Article

Electroanalytical Investigations on Formation of Thallium(I) Molybdates as a Function of pH

Shiva Prasad[*,a], André L.F. Brito[a], Valderí D. Leite[b] and Antônio G. Souza[c]

[a]*Departamento de Engenharia Química, Centro de Ciências e Tecnologia, Universidade Federal da Paraíba, CP 10108, 58109-970 Campina Grande - PB, Brazil*

[b]*Departamento de Química, CCT, Universidade Estadual da Paraíba, 58100-000 Campina Grande - PB, Brazil*

[c]*Departamento de Química, CCEN, Universidade Federal da Paraíba, 58059-900 João Pessoa - PB, Brazil*

A formação de molibdatos de tálio obtidos a partir de interação de nitrato de tálio(I) e molibdato de sódio nos valores específicos do pH 7,6; 5,5 e 4,1 foi estudada através de técnicas eletrométricas envolvendo titulações potenciométricas e condutométricas, em meios aquoso e alcoólico, com cada reagente usado alternadamente como titulante. As inflexões e degraus bem definidos nas curvas de titulação fornecem evidências incontestáveis sobre a formação de molibdatos *normal*-$Tl_2O.MoO_3$, *para*-$3Tl_2O.7MoO_3$ e o*cta*-$2Tl_2O.8MoO_3$ de tálio(I) nas vizinhanças de pH 6,8; 5,9 e 5,2 respectivamente. Estudos analíticos também foram realizados sobre os precipitados de molibdatos de tálio(I) confirmando os resultados obtidos pelas técnicas eletrométricas.

The formation of thallium(I) molybdates obtained by interaction of thallium(I) nitrate and sodium molybdate at specific pH levels 7.6, 5.5 and 4.1 has been studied by electrometric techniques involving potentiometric and conductometric titrations, in aqueous and alcoholic media using each reagent as titrant. Well defined breaks and inflections in the titration curves provide cogent evidence for formation of thallium *normal*-$Tl_2O.MoO_3$, *para*-$3Tl_2O.7MoO_3$ and *octa*-$2Tl_2O.8MoO_3$ molybdates in the vicinity of pH 6.8, 5.9 and 5.2, respectively. Analytical investigations of the precipitates of thallium(I) molybdates have also been carried out, which substantiate the results of the electrometric study.

Keywords: molybdates, thallium(I) molybdates, electrometry

Introduction

The chemistry of molybdenum is very prominent in both biological and industrial systems.[1,2] Recent studies have shown that certain molybdates have antiviral, including anti-AIDS, and antitumor activity.[3] Although a large number of studies have been done in the field of molybdate chemistry, the chemical state of isopolymolybdates, obtained on acidification of a molybdate solution, is not well understood because of the complexity in polymerization. Jander *et al*. claimed existence of $Mo_3O_{11}^{4-}$, $HMo_3O_{11}^{3-}$, $HMo_6O_{21}^{5-}$, $H_2Mo_6O_{21}^{4-}$, $H_3Mo_6O_{21}^{3-}$, $H_7Mo_{12}O_{41}^{3-}$, $H_7Mo_{24}O_{78}^{5-}$ and $H_9Mo_{24}O_{78}^{3-}$ from diffusion and optical experiments.[4] Bye claimed the existence of $Mo_7O_{24}^{6-}$, $Mo_6O_{20}^{4-}$, $Mo_4O_{13}^{2-}$ and $HMo_6O_{20}^{3-}$ by cryoscopic study.[5] In 1959, Sasaki *et al*. deduced from potentiometry that the main complex formed is $Mo_7O_{24}^{6-}$.[6] Subsequently mathematical analysis was applied to potentiometric equilibrium curves, and Sasaki *et al*. claimed the existence of $Mo_7O_{24}^{6-}$, $HMo_7O_{24}^{5-}$, $H_2Mo_7O_{24}^{4-}$ and $H_3Mo_7O_{24}^{3-}$ up to a value of Z (average number of H^+ being consumed by MoO_4^{2-}) of around 1.4.[7,8] Aveston *et al*.[9] by centrifuge data could only tell that in the range studied, the species probably contain more than 6 and less than 9 Mo atoms. Sasaki *et al*. proposed the presence of large isopolymolybdate anions of the order of 20 Mo in the solution of Z >1.5.[7] Numerous species such as $HMoO_4^-$, H_2MoO_4, $Mo_2O_7^{2-}$, $HMo_3O_{11}^{3-}$, $Mo_6O_{19}^{2-}$, $Mo_7O_{24}^{6-}$, $HMoO_{24}^{5-}$, $H_2Mo_7O_{24}^{4-}$, $Mo_8O_{26}^{4-}$, $HMo_8O_{26}^{3-}$, $Mo_{12}O_{37}^{2-}$, $H_7Mo_{24}O_{78}^{5-}$, $Mo_{36}O_{112}^{8-}$ etc. have been reported in many recent publications.[10-12]

