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Short Report

Potentiometric and Conductometric Studies on the Formation of Thorium Molybdates as a Function of pH

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A formação de molibdatos de tório obtidos pela interação de nitrato de tório com molibdato de sódio a níveis específicos de pH 7,8; 5,5 e 4,1 foi estudada por técnicas eletrométricas envolvendo titulações condutométricas e pH-métricas. As inflexões e degraus bem definidos nas curvas de titulações fornecem evidências incontestáveis sobre a formação de molibdatos *normal*-$ThO_2.2MoO_3$ e *para*-$3ThO_2.14MoO_3$ de tório nas vizinhanças dos pH's 5,3 e 4,4, respectivamente. As investigações analíticas sobre os precipitados de molibdatos de tório também foram realizadas, as quais confirmaram os resultados eletrométricos.

The formation of thorium molybdates obtained by interaction of thorium nitrate and sodium molybdate at specific pH levels 7.8, 5.5 and 4.1 have been studied by electrometric techniques involving pH and conductometric titrations. The well-defined inflections and breaks in titration curves provide cogent evidence for the formation of thorium *normal*-$ThO_2.2MoO_3$ and *para*-$3ThO_2.14MoO_3$ molybdates in the vicinity of pH 5.3 and 4.4, respectively. Analytical investigations on the precipitates of thorium molybdates have also been carried out, which support the electrometric results.

Keywords: molybdates, thorium 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. Numerous species such as $HMoO_4^-$, H_2MoO_4, $Mo_2O_7^{7-}$, $Mo_3O_{11}^{4-}$, $HMo_3O_{11}^{3-}$, $Mo_6O_{19}^{2-}$, $HMo_6O_{21}^{5-}$, $H_2Mo_6O_{21}^{4-}$, $H_3Mo_6O_{21}^{3-}$, $Mo_7O_{24}^{6-}$, $HMo_7O_{24}^{5-}$, $H_2Mo_7O_{24}^{4-}$, $H_3Mo_7O_{24}^{3-}$, $Mo_8O_{26}^{4-}$, $HMo_8O_{26}^{3-}$, $Mo_{12}O_{37}^{2-}$, $H_7Mo_{12}O_{41}^{3-}$, $H_7Mo_{24}O_{78}^{5-}$, $H_9Mo_{24}O_{78}^{3-}$, $Mo_{36}O_{112}^{8-}$, etc. have been proposed[4-11].

In earlier publication[12] one of us reported the effect of pH change on a solution of sodium molybdate and composition of mercuric molybdates. In view of the interesting results obtained, it was considered worthwhile to investigate the composition of thorium molybdates obtained by the action of Th^{4+} on various molybdate species at different pH levels by means of electrometric techniques, which have provided more conclusive evidence on condensation processes of vanadate, antimonate, thiotungstate and tungstate anions[13]. There is, however, no reference available in the literature on the formation of thorium molybdates as a function of pH.

Experimental

$Th(NO_3)_4$, $Na_2MoO_4.2H_2O$, oxine and different acids of extra-pure grade were used and their solutions were prepared in deionized distilled water. Concentration of sodium molybdate solutions was further verified by determining molybdenum with oxine as $MoO_2(C_9H_6ON)_2$[14a].

The pH measurements were carried out on a Metrohm Herisau (Switzerland) pH-meter using Scott Gerate glass combination electrode. Conductivity values were recorded by employing a Metrohm conductometer. 25 mL of the titre solution was placed in the cell each time and thermostated at 25.0±0.1ºC. Using different concentrations of the reactants,

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a series of pH and conductometric titrations was performed both by direct and reverse methods, *i.e.* when thorium nitrate solution from the microburette was added to the alkali molybdate solution and vice-versa. The observed pH changes were plotted as a function of volume of the titrant added. The inflections obtained by the curves were confirmed by the pronounced maxima in dpH/dV graphs. The breaks in the conductometric titrations are located by plotting corrected conductance as a function of volume of titrant added. The same concentrations of reactants were employed in the two techniques for the sake of comparison of results. The pH and conductometric titration curves are plotted together in the same figure for similar reasons and also for the sake of brevity. The electrometric titration results are summarized in Table 1.

The precipitates obtained at the end-points were also analyzed to substantiate the electrometric results. The different thorium molybdates were prepared by mixing stoichiometric amounts of thorium nitrate solution with the respective sodium molybdate solutions. The precipitates obtained were washed several times with 20% ethanolic solution and dried in a vacuum desiccator for 40 h. An amount exactly known (*ca.* 2.0 g) of each of the above precipitates was dissolved in minimum quantity of hydrochloric acid and then analyzed quantitatively for molybdenum by oxine[14a] and thorium as oxalate[14b]. The results of analysis are given in Table 2.

