerable quantities of strong acid by mechanism leading to formation of isopolytungstates [5]. Despite extensive investigations the problem of number and composition of the polymeric species has not been completely solved. It is reported [4,6] 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 $M_2^IO.nWO_3.mH_2O$, differing in the value of *n*, have been reported from the solutions at different pH's [6]. 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. A further verification of the tungstate 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 [7,8,9]. After establishing for suitable conditions for the stability of different tungstate polyanions, the investigations for the formation of lanthanum tungstates as a function of pH were also carried out as no reference could be traced out in the literature about their formation.

Experimental details

$Na_2WO_4.2H_2O$, $La(NO_3)_3$, HNO_3 and ethanol of extra-pure grade were used, and their solutions were prepared with deionized distilled water. Concentration of the sodium tungstate solution was further verified by tannin-antipyrine method [10a].

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. The sodium tungstate solution (25.00 mL) was placed in the cell each time and thermostated at 25.0±0.1°C. Using different concentrations of HNO_3 and Na_2WO_4, a series of glass electrode and conductometric titrations have been carried out.

The same concentrations of reactants were employed in conductometric and glass electrode titrations for the sake of comparison. The curves were plotted between pH and corrected conductance vs. volume of HNO_3 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. A summary of the electrometric titrations of the acid system is given in Table 1.

The formation of lanthanum tungstates was investigated by the action of lanthanum nitrate with different vanadate anions at specific pH levels 8.0, 5.9 and 4.0 using different concentrations of the reactants. A series of pH and conductometric titrations was performed by direct and reverse methods, i.e. when lanthanum nitrate solution from the microburette was added to sodium tungstate solution and vice versa (Table 2). 25.00 mL of ethanolic solution (20%) was taken in the cell, which was thermostated at 25.0±0.1°C.

The precipitates obtained at the end-points of titrations between lanthanum nitrate and sodium tungstates were also analyzed to substantiate the electrometric results. The different lanthanum tungstates were precipitated by mixing stoichiometric amounts of lanthanum nitrate solutions with sodium tungstate solutions at specific pH levels 8.0, 5.9 and 4.0. 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 precipitates was used for analysis tungsten and lanthanum. Tungsten [10a] was determined as oxinate and lan-

Table 1. Summary of results of electrometric titrations of HNO_3 with Na_2WO_4[a]

| Molarity of solutions | | Equivalence points (ml) for the formation of | | | | | |
| | | para-tungstate | | | meta-tungstate | | |
HNO_3	Na_2WO_4	Calculated	A[b]	B[b]	Calculated	A	B
M/10	M/100	2.92	2.92	2.92	3.75	3.75	3.77
M/20	M/225	2.59	2.60	2.58	3.33	3.35	3.35
M/50	M/525	2.78	2.78	2.75	3.57	3.60	3.60
M/100	M/1100	2.50	2.50	2.50	3.41	3.42	3.42

[a] Volume of Na_3WO_4 solution taken in the cell = 25 mL.
[b] A and B represent results obtained from pH and conductometric titrations, respectively. The titrations were performed in triplicate (sd = ±0.005).

Table 2. Summary of results of electrometric study on formation of lanthanum tungstates.
Volume of titre solution taken in the cell = 25.00 mL.