On account of the complexity of the relation of equilibrium between the polyanions or due to the experimental difficulty in early works, the conclusions of

* e-mail: prasad@deq.ufpb.br

earlier workers seem to be overstrained and hence it was considered worthwhile to make a careful and precise study on the formation of molybdates as a function of pH by electrometric techniques, which have provided more conclusive evidence on the condensation process of vanadate,[13] antimonite[14] thiotungstate[15] and tungstate anions.[16] In an earlier publication[17] Prasad and Gonçalves have reported the effect of pH change on composition of thorium molybdate. The results on formation of thallium molybdates as a function of pH are presented here.

Experimental

All the reagents including $TlNO_3$, $Na_2MoO_4.2H_2O$, HNO_3 and ethanol of extra-pure grade were used, and their solutions were prepared with deionized distilled water. Concentration of sodium molybdate solutions was further verified by determining molybdenum with oxime as $MoO_2(C_9H_6ON)_2$.[18] The variations of pH of Na_2MoO_4 solutions were obtained by progressive additions of determined quantities of nitric acid. pH measurements were carried out using a Metrohm Herisau pH-meter and Schott Gerate glass combined electrode. Stoichiometric points were obtained from the sharp inflections in the titration curves. The conductometric measurements were performed on a Metrohm conductometer. Conductivity values after correcting for dilution effect were plotted as a function of mL of titrant solution added and the end-points were judged from the breaks in titration curves. For each experiment, 25 mL of solution were taken in the cell and thermostated at $25\pm0.1^{\circ}C$. The same concentrations of reactants were employed in both techniques for the sake of comparison of results. The potentiometric and conductometric titration curves are plotted together in the same figure for similar reasons and also for the sake of brevity. The titrations were performed both by direct and reverse methods at three different concentrations. The electrometric titration results on formation of different thallium molybdates are summarized in Table 1.

Analytical investigations on precipitates were also carried out with a view to substantiate the electrometric results. Different molybdates of thallium(I) were prepared by mixing stoichiometric amounts of thallium nitrate solution with the respective sodium molybdate solutions at specific pH levels 7.6, 5.5 and 4.1. The precipitates obtained were washed several times with aqueous 30% (v/v) ethanolic solution and dried in a vacuum dessicator for 36 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 molybdenum[18] with dithiol and for thallium[18] with thionalide. The results are summarized in Table 2.

Table 1. Summary of results of electrometric study on formation of thallium molybdates. Volume of titre solution taken in the cell = 25 mL

