J. Braz. Chem. Soc., Vol. 9, No. 3, 253-259, 1998.
Printed in Brazil.

0103 – 5053 $6.00 + 0.00

Article

Electrometric Investigations on the System Acid-Molybdate and the Formation of Heavy Metal Molybdates

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Received: September 18, 1997

A natureza precisa dos poliânions formados pela ação de ácido clorídrico sobre soluções de molibdato de sódio foi estudada por meio de titulações de pH e condutométricas. As inflexões e degraus nas curvas de titulações indicaram a formação de ânions polimolibdatos *para*-$Mo_7O_{24}^{6-}$ e *octa*-$Mo_8O_{26}^{4-}$ ao redor do pH 5,5 e 4,1, correspondendo às razões 8H:7Mo e 3H:2Mo, respectivamente. Titulações semelhantes de pH e condutométricas entre Hg^{2+} e MoO_4^{2-}, $Mo_7O_{24}^{6-}$ e $Mo_8O_{26}^{4-}$ forneceram evidências incontestáveis sobre a formação de molibdato normal $HgO.MoO_3$, paramolibdato $3HgO.7MoO_3$ e octamolibdato $2HgO.8MoO_3$ de mercúrio(II) nas vizinhanças de pH 4,9; 4,2 e 3,7 respectivamente. Estudos analíticos também foram realizados sobre precipitados de molibdatos de mercúrio(II) confirmando os resultados obtidos pelas técnicas eletrométricas.

The precise nature of the polyanions formed by the action of hydrochloric acid on sodium molybdate solutions has been studied by pH and conductometric measurements involving glass electrode and conductometric titrations. The inflections and breaks in the titration curves indicate the formation of *para*-$Mo_7O_{24}^{6-}$ and *octa*-$Mo_8O_{26}^{4-}$ polymolybdate anions around pH 5.5 and 4.1, corresponding to the molar ratio 8H:7Mo and 3H:2Mo, respectively. Similar pH and conductometric titrations between Hg^{2+} and MoO_4^{2-}, $Mo_7O_{24}^{6-}$, and $Mo_8O_{26}^{4-}$ provide definite evidence for the formation of normal molybdate $HgO.MoO_3$, paramolybdate $3HgO.7MoO_3$ and octamolybdate $2HgO.8MoO_3$ of mercury(II) in the vicinity of the pH 4.9, 4.2 and 3.7, respectively. The analytical investigations of the precipitates of mercuric molybdates have also been carried out, which substantiate the results of the electrometric study.

Keywords: *molybdate anions, mercuric molybdates, electrometric techniques*

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]. Altough 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 equilibria between the polyanions or due to the experimental difficulty in early works, the conclusions of earlier workers seem to be overstrained and hence it was considered worthwhile to make a careful and precise study of the acid-molybdate system by electrometric techniques, which have provided more conclusive evidence on the condensation process of vanadate, antimonate, thiotungstate and tungstate anions[13]. After establishing the suitable conditions for the stability of different molybdate isopolyanions, the investigations of formation of molybdates of mercury, chromium and nickel as a function of the pH were also carried out.

Experimental

$Na_2MoO_4.2H_2O$, $Hg(NO_3)_2$, $CrCl_3.6H_2O$, $NiCl_3.6H_2O$, $Na_2B_4O_7.10H_2O$ and hydrochloric acid 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 hydrochloric acid solutions were standardized with recrystallized sodium tetraborate decahydrate[14b].

The pH measurements were carried out on Metrohm Herisau (Switzerland) pH-meter using a 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 ± 0.1 °C. Using different concentrations of the reactants, a series of glass electrode and conductometric titrations was performed. The observed pH changes were plotted as a function of volume of titrant added. The inflections obtained in the curves were confirmed by the pronounced maxima in dpH/dV and zero in d^2pH/dV^2 graphs. The breaks in the conductometric titrations were 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 for the formation of molybdate polyanions and mercuric molybdates are summarized in Tables 1 and 2, respectively.