Molarity of solutions		Equivalence points (mL)			Formula supported
		Calculated	Observed from		
			pH	Conductance	
$La(NO_3)_3$	Na_2WO_4	Direct titrations*			
M/30	M/250	2.00	2.00	2.00	$La_2O_3.3WO_3$
M/50	M/400	2.08	2.08	2.10	
M/80	M/650	2.05	2.05	2.05	
		Reverse titrations*			
M/375	M/20	2.00	2.00	2.00	$La_2O_3.3WO_3$
M/675	M/40	2.40	2.40	2.38	
M/900	M/60	2.50	2.50	2.50	
$La(NO_3)_3$	$Na_{10}W_{12}O_{41}$	Direct titrations*			
M/30	M/1200	2.08	2.08	2.06	$5La_2O_3.36WO_3$
M/50	M/1750	2.38	2.38	2.38	
M/80	M/3000	2.22	2.20	2.20	
		Reverse titrations*			
M/900	M/240	2.22	2.22	2.22	$5La_2O_3.36WO_3$
M/1600	M/480	2.25	2.25	2.25	
M/2000	M/650	2.44	2.40	2.42	
$La(NO_3)_3$	$Na_6W_{12}O_{39}$	Direct titrations*			
M/30	M/750	2.00	-	2.00	$La_2O_3.12WO_3$
M/50	M/1000	2.50	-	2.50	
M/80	M/1750	2.29	-	2.28	
		Reverse titrations*			
M/1500	M/240	2.00	-	2.00	$La_2O_3.12WO_3$
M/2800	M/480	2.14	-	2.15	
M/3600	M/600	2.08	-	2.10	

* Typical curves of these titrations of normal- para- and meta- tungstates are shown in Figs. 2, 3 and 4, respectively.

thanum [10b] with oxalate. From the proportions of lanthanum and tungsten in the compounds thus obtained their composition was established. The results are summarized in Table 3. The analytical results were also confirmed by atomic absorption spectroscopy.

Results and Discussions

The pH titrations of the acid against sodium tungstate are shown in Fig. 1 (curves 1 and 2). Two points of inflection were obtained; the first at $H^+:WO_4^{2-}$ as 7:6 corresponding to the for-

Table 3. Summary of analytical results of the lanthanum tungstate precipitates.

Proposed formula of the compound	Mode of synthesis	Analysis %: Found (Calculated)	
		La	W
	Analysis of the normal-tungstate precipitates		
$La_2O_3.3WO_3$	Direct*	27.17(27.20)	54.05(54.00)
	Reverse*	27.24	53.96
	Analysis of the para-tungstate precipitates		
$5La_2O_3.36WO_3$	Direct	13.92(13.93)	66.40(66.35)
	Reverse	13.95	66.31
	Analysis of the meta-tungstate precipitates		
$La_2O_3.12WO_3$	Direct	8. 92(8.94)	71.04(70.98)
	Reverse	8.96	70.93

*Direct – Lanthanum nitrate solution added to sodium tungstate solution.
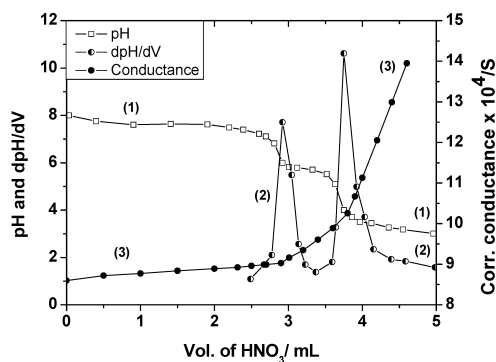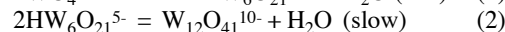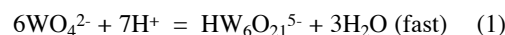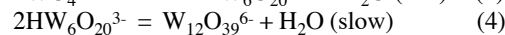*Reverse – Sodium tungstate solution added to lanthanum nitrate solution.

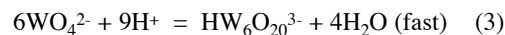**Figure 1.** pH and conductometric titrations of 25 mL of M/100 N_2WO_4 with M/10 HNO_3.