Concentration of solutions (x 10^3 mol L^{-1})		Equivalence points (mL) Calcd.	Observed from pH	Conductance	Formula Supported
$TlNO_3$	Na_2MoO_4	Direct titrations. Figure 2, curves 1 and 2			
100.00	4.00	2.00	2.00	2.00	$Tl_2O.MoO_3$
50.00	2.50	2.50	2.48	2.50	
33.33	1.43	2.14	2.14	2.12	
		Reverse titrations. Figure 2, curves 3 and 4			
16.67	100.00	2.08	2.10	2.10	$Tl_2O.MoO_3$
10.00	50.00	2.50	2.50	2.52	
5.71	33.33	2.15	2.15	2.15	
$TlNO_3$	$Na_6Mo_7O_{24}$	Direct titrations. Figure 3, curves 1 and 2			
100.00	1.33	2.00	2.00	2.00	$3Tl_2O.7MoO_3$
50.00	0.71	2.14	2.15	2.15	
33.33	0.50	2.25	2.25	2.20	
		Reverse titrations. Figure 3, curves 3 and 4			
12.50	25.00	2.08	2.10	2.10	$3Tl_2O.7MoO_3$
6.67	12.50	2.22	2.20	2.25	
4.00	8.33	2.00	2.00	2.05	
$TlNO_3$	$Na_4Mo_8O_{26}$	Direct titrations. Figigure 4, curves 1 and 2			
100.00	2.00	2.00	2.00	2.00	$2Tl_2O.8MoO_3$
50.00	1.11	2.22	2.20	2.20	
33.33	0.71	2.14	2.12	2.15	
		Reverse titrations. Figure 4, curves 3 and 4			
16.67	50.00	2.08	2.10	2.10	$2Tl_2O.8MoO_3$
7.41	20.00	2.33	2.35	2..35	
4.00	10.00	2.50	2.52	2.50	

Table 2. Summary of analytical results of the precipitates of thallium molybdates

Proposed formula of the compound	Mode of synthesis	Analysis %: Found (calculated)	
		Tl	Mo
	Analysis of the *normal*-molybdate precipitates.		
$Tl_2O.MoO_3$	Direct[*]	71.79(71.88)	16.83(16.87)
	Reverse[*]	71.95	16.90
	Analysis of the *para*-molybdate precipitates.		
$3Tl_2O.7MoO_3$	Direct	53.66(53.74)	29.49(29.43)
	Reverse	53.81	29.39
	Analysis of the *octa*-molybdate precipitates.		
$2Tl_2O.8MoO_3$	Direct	40.78(40.85)	38.41(38.36)
	Reverse	40.91	38.32

[*] Direct - Thallium nitrate solution added to sodium molybdate solution. Reserve - Sodium molybdate solution added to mercuric nitrate solution.

Results and Discussion

When nitric acid is gradually added to Na_2MoO_4 solution, it changes to *para*-molybdate $Mo_7O_{24}^{6-}$ and *octa*-molybdate $Mo_8O_{26}^{4-}$ polyanions around pH 5.5 and 4.1, respectively. Figure 1 illustrates the curves of pH and conductometric titrations of Na_2MoO_4 solution with nitric acid. The titration curves of both the techniques show two inflections at 7Mo:8H and 8Mo:12H corresponding to the formation of the polyanions *para*-$Mo_7O_{24}^{6-}$ and *octa*-$Mo_8O_{26}^{4-}$, respectively (see Figure 1, points A, B and A', B'). The results are similar to those obtained for the interaction of hydrochloric acid with sodium molybdate[17] and are also in conformity with the results of the temperature-jump studies by Honing and Kustin[19] and the Raman spectra studies by Ozeki *et al.*[20] The stepwise condensation of MoO_4^{2-} by gradual addition of nitric acid can be represented by the following equations:[17]

