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# Electrometric studies on uranyl molybdates as a function of pH

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**ABSTRACT:** The formation and composition of uranyl molybdates obtained by the interaction of uranyl acetate and sodium molybdate at specific pH levels 7.6, 5.5 and 4.1 have been studied by employing electrometric techniques involving pH and conductometric titrations. The results provide cogent evidence for the formation of three uranyl molybdates having the molecular formulae $UO_2O.MoO_3$, $3UO_2O.7MoO_3$ and $2UO_2O.8MoO_3$ in the vicinity of pH 5.7, 4.6 and 3.8, respectively. Analytical investigations of the compounds have also been carried out which substantiate the results of electrometric study.

**KEYWORDS:** Molybdates; uranyl; electrometric study.

## Introduction

The chemistry of molybdenum is very prominent in both biogical and industrial systems.[4,16] Recent studies have shown that certain molybdates have antiviral, including anti-AIDS, and antitumor activity.[6] 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.[5] 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.[3] In 1959, Sasaki et al. deduced from potentiometry that the main complex formed is $Mo_7O_{24}$. [6-13] 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 $MoO4^{2-}$) of around 1.4.[14,15] Aveston et al.[1] 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 $Z > 1.5$[14]. Numerous species such as $HMoO_4^-$, $H_2MoO_4$, $Mo_2O_7^{2-}$, $HMo_3O_{11}^{3-}$, $Mo_6O_{19}^{2-}$, $Mo_7O_{24}^{6-}$, $HMo_7O_{24}^{5-}$, $H_2Mo_7O_{24}^{4-}$, $Mo_8O_{26}^{4-}$, $HMo_8O_{26}^{3-}$, $Mo_{12}O_{37}^{2-}$, $H_7Mo_{24}O_{78}^{5-}$, $Mo_{36}O_{112}^{8-}$, etc. have been reported in many recent publications.[7,8]

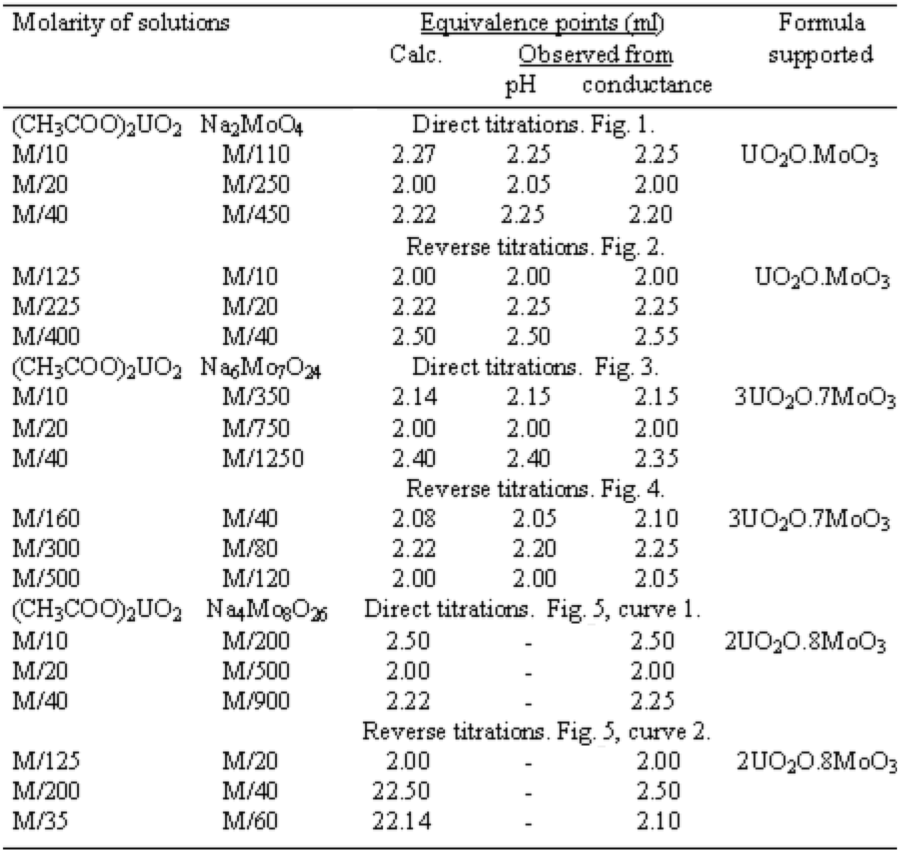
On account of the complexity of the relation of equilibria between the polyanions or due to the experimental difficulty in early works, the conclusions of earlier workers seem to be overstrained and hence it was considered worthwhile to make a careful and precise study of the acid-molybdate system by electrometric techniques, which have provided more conclusive evidence on the condensation process of vanadate, antimonate, thiotungstate and tunsgtate anions.[9] In earlier publications the author has reported the effect of pH change on a solution of $Na_2MoO_4$ and composition of mercuric molybdates.[11,12] In view of the interesting results obtained, it was considered worthwhile to investigate the composition of uranyl molybdates obtained by the action of uranyl cations on different molybdate anions at specific pH levels by means of the electrometric techniques.