mation of paratungstate and the second at $H^+:WO_4^{2-}$ as 9:6 due to the formation of paratungstate anions. In the first stage of the formation, when $H^+:WO_4^{2-}$ 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 ($HW_6O_{21}^{5-}$) to a more stable ion, paratungstate Z ($W_{12}O_{41}^{10-}$). The increase in pH value observed on standing should be the result of an increase in negative charge (from -5 on $HW_6O_{21}^{5-}$ to -10 on $W_{12}O_{41}^{10-}$) on the formation of higher polymer of a weaker acid. The existence of these two species is in agreement with the ultracentrifuge results [11-14]. The paratungstate formation may be represented in a simplified way as follows:

$$6WO_4^{2-} + 7H^+ = HW_6O_{21}^{5-} + 3H_2O \text{ (fast)} \quad (1)$$
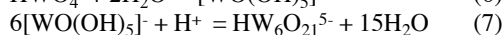$$2HW_6O_{21}^{5-} = W_{12}O_{41}^{10-} + H_2O \text{ (slow)} \quad (2)$$

During the region of the second inflection in the titration curves, corresponding to the formation of metatungstate isopolyanions, 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 formation of an unstable species $HW_6O_{20}^{3-}$, psedo-metatungstate [5,6]. The two stage reaction may be represented as follows:

$$6WO_4^{2-} + 9H^+ = HW_6O_{20}^{3-} + 4H_2O \text{ (fast)} \quad (3)$$
$$2HW_6O_{20}^{3-} = W_{12}O_{39}^{6-} + H_2O \text{ (slow)} \quad (4)$$

It was observed that after passing the second inflection the pH value 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 [2b].

Conductometric titrations between HNO_3 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. 1, curve 3) of corrected conductance as a function of the 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 suggested by the preceding pH study. In all these titrations the break corresponding to the addition of 1.5 equivalents of the acid per Na_2WO_4 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.

When a basic tungstate solution containing WO_4^{2-} 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.

$$WO_4^{2-} + H^+ = HWO_4^- \qquad (5)$$
$$HWO_4^- + 2H_2O = [WO(OH)_5]^- \qquad (6)$$
$$6[WO(OH)_5]^- + H^+ = HW_6O_{21}^{5-} + 15H_2O \qquad (7)$$

The condensation process may be represented by the following general equation, which is almost similar to the one proposed by MacInnis and Kim [15]:

$$aH^+ + bWO_4^{2-} = cW_xO_yH_z^{n-} + dH_2O \qquad (8)$$

with the values for a and b as represented in Table 4.

It is quite probable that the highly charged species given in Table 4 may be hydrated; e.g., $W_{12}O_{41}^{10-}$ as $H_{10}W_{12}O_{46}^{10-}$, and $W_{12}O_{39}^{6-}$ as $H_2W_{12}O_{40}^{6-}$ as suggested by Cotton and Wilkinson [6] or $W_{12}O_{41}^{10-}$ as $W_{12}O_{40}(OH)_2^{10-}$ [16] and $W_{12}O_{39}^{6-}$ as $W_{12}O_{38}(OH)_2^{6-}$ as recently reported by Rozantsev and Sazonova [17].

The results of a careful pH and conductometric study on the acid tungstate system provided definite evidence for the formation of para-$W_{12}O_{41}^{10-}$ (via $HW_6O_{21}^{5-}$) and meta-$W_{12}O_{39}^{6-}$ (via $HW_6O_{20}^{3-}$) in the pH ranges 5.7-6.0 and 3.6-4.1, respectively. The observation of MacInnis and Kim [15] about the formation of $W_{12}O_{46}^{20-}$, $W_3O_{11}^{4-}$ and $WO_3.H_2O$, of Meier and Schwarzenbach [18] about $H_5W_4O_{16}^{3-}$, of Simons [19] about $W_2O_7^{2-}$ and of Timofeeva et al. [20] about $W_7O_{24}^{6-}$ could not be confirmed by the study.