$$8H^+ + 7MoO_4^{2-} = Mo_7O_{24}^{6-} + 4H_2O \qquad (1)$$

$$12H^+ + 8MoO_4^{2-} = Mo_8O_{26}^{4-} + 6H_2O \qquad (2)$$
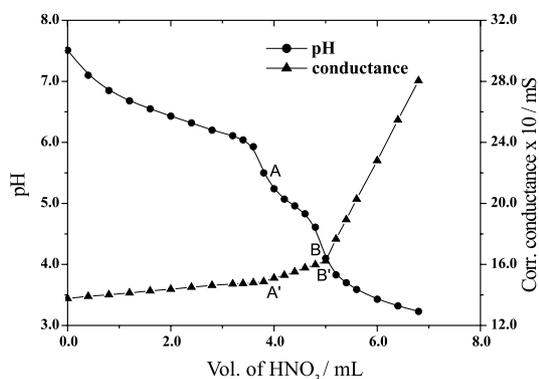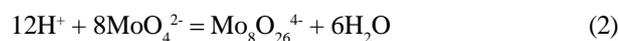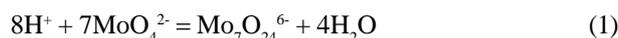
Figure 1. Potentiometric (curve 1) and conductometric (curve 2) titrations of acid-molybdate system. 25 mL of 1.33×10^{-2} mol L^{-1} Na_2MoO_4 titrated with 1.00×10^{-1} mol L^{-1} HNO_3 (stoichiometric points are A, B and A', B').

Thallium normal-molybdate

Using different concentrations of Na_2MoO_4 (pH 7.6) and thallium(I) nitrate (pH 6.1) solutions, a series of potentiometric titrations was carried out. In direct titrations (Figure 2, curve 1), when Na_2MoO_4 solution was used as titrate, a gradual decrease in pH value was observed till at the stoichiometric end-point (the stage at which the
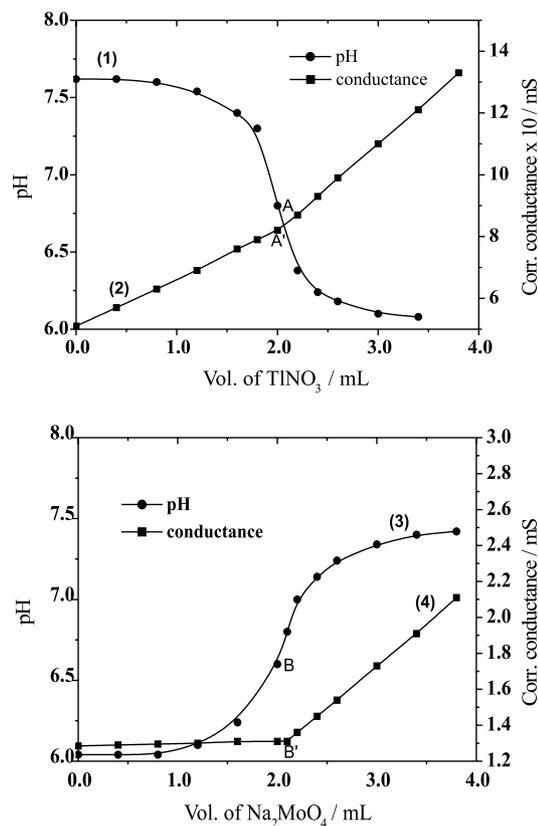

Figure 2. *Normal*-molybdate direct (1 and 2) and reverse (3 and 4) titrations. 1, 2: 25 mL of 4.00×10^{-3} mol L^{-1} Na_2MoO_4 titrated with 1.00×10^{-1} mol L^{-1} $TlNO_3$. 3, 4: 25 mL of 1.67×10^{-2} mol L^{-1} $TlNO_3$ titrated with 1.00×10^{-1} mol L^{-1} Na_2MoO_4 (stoichiometric points: A, B and A',B').

reaction ends if simple double decomposition takes place) a sharp fall in pH was observed (see point A in Figure 2) when the molar ratio of $Tl^+:MoO_4^{2-}$ is 2:1 corresponding to the formation of thallium *normal*-molybdate, $Tl_2O.MoO_3$, in the neighborhood of pH 6.8. In case of inverse titrations (Figure 2, curve 3), the pH at first gradually increases till in the vicinity of stoichiometric end-point when the last traces of thallium ions have been removed by precipitation, further addition of alkali molybdate causes a marked upward jump in pH and the inflection corresponds to the molar ratio for the formation of $Tl_2O.MoO_3$ according to the reaction:

$$2TlNO_3 + Na_2MoO_4 = Tl_2O.MoO_3 + 2NaNO_3 \qquad (3)$$

Employing similar concentrations of the reactants, direct (Figure 2, curve 2) and reverse (Figure 2, curve 4) conductometric titrations between the solutions of thallium nitrate and sodium molybdate gave well-defined breaks at 2:1 molar ratio of $Tl^+:MoO_4^{2-}$ confirming the formation of the same compound $Tl_2O.MoO_3$ as indicated by the pH study.