Job's method of continuous variation was employed using electrical conductance measurements for determining the composition of the polyanions formed by the interaction of sodium molybdate with hydrochloric acid. This consists in 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. From the maxima obtained in such plots, the stoichiometry of the compound formed was established.

The precipitates obtained at the end-points of titrations between mercuric nitrate and sodium molybdates were also analyzed to substantiate the electrometric results. The different mercuric molybdates were prepared by mixing stoichiometric amounts of mercuric nitrate solution with the respective sodium molybdate solutions. The precipitates obtained were washed several times with aqueous 20% (v/v) ethanolic solution and dried in a vacuum dessicator for 40 h. A known amount (2 g) of each of the above precipitates was dissolved in a minimum quantity of hydrochloric acid and then analyzed quantitatively for mercury[14c] with ethylenediamine and molybdenum[14a] with oxine. From the proportion of mercury and molybdenum in the compounds thus obtained their composition was established. The results are summerized in Table 3.

Results and discussion

Isopolymolybdate anions

Figure 1, curve 1 represents the changes occurring in H^+ concentration on the addition of HCl to sodium molybdate solution. It is noted that the smallest addition of the acid in the beginning causes a sharp fall in the pH (not

Table 1. Summary of results of electrometric titrations of the acid-molybdate system. Volume of titre solution taken in the cell = 25 mL.

Molarity of solutions		Equivalence points (mL) for the formation of					
		paramolybdate			octamolybdate		
HCl	Na_2MoO_4	Calc.	A*	B*	Calc.	A	B
M/5	M/50	2.86	2.85	2.90	3.75	3.75	3.75
M/10	M/80	3.57	3.55	3.55	4.69	4.70	4.70
M/20	M/250	2.29	2.30	2.25	3.00	3.00	3.05
M/40	M/450	2.54	2.55	2.55	3.33	3.35	3.35
M/100	M/1000	2.86	2.85	2.85	3.75	3.75	3.80
M/200	M/2200	2.60	2.60	2.55	3.41	3.40	3.40

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

Table 2. Summary of results of electrometric study on the formation of mercuric molybdates. Volume of titre solution taken in the cell = 25 mL.

Molarity of solutions		Equivalence points (mL)			Formula supported
			pH	Conductance	
$Hg(NO_3)_2$	Na_2MoO_4	Direct titrations. Fig. 3, curves 1 and 2			
M/10	M/100	2.50	2.50	2.50	$HgO.MoO_3$
M/20	M/250	2.00	2.00	2.05	
M/30	M/350	2.14	2.10	2.10	
		Reverse titrations. Fig. 3, curves 3 and 4			
M/125	M/10	2.00	2.00	2.00	$HgO.MoO_3$
M/200	M/20	2.50	2.50	2.55	
M/350	M/30	2.15	2.15	2.15	
$Hg(NO_3)_2$	$Na_6Mo_7O_{24}$	Direct titrations. Fig. 4, curves 1 and 2			
M/10	M/350	2.14	2.15	2.10	$3HgO.7MoO_3$
M/20	M/750	2.00	2.00	2.05	
M/30	M/1000	2.25	2.20	2.20	
		Reverse titrations. Fig. 4, curves 3 and 4			
M/160	M/40	2.08	2.10	2.10	$3HgO.7MoO_3$
M/300	M/80	2.22	2.20	2.15	
M/500	M/120	2.00	2.05	2.05	
$Hg(NO_3)_2$	$Na_4Mo_8O_{26}$	Direct titrations. Fig. 5			
M/10	M/200	2.50	2.45	2.45	$2HgO.8MoO_3$
M/20	M/500	2.00	2.00	1.95	
M/30	M/700	2.14	2.10	2.15	

Table 3. Summary of analytical results of the precipitates of mercuric molybdates.