Formation of lanthanum tungstates

The above studies show that the addition of acid to Na_2WO_4 solution under suitable condition causes the formation of paratungstate $W_{12}O_{41}^{10-}$ and metatungstate $W_{12}O_{39}^{6-}$ anions. 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 lanthanum nitrate and different alkali tungstates has therefore been studied by means of pH and conductometric titrations. The solution of Na_2WO_4 was prepared in deionized distilled water. The solutions of sodium para- and meta-tungstates were prepared by adding 7 and 9 mol of HNO_3 to 6 mol of Na_2WO_4.
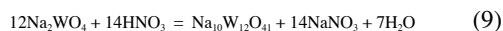
$$12Na_2WO_4 + 14HNO_3 = Na_{10}W_{12}O_{41} + 14NaNO_3 + 7H_2O \qquad (9)$$

Table 4: Summary of isopolytungstate ions represented by equation 8

$H^+:WO_4^{2-}$	a*	b*	pH range	polytungstate	common name	rate
7:6	7	6	5.5-6.0	$HW_6O_{21}^{5-}$	Paratungstate A	Fast
7:6	14	12	5.7-6.0	$W_{12}O_{41}^{10-}$	Paratungstate Z	Slow
9:6	9	6	3.5-4.1	$HW_6O_{20}^{3-}$	Pseudo-metatungstate	Fast
9:6	18	12	3.6-4.1	$W_{12}O_{39}^{6-}$	Metatungstate	Slow

$$12Na_2WO_4 + 18HNO_3 = Na_6W_{12}O_{39} + 18NaNO_3 + 9H_2O \qquad (10)$$
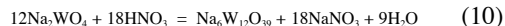
Lanthanum normal tungstate

Figure 2 illustrates the curves of the pH and conductometric titrations performed between the solutions of the normal tungstate and lanthanum nitrate. In direct titrations (curve 1), when $La(NO_3)_3$ solution (pH 4.3) was added to the Na_2WO_4 solution (pH 8.0) a sharp fall in pH was noted with an inflection at molar ratio of $La^{3+}:WO_4^{2-}$ as 2:3 in the vicinity of pH 6.3, corresponding to the stoichiometry for the formation of lanthanum tungstate, $La_2O_3.3WO_3$. This sharp fall in pH occurs because of the presence of unreacted acidic (pH 4.3) $La(NO_3)_3$ in the cell just after completion of precipitation of lanthanum tungstate. In reverse titrations (curve 3), when Na_2WO_4 solution was added to the lanthanum nitrate solution, the pH first changed very slowly, but at the end-point it jumped upwards corresponding to the formation of the same compound in accordance with the following equation:

$$2La(NO_3)_3 + 3Na_2WO_4 = La_2O_3.3WO_3 + 6NaNO_3 \quad (11)$$
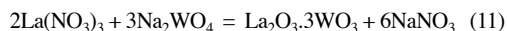
Employing similar concentrations of the reactants, both direct (curve 2) and reverse (curve 3) conductometric titrations between the solutions of $La(NO_3)_3$ and Na_2WO_4 gave well-defined breaks at 2:3 molar ratio of $La^{3+}:WO_4^{2-}$, confirming the stoichiometry for formation of the cerium tungstate $La_2O_3.3WO_3$, as suggested by the pH study.