Thallium para-molybdate

Sodium *para*-molybdate solution was prepared by addition of nitric acid to Na_2MoO_4 in molar ratio 8H:7Mo. Using different concentrations of sodium *para*-molybdate (pH 5.5) and thallium(I) nitrate (pH 6.1) solutions, a series of potentiometric titrations was carried out. In direct titrations (Figure 3, curve 1), when the *para*-molybdate solution was used as titrate, a gradual change in pH value was observed till at the stoichiometric end-point a sharp upward jump in pH was observed when the molar ratio of $Tl^+:Mo_7O_{24}^{6-}$ is 6:1 corresponding to the formation of thallium *para*-molybdate, $3Tl_2O.7MoO_3$, in the neighborhood of pH 5.9. In case of inverse titrations (Figure 3, curve 3), when thallium nitrate solution was used as titrate, a gradual decrease in pH was observed till at the stoichiometric point a downward jump in pH was noted and the inflection corresponds to the molar ratio for formation of $3Tl_2O.7MoO_3$. The formation of the *para*-molybdate can be represented as follows:

$$6TlNO_3 + Na_6Mo_7O_{24} = 3Tl_2O.7MoO_3 + 6NaNO_3 \qquad (4)$$
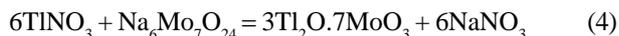
Employing similar concentrations of the reactants a series of direct (Figure 3, curve 2) and reverse (Figure 3, curve 4) conductometric titrations was performed between the solutions $TlNO_3$ and $Na_6Mo_7O_{24}$. The titration curves provide well-defined breaks at a point where the molar
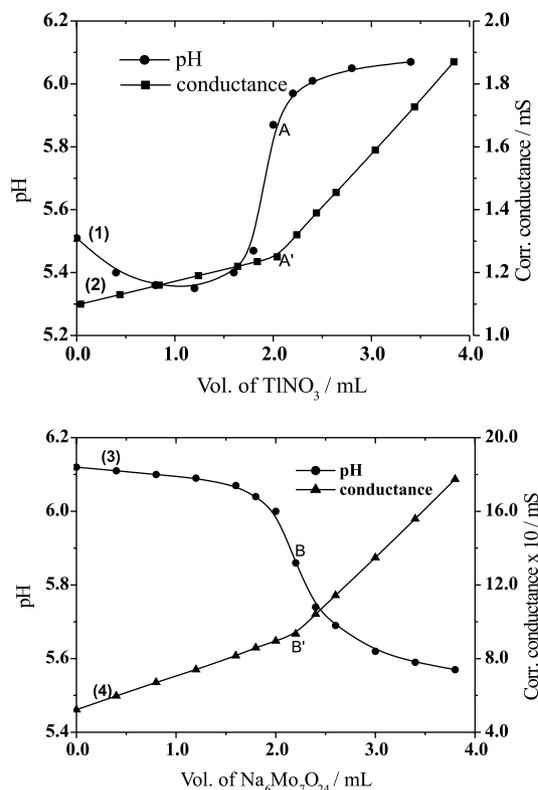

Figure 3. *Para*-molybdate direct (1 and 2) and reverse (3 and 4) titrations. 1, 2: 25 mL of 1.33×10^{-3} mol.L^{-1} $Na_6Mo_7O_{24}$ titrated with 1.00×10^{-1} mol L^{-1} $TlNO_3$. 3, 4: 25 mL of 6.67×10^{-3} mol L^{-1} $TlNO_3$ titrated with 1.25×10^{-2} mol L^{-1} $Na_6Mo_7O_{24}$ (stoichiometric points: A, B and A',B').

ratio of $Tl^+:Mo_7O_{24}^{6-}$ is 6:1 (Table 1), thus confirming formation of *para*-molybdate, as suggested by the pH study.