Proposed formula of the compound	Mode of synthesis	Analysis %: Hg	Found (calculated) Mo
	Analysis of the normal molybdate precipitates.		
$HgO.MoO_3$	Direct*	55.52(55.64)	26.69(26.61)
	Reverse*	55.71	26.53
	Analysis of the paramolybdate precipitates.		
$3HgO.7MoO_3$	Direct	36.23(36.31)	24.58(40.52)
	Reverse	36.40	40.46
	Analysis of the octamolybdate precipitates.		
$2HgO.80MoO_3$	Direct	25.20(25.32)	48.54(48.43)

*Direct - Mercuric nitrate solution added to sodium molybdate solution. Reserve - Sodium molybdate solution added to mercuric nitrate solution.

shown in the figure), whilst further reaction with HCl produces buffer action between pH 6.2 and 5.7 showing strong affinity for the hydrogen ions in this region; subsequent addition of HCl shows a sudden fall in pH at a ratio 8H:7Mo around pH 5.5 corresponding to the stoichiometry for the formation of *para*-$Mo_7O_{24}^{6-}$ molybdate anions. Further addition of acid yields one more inflection indicating the consumption of 1.5 moles of HCl per mole of Na_2MoO_4 and suggesting the formation of *octa*-$Mo_8O_{26}^{4-}$ molybdate anions in the vicinity of pH 4.1. The pH of such acidified solutions became steady after a lapse of some time indicating that the reaction proceeds by way of some intermediate species. Each time the pH value was recorded only after waiting enough for its stabilization. It was noted that in the

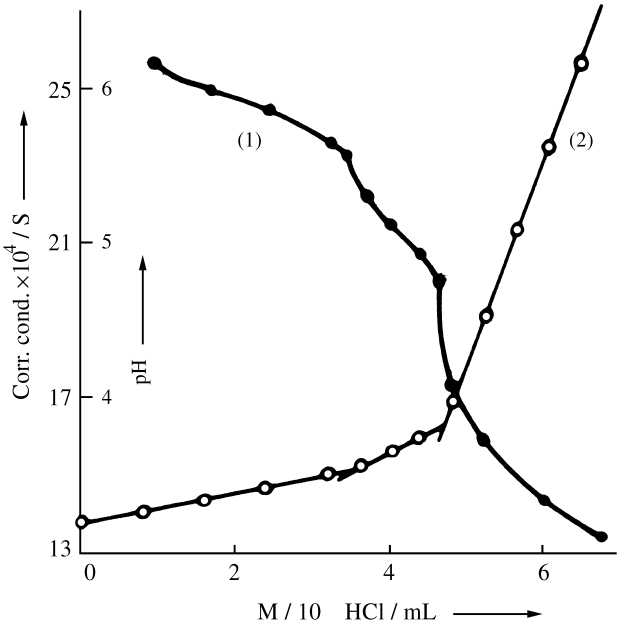

Figure 1. pH (curve 1) and conductometric (curve 2), titrations. 25 mL of M/80 Na_2MoO_4 titrated with M/10 HCl.

case of moderately concentrated solutions, the curves were steeper than for dilute reactants. Out of the two inflections in the curves, the one corresponding to the conversion into octamolybdate is more pronounced.

Conductometric titrations between HCl and Na_2MoO_4 solutions were also carried out using similar concentrations as in the pH titrations. The observed breaks (Fig. 1, curve 2) correspond to the formation of the same polyanions, *para*-$Mo_7O_{24}^{6-}$ and *octa*-$Mo_8O_{26}^{4}$, as suggested by the preceding pH study. The slow increase in conductance values on addition of HCl to Na_2MoO_4 till the point 8H:7Mo may be ascribed to the formation of the highly charged $Mo_7O_{24}^{6-}$ anions of the relatively weak acid. The break corresponding to the addition of 1.5 moles of HCl per mole of Na_2MoO_4 is strongly defined, after which a sharp rise in conductance was observed which was determined to be the same as expected for the addition of free HCl to the system.