Lanthanum paratungstate

The solution of sodium paratungstate, $Na_{10}W_{12}O_{41}$, was prepared by addition of nitric acid to Na_2WO_4 in the molar ratio 7:6. Figure 3 illustrates the changes occurring in pH and conductance when $La(NO_3)_3$ solution (pH 4.3) is treated with $Na_{10}W_{12}O_{41}$ solution (pH 5.9). In direct titrations (curve 1) when $La(NO_3)_3$ solution was added from microburette to $Na_{10}W_{12}O_{41}$ solution, a gradual change in pH was observed till at the stoichiometric end-point (the stage at which the reaction ends if simple double decomposition takes place), a sharp fall in pH was noted with the inflection corresponding to the molar ratio of $La^{3+}:W_{12}O_{41}^{10-}$ as 10:3, suggesting the formation of lanthanum paratungstate $5La_2O_3.36WO_3$ in the vicinity of pH 5.0. In case of reverse titrations (curve 3) the first addition of $Na_{10}W_{12}O_{41}$ solution to $La(NO_3)_3$ caused a slight decrease in pH till about half the volume of titrant required for the precipitation of lanthanum paratungstate was added. This initial lowering in pH value was due to the presence of hydrolyzed acid from the lanthanum salt. Later on, with the progress of the reaction, pH began to rise and a pronounced upward jump was obtained at the stoichiometric point corresponding to the formation of lanthanum paratungstate. Employing similar concentrations of the reactants a series of direct (curve 2) and reverse (curve 4) conductometric titrations were performed between the solutions of $La(NO_3)_3$ and $Na_{10}W_{12}O_{41}$. The titration curves provide well-defined breaks at a point where the molar ratio of $La^{3+}:W_{12}O_{41}^{10-}$ is 10:3 (Table 2), thus confirming formation of the paratungstate as suggested by the pH study. The
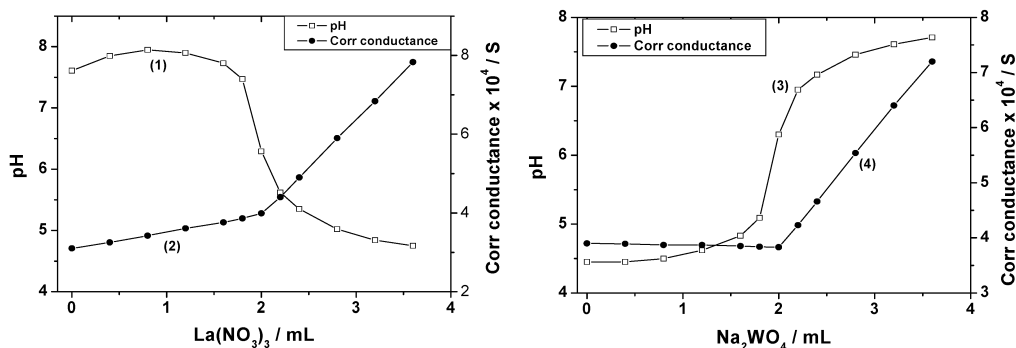

Figure 2. Normal-tungstate direct (1 and 2) and reverse (3 and 4) titrations. 1, 2: 25 mL of M/250 Na_2WO_4 titrated with M/30 $La(NO_3)_3$. 3, 4: 25 mL of M/375 $La(NO_3)_3$ titrated with M/20 Na_2WO_4
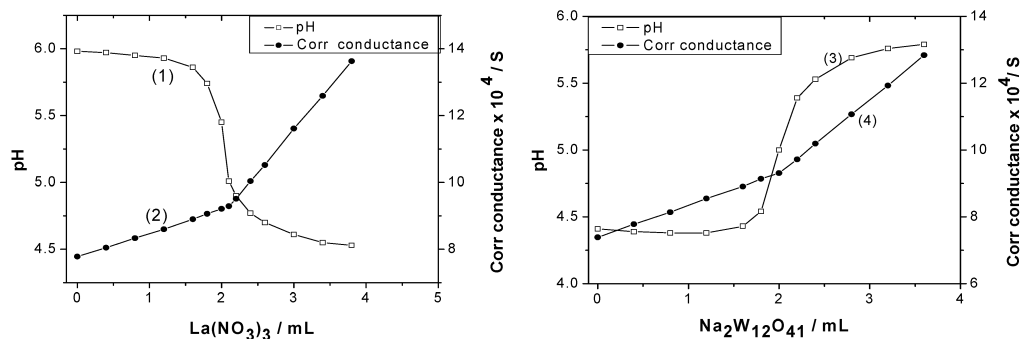
Figure 3. Para-tungstate direct (1 and 2) and reverse (3 and 4) titrations. 1, 2: 25 mL of M/1200 $Na_{10}W_{12}O_{41}$ titrated with M/30 $La(NO_3)_3$. 3, 4: 25 mL of M/900 $La(NO_3)_3$ titrated with M/240 $Na_{10}W_{12}O_{41}$

formation of the paratungstate can be represented as follows:

$$10La(NO_3)_3 + 3Na_{10}W_{12}O_{41} = (5La_2O_3.36WO_3) + 30NaNO_3 \quad (12)$$