Thallium octa-molybdate

Sodium *octa*-molybdate solution was prepared by addition of nitric acid to Na_2MoO_4 in molar ratio 3H:2Mo. Using different concentrations of the solutions of $TlNO_3$ and $Na_4Mo_8O_{26}$, a series of potentiometric and conductometric titrations was carried out. The slope and nature of these titration curves (Figure 4) are similar to those of the *para*-molybdate. The curves provide well-defined inflections at molar ratio 4:1 of $Tl^+:Mo_8O_{26}^{4-}$ (see points A, B and A', B' in Figure 4) corresponding to stoichiometry for formation of thallium *octa*-molybdate $2Tl_2O.8MoO_3$ in the vicinity of pH 5.2, according to the reaction:

$$4TlNO_3 + Na_4Mo_8O_{26} \rightarrow 2Tl_2O.8MoO_3 + 4NaNO_3 \qquad (5)$$

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 the neighborhood
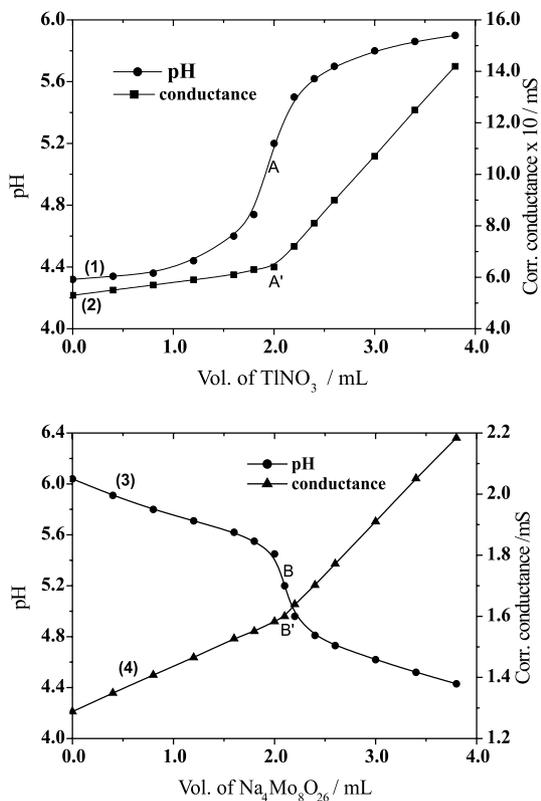
Figure 4. *Octa*-molybdate direct (1 and 2) and reverse (3 and 4) titrations. 1, 2: 25 mL of 2.00 x 10⁻³ mol L⁻¹ Na₄Mo₈O₂₆ titrated with 1.00 x 10⁻¹ mol L⁻¹ TlNO₃, 3, 4: 25 mL of 1.67 x 10⁻² mol L⁻¹ TlNO₃ titrated with 2.00 x 10⁻² mol L⁻¹ Na₄Mo₈O₂₆ (stoichiometric points: A, B and A',B').

of the equivalence point has a favorable effect. The presence of ethanol (30%) improves the position of end-point and increase the magnitude of the jump in pH curves as it decreases the solubility of the precipitates formed and minimizes hydrolysis and adsorption. The results obtained were precise. The relative standard deviation of the results reported in Table 1 was <1%.

Quantitative analysis of precipitates

The results of the quantitative elemental analyses 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 2).

The present electroanalytical investigations and the quantitative analysis of the precipitates confirm the formation and precipitation of three thallous molybdates *viz. normal*-Tl₂O.MoO₃, *para*-3Tl₂O.7MoO₃ and *octa*-2Tl₂O.8MoO₃ in the vicinity of pH 6.8, 5.9 and 5.2, respectively.

As the structure of these compounds are not known they are represented as double oxides, the manner which is usually adopted for such compounds.[21,22]

Acknowledgement

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