The course of the isopolyanion formation of molybdate by the acid was also followed by employing Job's method of continuous variation using electrical condutance measurements. The plot of difference in specific conductivity values against composition of mixtures produced a sharp peak (Fig. 2) at the molar ratio 3H:2Mo providing further evidence for the formation of the octamolybdate polyanions.

The formation of the polyanions, as suggested by the electrometric study, may be represented as follows:

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

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

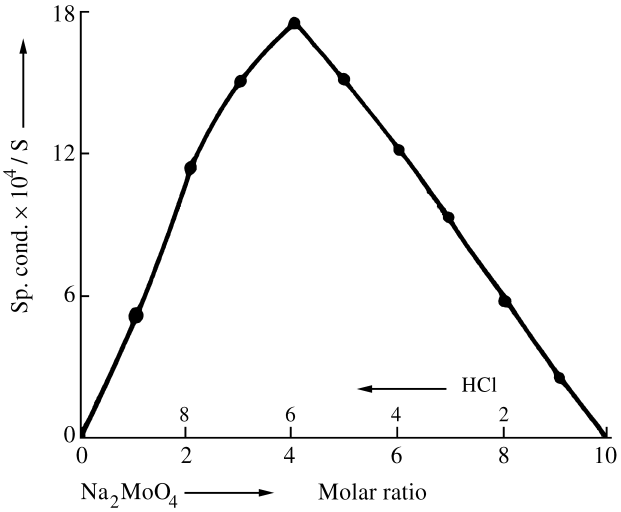

Figure 2. Continuous variation study by Job's method using equimolar (0.02 M) solutions.

The existence of $Mo_7O_{26}^{6-}$ and $Mo_8O_{26}^{4-}$ is in conformity with the results of the temperature-jump studies by Honing and Kustin[15] and the Raman spectra studies by Ozeki *et al.*[16] Murata *et al.*[17], however, claimed that the octamolybdate underwent further reaction with acid ($Z \geq 1.7$) to form $Mo_{12}O_{37}^{2-}$ and $Mo_6O_{19}^{6-}$, but this observation could not be confirmed by our results.

When a dilute solution of MoO_4^{2-} ($< 10^{-4}$ M) is acidified, it yields $HMoO_4^-$ and "H_2MoO_4". It has been confirmed[10,18] that the tetrahedral ion MoO_4^{2-} transforms into an octahedral especies at the stage of second protonation.

$$MoO_4^{2-} + H^+ = [MoO_3(OH)]^-$$

$$[MoO_3(OH)]^- + H^+ + 2H_2O = Mo(OH)_6 \text{ or } MoO_2(OH)_2(H_2O)_2$$

When a basic molybdate solution at millimolar or higher concentrations is acidified, the molybdate ions have been found to condense in definite steps, as evidenced by the foregoing electrometric study, to form different isopolymolybdate species. The condensation process may be considered as rapid aggregation of the protonated species. Six monoprotonated $[MoO_3(OH)]^-$ can easily link to the dipronated species, each one sharing a weak corner of octahedral $Mo(OH)_6$. And, when six tetrahedra have been accomodated, all of these peripheral tetrahedra can expand to octahedra simply by folding at the common corners to share the octahedral edge along with a considerable decrease in enthalpy[10,12]. This negative enthalpy change can be expected to stabilize the resultant product $Mo_7O_{24}^{6-}$.

$$Mo(OH)_6 + 6[MoO_4(OH)]^- = Mo_7O_{24}^{6-} + 6H_2O$$

The condensation process, for formation of the unprotonated polyanions, may be represented by the following general equation:

$$aH^+ + bMoO_4^{2-} = (MoO_4^{2-})_{b-a/2}(MoO_3)_{a/2} + (a/2)H_2O$$

The values of *a* and *b* are 8 and 7 for heptamer and 12 and 8 for octamer, respectively.