## Materials and methods

$Na_2MoO_4.2H_2O$, $(CH_3COO)_2UO_2.2H_2O$, $Na_2B_4O_7.10H_2O$ 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 $MoO_2(C_9H_6ON)_2$.[18a] The hydrochloric acid solutions were standardized with recrystallized sodium tetraborate decahydrate.[18b]

The pH-meter, conductometer, electrodes and titration cells were used as reported earlier.[10] 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 by the curves were confirmed by the pronounced maxima in dpH/dV 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. Only a limited number of experimental points are shown in the curves to maintain legibility and to avoid overlapping. The electrometric titration results for the formation of uranyl molybdates are summarized in Tables 1.

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



| Molarity of solutions | | Equivalence points (ml) | | | Formula supported |
|---|---|---|---|---|---|
| | | Calc. | Observed from | | |
| | | | pH | conductance | |
| $(CH_3COO)_2UO_2$ | $Na_2MoO_4$ | Direct titrations. Fig. 1. | | | |
| M/10 | M/110 | 2.27 | 2.25 | 2.25 | $UO_2O.MoO_3$ |
| M/20 | M/250 | 2.00 | 2.05 | 2.00 | |
| M/40 | M/450 | 2.22 | 2.25 | 2.20 | |
| | | Reverse titrations. Fig. 2. | | | |
| M/125 | M/10 | 2.00 | 2.00 | 2.00 | $UO_2O.MoO_3$ |
| M/225 | M/20 | 2.22 | 2.25 | 2.25 | |
| M/400 | M/40 | 2.50 | 2.50 | 2.55 | |
| $(CH_3COO)_2UO_2$ | $Na_6Mo_7O_{24}$ | Direct titrations. Fig. 3. | | | |
| M/10 | M/350 | 2.14 | 2.15 | 2.15 | $3UO_2O.7MoO_3$ |
| M/20 | M/750 | 2.00 | 2.00 | 2.00 | |
| M/40 | M/1250 | 2.40 | 2.40 | 2.35 | |
| | | Reverse titrations. Fig. 4. | | | |
| M/160 | M/40 | 2.08 | 2.05 | 2.10 | $3UO_2O.7MoO_3$ |
| M/300 | M/80 | 2.22 | 2.20 | 2.25 | |
| M/500 | M/120 | 2.00 | 2.00 | 2.05 | |
| $(CH_3COO)_2UO_2$ | $Na_4Mo_8O_{26}$ | Direct titrations. Fig. 5, curve 1. | | | |
| M/10 | M/200 | 2.50 | - | 2.50 | $2UO_2O.8MoO_3$ |
| M/20 | M/500 | 2.00 | - | 2.00 | |
| M/40 | M/900 | 2.22 | - | 2.25 | |
| | | Reverse titrations. Fig. 5, curve 2. | | | |
| M/125 | M/20 | 2.00 | - | 2.00 | $2UO_2O.8MoO_3$ |
| M/200 | M/40 | 22.50 | - | 2.50 | |
| M/35 | M/60 | 22.14 | - | 2.10 | |

The precipitates obtained at the end-points of titrations between uranyl acetate and sodium molybdates were also analyzed to substantiate the electrometric results. The different uranyl 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 sulfuric acid and then analyzed quantitatively for molybdenum by precipitating with **a**-benzoinoxime and weighing as molybdic oxide.[18c] Uranium was determined from the filtrate with oxine.[18d] From the proportion of uranium and molybdenum in the compounds thus obtained their composition were established. The results are summarized in Table 2.