Lanthanum metatungstate

Sodium metatungstate, $Na_6W_{12}O_{39}$, solution was prepared by addition of nitric acid to Na_2WO_4 in the molar ratio 3H:2W. Using different concentrations of the solutions of $La(NO_3)_3$ and $Na_6W_{12}O_{39}$, a series of direct and reverse conductometric titrations was carried out. The nature of these titration curves (Figure 4) is similar to those of the paratungstate. The curves provide breaks at molar ratio 2:1 of $La^{3+}:W_{12}O_{39}{}^{6-}$ corresponding to the stoichiometry for formation of lanthanum
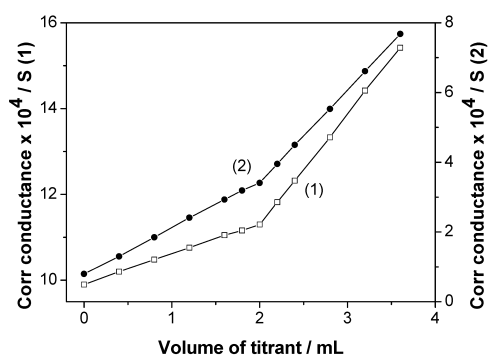

Figure 4. Meta-tungstate direct (1) and reverse (2) titrations. 1: 25 mL of M/750 $Na_6W_{12}O_{39}$ titrated with M/30 $La(NO_3)_3$. 2: 25 mL of M/1500 $La(NO_3)_3$ titrated with M/240 $Na_6W_{12}O_{39}$

metatungstate $La_2O_3.12WO_3$ in the vicinity of pH 4.2, according to the reaction:

$$2La(NO_3)_3 + Na_6W_{12}O_{39} = La_2O_3.12WO_3 + 6NaNO_3 \quad (13)$$

The pH titrations of this system did not provide reliable results for the formation of lanthanum metatungstate, which may be ascribed to very close pH values of the reactants involved.

It was noted that after each addition of the titrant, it takes a little time for the pH and conductance values to become steady. A thorough stirring in neighborhood of the equivalence point has a favorable effect. The presence of ethanol (20%) improves position of the end-point and increases magnitude of the jump in pH curves, as it decreases solubility of the precipitates formed and minimizes hydrolysis and adsorption. For this reason all the titrations were performed in presence of 20% ethanol.

Conclusions

The results of the quantitative elemental analysis of the precipitates were used to calculate the proportions of the elements present in the compounds. From these proportions, the composition of the compounds was established which was found to be the same as obtained by the electrometric techniques (see Table 3).

The present electrometric and analytical investigations confirm the formation and precipitation of three lanthanum tungstates, viz. *normal*-$La_2O_3.3WO_3$, *para*-$5La_2O_3.36WO_3$ and

meta-$La_2O_3.12WO_3$ in the vicinity of pH 6.3, 5.0 and 4.2, respectively. The pH values reported correspond to the 20% ethanol medium. As structure of these compounds is not known they are represented as double oxides, the manner which is usually adopted for such compounds [21].

S. Prasad, R. A.C. Santana, A. R.N. Campos , V. D. Leite. Estudos eletrométricos sobre o sistema ácido-tungstato e a formação de tungstatos de metais pesados.