Mercury molybdates

The solution of Na_2MoO_4 was prepared in deionized distilled water. Sodium paramolybdate (pH 5.5) and octamolybdate (pH 4.1), as suggested by the preceding studies, were prepared by progressive additions of hydrochloric acid to Na_2MoO_4 solutions in the molar ratios 8H:7Mo and 3H:2Mo, respectively.

$$8HCl + 7Na_2MoO_4 = Na_6Mo_7O_{24} + 8NaCl + 4H_2O$$

$$12HCl + 8Na_2MoO_4 = Na_4Mo_8O_{26} + 12NaCl + 6H_2O$$

Figure 3 illustrates the curves of the pH and conductometric titrations performed between the solutions of the normal molybdate and mercuric nitrate. In direct titrations (curve 1), when $Hg(NO_3)_2$ solution (pH 2.6) was added to the Na_2MoO_4 solution (pH 7.6) a sharp fall in pH was noted with an inflection at the molar ratio of Hg^{2+}:MoO_4^{2-} as 1:1 in the vicinity of pH 4.9, corresponding to the stoichiometry for the formation of mercuric molybdate, $HgO.MoO_3$. This sharp fall in pH occurs because of the presence of unreacted acidic (pH 2.6) $Hg(NO_3)_2$ in the cell just after completion of precipitation of mercuric molybdate. In reverse titrations (curve 3), when Na_2MoO_4 solution was added to the mercuric 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:

$$Hg(NO_3)_2 + Na_2MoO_4 = HgO.MoO_3 + 2NaNO_3$$

Employing similar concentrations of the reactants, both direct (curve 2) and reserve (curve 4) conductometric titrations between the solutions of $Hg(NO_3)_2$ and Na_2MoO_4 gave well-defined breaks at 1:1 molar ratio of Hg^{2+}:MoO_4^{2-}, confirming the formation of the mercuric molybdate $HgO.MoO_3$, as suggested by the pH study.

Figure 4 (curves 1 and 3) illustrates the changes occurring in H^+ concentration when $Hg(NO_3)_2$ solution (pH 2.6) is treated with $Na_6Mo_7O_{24}$ solution (pH 5.5). In direct titrations, curve 1, when $Hg(NO_3)_2$ solution was added from the microburette to $Na_6Mo_7O_{24}$ solution, a gradual change in pH was observed till at the stoichiometric endpoint (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 Hg^{2+}:$Mo_7O_{24}^{6-}$ as 3:1, suggesting the formation of mercu-