Results and Discussion

When hydrochloric acid is gradually added to Na_2MoO_4, 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[12]. The formation of the polyanions may be represented as follows:

$$8H^+ + 7MoO_4^{2-} = Mo_7O_{24}^{6-} + 4H_2O$$
$$12H^+ + 8MoO_4^{2-} = Mo_8O_{26}^{4-} + 6H_2O$$

Normal-molybdate titrations

Using different concentrations of Na_2MoO_4 (pH 7.8) and thorium nitrate (pH 2.9) solutions, a series of pH titrations was carried out. In direct titrations (Figure 1, curve 1), when Na_2MoO_4 solution was used as titre, a gradual decrease in pH value was observed till at the stoichiometric end-point (the stage at which the reaction ends if simple double decomposition takes place), a sharp downward jump in pH was observed when the molar ratio of Th^{4+}:MoO_4^{2-} is 1:2, corresponding to the formation of white colored precipitate of thorium normal-molybdate, $ThO_2.2MoO_3$, in the neighborhood of pH 5.3. In case of inverse titrations (Figure 1, curve 3) the pH at first gradually changes till in the vicinity of the stoichiometric end-point, when the last traces of thorium 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 $ThO_2.2MoO_3$ according to the reaction:

$$Th(NO_3)_4 + 2Na_2MoO_4 = ThO_2.2MoO_3 + 4NaNO_3$$

Employing similar concentrations of the reactants, direct (Figure 1, curve 2) and reverse (Figure 1, curve 4) conductometric titrations between the solutions of thorium

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

Solutions concentrations		Equivalence points (mL)			Formula supported
$\times 10^3$ mol L^{-1}		Calcd.	Observed from pH	Observed from Cond.	
$Th(NO_3)_4$	Na_2MoO_4	Direct titrations. Fig. 1, curves 1 and 2			
50.00	10.00	2.50	2.50	2.50	$ThO_2.2MoO_3$
25.00	4.00	2.00	2.00	2.00	
12.50	2.22	2.22	2.20	2.20	
		Reverse titrations. Fig. 1, curves 3 and 4			
4.00	100.00	2.00	2.00	2.00	$ThO_2.2MoO_3$
2.22	50.00	2.22	2.25	2.20	
1.25	25.00	2.50	2.55	2.55	
$Th(NO_3)_4$	$Na_6Mo_7O_{24}$	Direct titrations. Fig. 2, curves 1 and 2			
25.00	1.33	2.00	2.00	2.00	$3ThO_2 14MoO_3$
14.29	0.80	2.10	2.10	2.10	
10.00	0.57	2.14	2.15	2.15	
		Reverse titrations. Fig. 2, curves 3 and 4			
1.67	12.50	2.22	2.25	2.25	$3ThO_2.14MoO_3$
1.00	6.67	2.50	2.50	2.55	
0.50	4.00	2.08	2.10	2.10	

Table 2. Summary of analytical results of the precipitates

Proposed formula of the compound	Mode of synthesis	Analysis % Found (Calculated) Th	Mo
	Analysis of the normal molybdate precipitates		
$ThO_2.2MoO_3$	Direct*	41.98(42.04)	34.82(34.77)
	Reverse*	42.07	34.74
	Analysis of the paramolybdate precipitates		
$3ThO_2.14MoO_3$	Direct	24.75(24.80)	47.91(47.85)
	Reverse	24.84	47.80

*Direct – Thorium nitrate solution added to sodium molybdate solution. Reverse – Sodium Molybdate solution added to thorium nitrate solution.

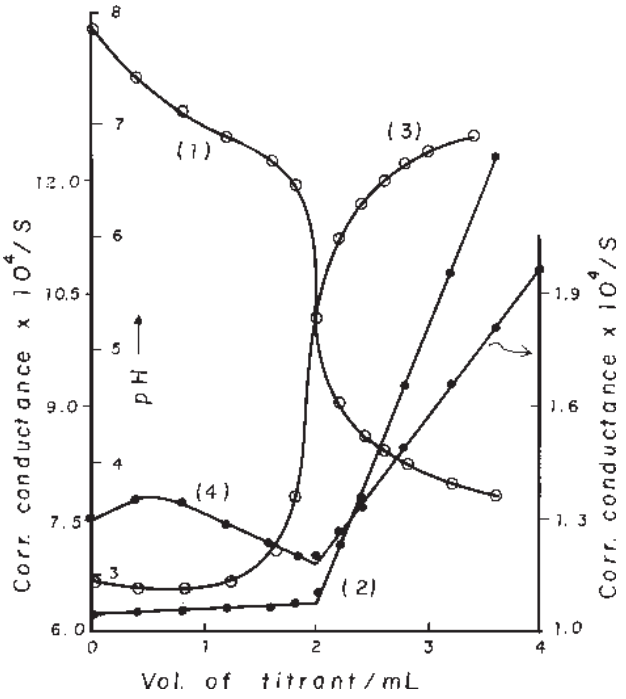

Figure 1. Normal-molybdate titrations. (1 and 2) M/40 $Th(NO_3)_4$ added to 25 mL of M/250 Na_2MoO_4. (3 and 4) M/10 Na_2MoO_4 added to 25 mL of M/250 $Th(NO_3)_4$.