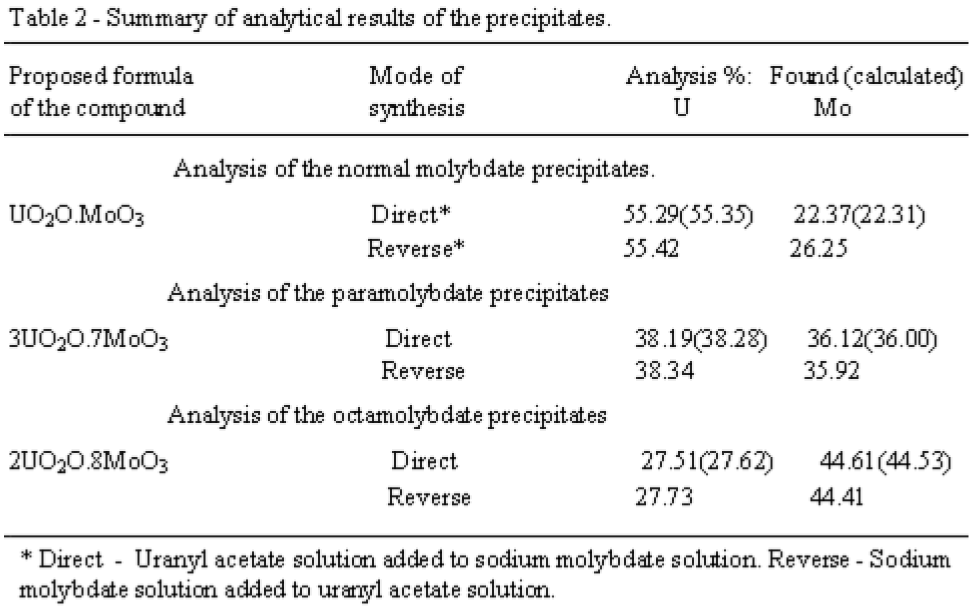


Table 2 - Summary of analytical results of the precipitates.

| Proposed formula of the compound | Mode of synthesis | Analysis %: Found (calculated) U | Mo |
|---|---|---|---|
| Analysis of the normal molybdate precipitates. | | | |
| $UO_2O.MoO_3$ | Direct* | 55.29(55.35) | 22.37(22.31) |
| | Reverse* | 55.42 | 26.25 |
| Analysis of the paramolybdate precipitates | | | |
| $3UO_2O.7MoO_3$ | Direct | 38.19(38.28) | 36.12(36.00) |
| | Reverse | 38.34 | 35.92 |
| Analysis of the octamolybdate precipitates | | | |
| $2UO_2O.8MoO_3$ | Direct | 27.51(27.62) | 44.61(44.53) |
| | Reverse | 27.73 | 44.41 |

* Direct - Uranyl acetate solution added to sodium molybdate solution. Reverse - Sodium molybdate solution added to uranyl acetate solution.

## Results and Discussion

The solution of $Na_2MoO_4$ was prepared in deionized distilled water. Sodium paramolybdate (pH 5.5) and octamolybdate (pH 4.1), as reported by recent studies,[11,12] were prepared by progressive additions of hydrochloric acid to $Na_2MoO_4$ solutions in the molar ratios 8H:7Mo and 3H:2Mo, respectively.

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

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

### Uranyl normal molybdate

Figures 1 and 2 illustrate the curves of pH and conductometric titrations performed between the solutions of sodium normal molybdate and uranyl acetate.