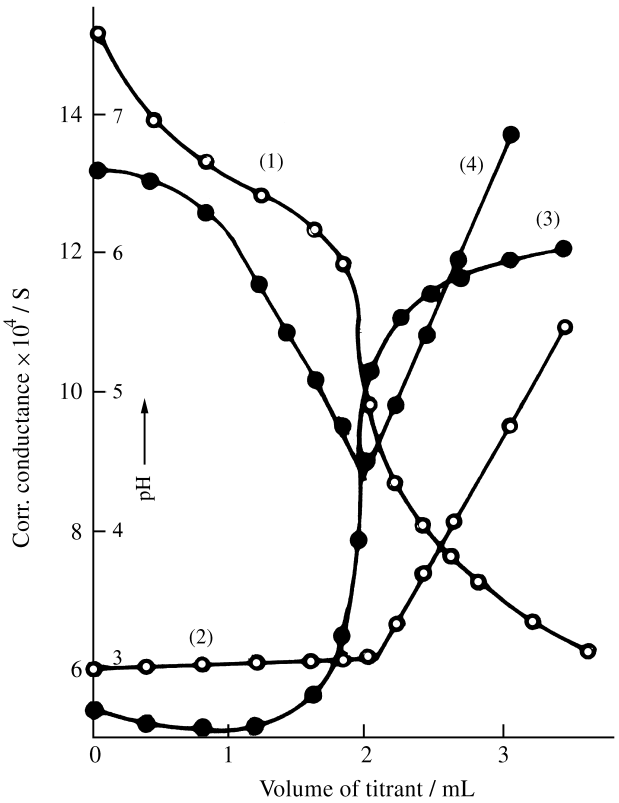

Figure 3. Normal molybdate titrations. (1 and 2) M/20 $(HgNO_3)_2$ to 25 mL of M/250 Na_2MoO_4. (3 and 4) M/10 Na_2MoO_4 to 25 mL of M/125 $Hg(NO_3)_2$.

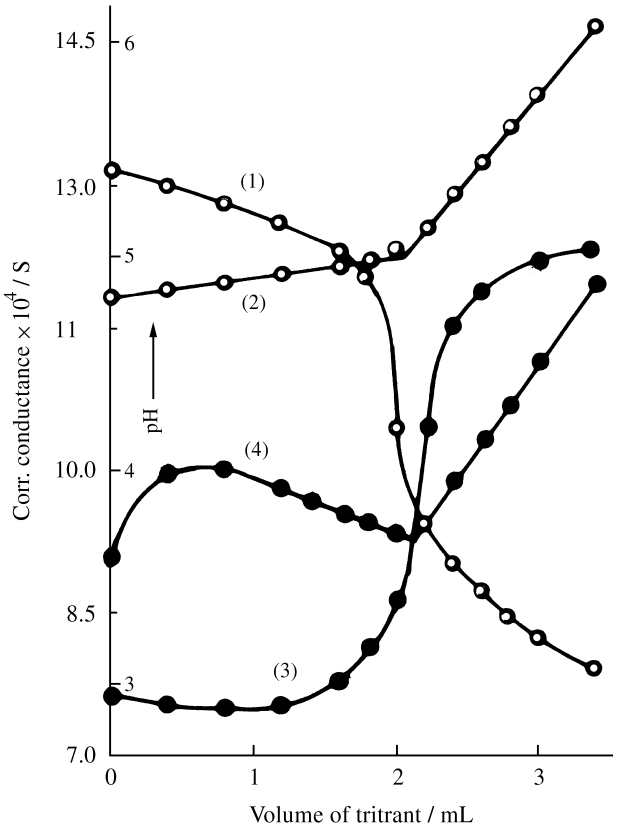

Figure 4. Paramolybdate titrations. (1 and 2) M/20$(HgNO_3)_2$ to 25 mL of M/750 $Na_6Mo_7O_{24}$. (3 and 4) M/80 $Na_6Mo_7O_{24}$ to 25 mL of M/300 $Hg(NO_3)_2$.

ric paramolybdate $3HgO.7MoO_3$ in the vicinity of pH 4.2. In the case of reverse titrations (curve 3) when $Na_6Mo_7O_{24}$ solution was used as titrant, the pH first changes slowly but at the stoichiometric end-point a marked jump in pH was observed, suggesting the formation of the same compound. Employing similar concentrations of the reactants a series of direct (Fig. 4, curve 2) and reverse (Fig. 4, curve 4) conductometric titrations were performed between the solutions of $Hg(NO_3)_2$ and $Na_6Mo_7O_{24}$. The titration curves provide well-defined breaks at a point (Table 2), where the molar ratio of Hg^{2+}:$Mo_7O_{24}^{6-}$ is 3:1, confirming the formation of mercuric paramolybdate as suggested by the pH study. The reaction can be represented as follows:

$$3Hg(NO_3)_2 + Na_6Mo_7O_{24} = (3HgO.7MoO_3) + 6NaNO_3$$

Figure 5 illustrates the changes occurring in the pH and conductance values when $Hg(NO_2)_2$ solution is added to sodium octamolybdate solution. The titration curves provide inflections and breaks at the point where the molar ratio of Hg^{2+}:$Mo_8O_{26}^{4-}$ is 2:1, which corresponds to the stoichiometry for the formation of $2HgO.8MoO_3$ in the neighbourhood of pH 3.7. The reaction can be represented by the following equation:

$$2Hg(NO_3)_2 + Na_4Mo_8O_{26} = (2HgO.8MoO_3) + 4NaNO_3$$

Reserve titrations on the formation of mercuric octamolybdate did not give dependable results which may be ascribed to a considerable solubility of the product in excess of mercuric nitrate.