Resumo: A estequiometria de poliânions formados pela ação do ácido nítrico sobre a solução de tungstato de sódio (≤ 0,01M) foi estudada por meio de técnicas eletrométricas envolvendo titulações potenciométricas e condutométricas. As inflexões e degraus bem definidas nas curvas de titulações forneceram evidências convincentes pela existência de poliânions, *para*-$W_{12}O_{41}^{10-}$ e *meta*-$W_{12}O_{39}^{6-}$ nas faixas do pH 5,7-6,0 e 3,6-4,1; correspondendo a razão H^+:WO_4^{2-} como 7:6 e 9:6, respectivamente. A interação entre soluções de nitrato de lantânio e tungstato de sódio a específicos níveis de pH 8,0; 5,9 e 4,0 também foi estudada por titulações potenciométricas e condutométricas, nos meios aquoso e etanólico, com cada reagente usado alternadamente como titulante. Os experimentos eletrométricos forneceram evidências incontestáveis sobre a formação de tungstatos *normal*-$La_2O_3.3WO_3$, *para*-$5La_2O_3.36WO_3$ e *meta*-$La_2O_3.12WO_3$ nas proximidades de valores de pH 6,3; 5,0 e 4,2; respectivamente. Investigações analíticas sobre os precipitados formados confirmam os resultados do estudo eletrométrico.

Palavras-chave: isopolitungstatos; lantânio; eletrometria.

References

[1] M. T. Pope, B. W. Dale, Q. Revs. 22 (1968) 527.
[2] D. L. Kepert, in: A. F. Trotman-Dickenson, (Ex. Ed.), Comprehensive Inorganic Chemistry, Vol. 4, Pergamon Press, Oxford, 1973, pp. (a) 641, (b) 642, (c) 646.
[3] H. R. Craig, S. Y. Tynee, Inorg. Chem. 4 (1965) 997.
[4] M., Grayson, (Ex. Ed.), Kirk-Othmer Encyclopedia of Chemical Technology. Vol.23, Wiley-Interscience, New York, 3rd edn., 1993, p.431.
[5] D. L. Kepert, in: F. A. Cotton, (Ed.), Progress in Inorganic Chemistry, Vol. 4, Interscience Publishers, New York, 1962, p. 199.
[6] F. A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, Interscience Publishers, New York, 3rd edn., 1972, p.952.
[7] S. Prasad, Can. J. Chem. 59 (1981) 563.
[8] S. Prasad, S. B. Gonçalves, J. B. Brito, Catal. Today, 57 (2000) 343.
[9] S. Prasad, T. L. M. Guimarães, J. Braz. Chem. Soc. 9 (1998) 253.

[10] A. I. Vogel, A Textbook of Quantitative Inorganic Analysis, Longmans, London, 3rd. Edn.,1968, p. (a) 567, (b) 541.
[11] K. F. Jahr, J. Fuchs, Angew. Chem. Intern. Ed. 5 (1966) 689.
[12] J. Aveston, Inorg. Chem. 3 (1964) 981.
[13] O. Glemser, W. Holtje, Z. Naturforsch. 20b (1965) 398.
[14] O. Glemser, W. Holznagel, W. Holtje, E. Schwarzmann, Z. Naturforsch. 20b (1965) 725.
[15] M. B. MacInnis, T. K. Kim, J. Chem. Tech. Biotechnol. 29 (1979) 225.
[16] M. del Arco, D. Carriazo, S. Gutierrez, C. Martin, V. Rives, Inorg. Chem. 43 (2004) 375.
[17] G. M. Rozantsev, O. I. Sazonova, Russ. J. Coord. Chem. 31 (2005) 552.
[18] J. Meier, G. Schwarzenbach, J. Inorg. Nucl. Chem. 8 (1958) 302.
[19] E. L. Simons, Inorg. Chem. 3 (1964) 1079.
[20] E. V. Timofeeva, G. A. Tsirlina, O. A. Petrii, Russ. J. Electrochem. 39 (2003) 716.
[21] A. Standen, (Ex. Ed.), Kirk-Othmer Encyclopedia of Chemical Technology, Vol.13, IntersciencePublishers, New York, 2nd Edn., 1967, p.782.