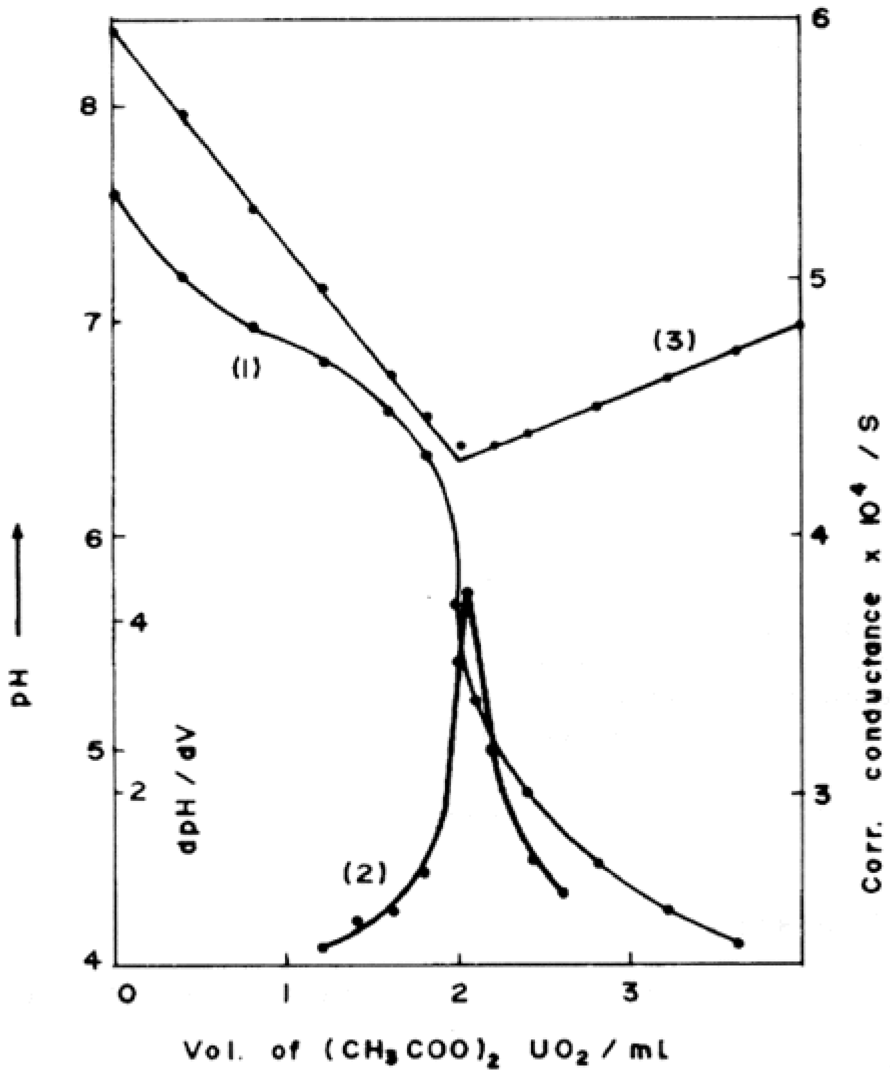


FIGURE 1 - Direct titrations of normal molybdate (M/20 $(CH_3COO)2UO_2$ vs M/250 $Na_2MoO_4$). (1) pH, (2) dpH/dV, and (3) conductometric.