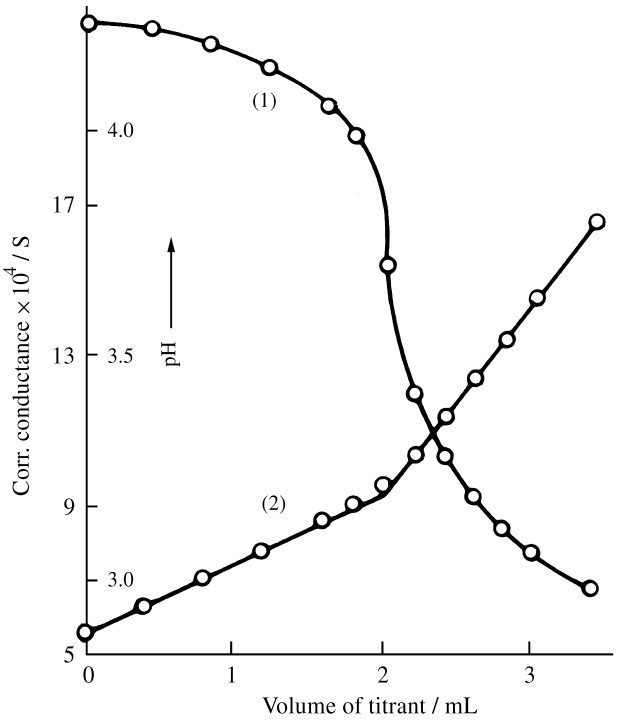

Figure 5. Octamolybdate titrations. M/20 $Hg(NO_3)_2$ to 25 mL of M/500 $Na_2Mo_8O_{26}$.

It is 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 neighbourhood of the equivalence point has a favourable effect. The presnce of ethanol (20%) improves the position of the end-points and increases the magnitude of the jump in pH curves, as it decreases the solubility of the precipitates formed and minimises hydrolysis and adsorption. It was found that the presence of 20% ethanol checked the hydrolysis, as a concentration higher than this could not make any change in the results. Similar studies of this system were carried out in the presence of electrolytes such as NaCl and $NaNO_3$. But the presence of these salts did not have a significant effect on the position of the end points.

Similar investigations on the interaction of solutions of chromium chloride with sodium molybdate at different pH levels confirmed the precipitation of $Cr_2O_3.3MoO_3$ (pH 5.6), $Cr_2O_3.7MoO_3$ (pH 4.4) and $Cr_2O_3.24MoO_3$ (pH 3.8) molybdates[19]. Electrometric studies on interaction of nickel chloride and different sodium molybdate solutions did not suggest the formation of nickel molybdates which is in accord with the observations of Sleight and Chamberland[20].

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

Conclusion

The results of the electrometric investigations on acid-molybdate system, at the studied concentration levels, suggest the formation of *para*-$Mo_7O_{24}^{6-}$ and *octa*-$Mo_8O_{26}^{4-}$ molybdate polyanions in the vicinity of pH 5.5 and 4.1, respectively. The electrometric and analytical investigations on the interaction of mercuric nitrate and alkali molybdates indicate the formation of $HgO.MoO_3$, $3HgO.7MoO_3$ and $2HgO.8MoO_3$ mercuric molybdates in the neighbourhood of pH 4.9, 4.2, and 3.7, respectively.

Acknowledgement

The authors wish to express their sincere thanks to CNPq for financial assistance.

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