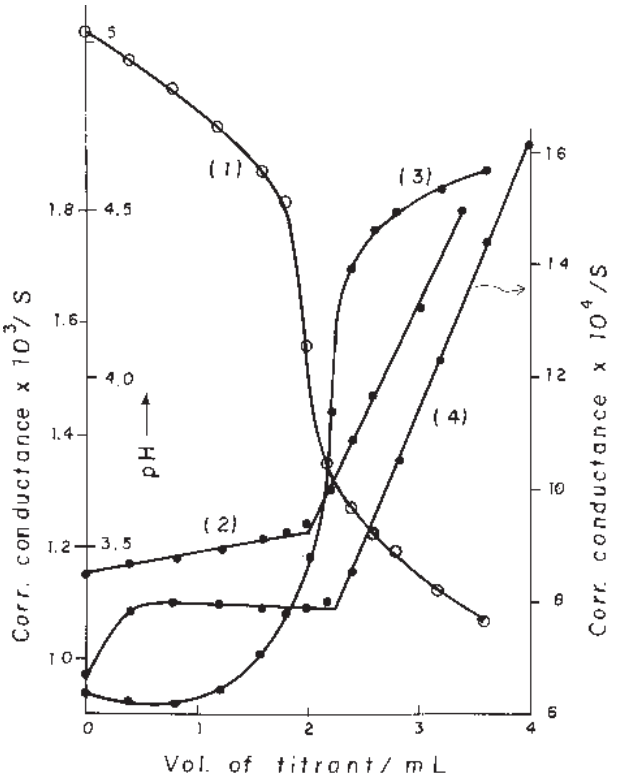

Figure 2. Para-molybdate titrations. (1 and 2) M/40 $Th(NO_3)_4$ added to 25 mL of M/750 $Na_6Mo_7O_{24}$. (3 and 4) M/80 $Na_6Mo_7O_{24}$ added to 25 mL of M/600 $Th(NO_3)_4$.

nitrate and sodium molybdate gave well-defined breaks at 1:2 molar ratio of Th^{4+}:MoO_4^{2-} confirming the formation of thorium normal-molybdate.

Para-molybdate titrations

Sodium para-molybdate solution was prepared by addition of hydrochloric acid to Na_2MoO_4 in the molar ratio 8H:7Mo. Using different concentrations of $Th(NO_3)_4$ and $Na_6Mo_7O_{24}$, a series of pH and conductometric titrations was carried out. The slope and nature of these titration curves (Figure 2) are similar to those of the normal-molybdate. The curves provide well-defined inflections at molar ratio 3:2 of Th^{4+}:$Mo_7O_{24}^{6-}$ corresponding to the stoichiometry for the formation of para-molybdate of thorium $3ThO_2.14MoO_3$ in the neighborhood of pH 4.4. The reaction can be represented as follows:

$$3Th(NO_3)_4 + 2Na_6Mo_7O_{24} =$$

$$(3ThO_2.14MoO_3) + 12NaNO_3$$

An interesting phenomenon was observed, in both pH and conductometric reverse titrations, *i.e.*, when thorium nitrate solution was taken as titre in the cell. In the initial part of the titration the pH slightly decreases (curve 3) and conductance value increases (curve 4). This may be ascribed to the liberation of the strong acid by hydrolysis of thorium nitrate under experimental conditions. This phenomenon may further be clarified by the fact that the white turbid precipitate of thorium molybdates, which starts from the very beginning in the case of direct titrations, starts only at the stoichiometric end-point in these reverse titrations. After passing the end-point the white precipitate gets flocculated.

Similar studies on the reaction between thorium nitrate and sodium octa-molybdate did not exhibit any

appreciable inflections. This may be ascribed to the small difference in pH value of the reactants; and the presence of sodium nitrate in appreciable amounts preventing the occurrence of breaks in the conductometric titration curves.

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 of the equivalence point has a favorable effect. The presence of ethanol (20%) improves the position of the end-point and increases the magnitude of the jump in pH curves, as it decreases the solubility of the precipitates formed and minimizes hydrolysis and adsorption.

Analytical results

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 compositions of the compounds were established which were found to be the same as obtained by the electrometric techniques (see Table 2).

The present electrometric and analytical investigations confirm the formation and precipitation of two thorium molybdates, viz. *normal*-$ThO_2.2MoO_3$ and *para*-$3ThO_2.14MoO_3$ in the vicinity of pH 5.3 and 4.4, respectively.

As structure of these compounds is not known they are represented as double oxides, the manner which is usually adopted for such compounds[15,16].

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