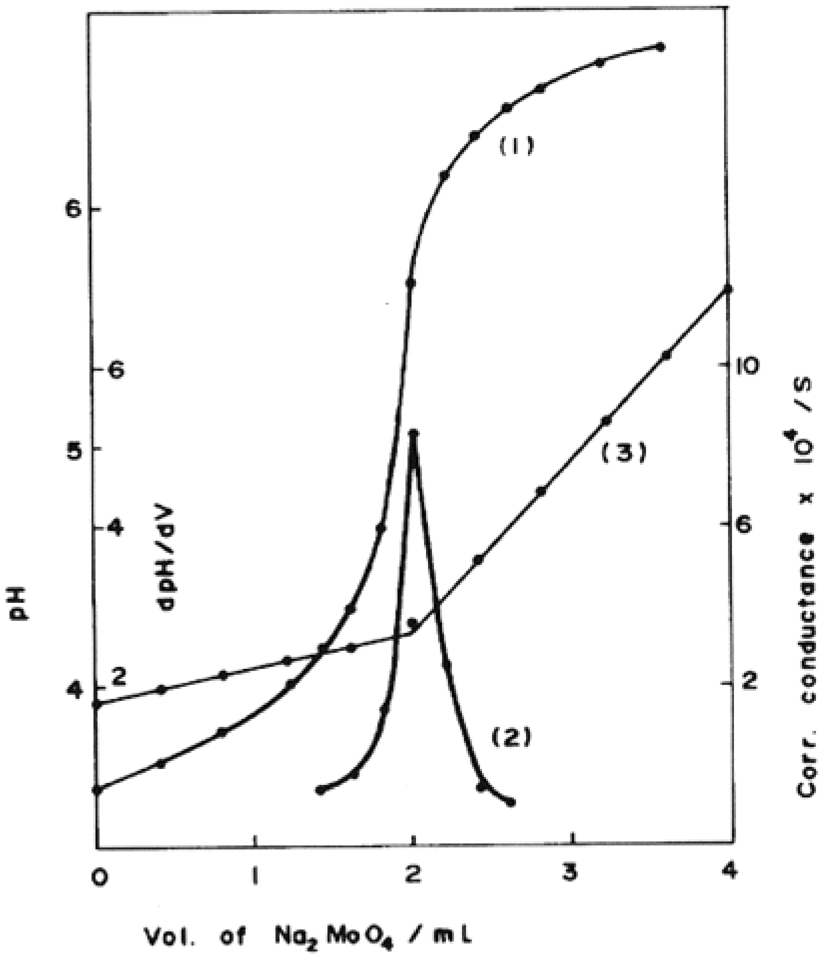


FIGURE 2 - Reverse titrations of normal molybdate (M/10 $Na_2MoO_4$ vs M/125 $(CH_3COO)_2UO_2$). (1) pH, (2) dpH/dV, and (3) conductometric.

In direct titrations (Figure 1, curve 1), when uranyl acetate solution (pH 3.6) 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 $UO_2^{2+}$:$MoO_4^{2-}$ as 1:1 in the vicinity of pH 5.7, corresponding to the stoichiometry for the formation of uranyl molybdate, $UO_2O.MoO_3$. The inflection of the curve is located by the pronounced maxima in dpH/dV graph (Figure 1, curve 2). In case of inverse titrations (Figure 2, curves 1 and 2), when $Na_2MoO_4$ solution was used as titrant, the pH first changed very slowly, but at the end-point it jumped upwards producing a sharp maxima in dpH/dV corresponding to the formation of the same compound in accordance with the following equation:

$$(CH_3COO)_2UO_2 + Na_2MoO_4 = UO_2O.MoO_3 + 2CH_3COONa$$

Employing similar concentrations of the reactants, both direct (Figure 1, curve 3) and reverse (Figure 2, curve 3) conductometric titrations between the solutions of uranyl acetate and $Na_2MoO_4$ gave well-defined breaks at 1:1 molar ratio of $UO_2^{2+}$: $MoO_4^{2-}$, confirming the formation of the uranyl molybdate $UO_2O.MoO_3$ as suggested by the pH study.

**Uranyl paramolybdate**

Figures 3 and 4 illustrate the curves of the pH and conductometric titrations performed between the solutions of sodium paramolybdate and uranyl acetate.

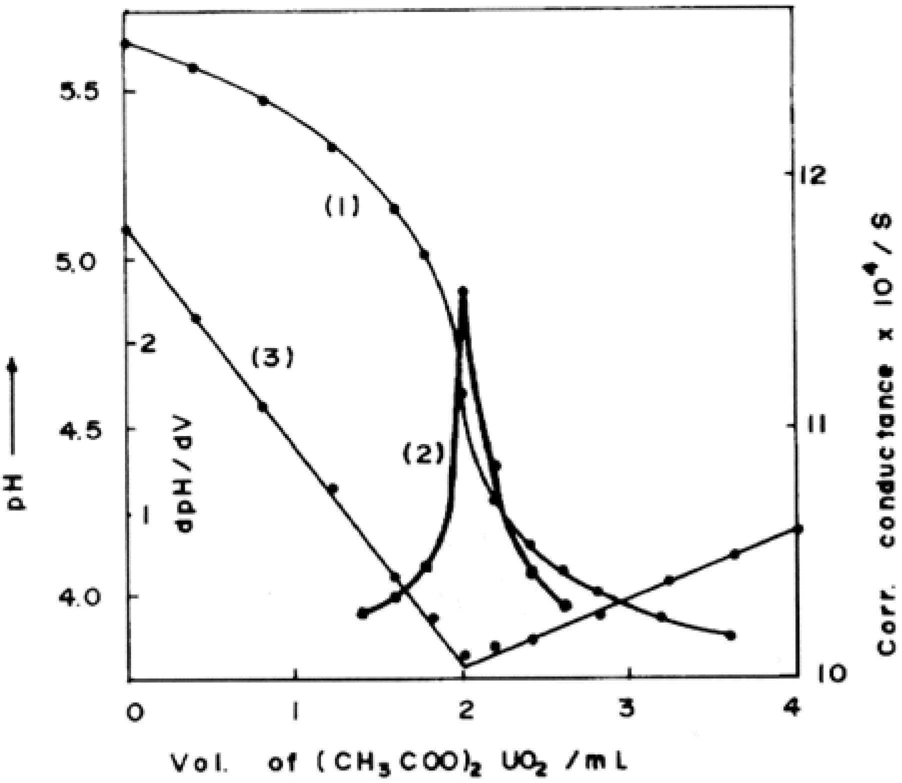


FIGURE 3 - Direct titrations of paramolybdate (M/20 $(CH_3COO)_2UO_2$ vs M/750 $Na_6Mo_7O_{24}$). (1) pH, (2) dpH/dV, and (3) conductometric.

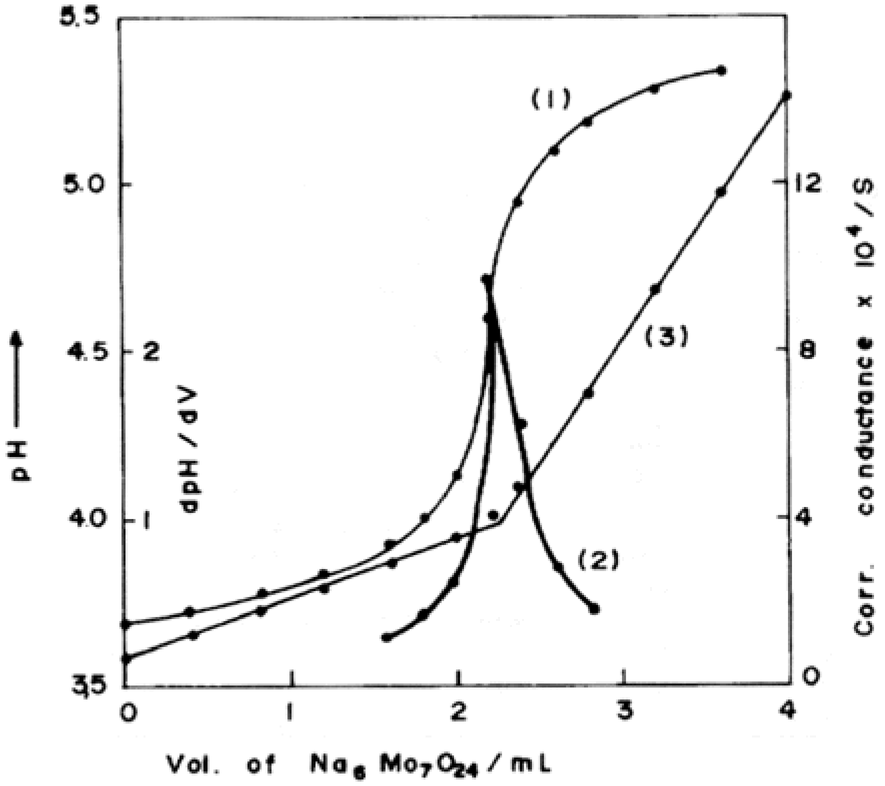


FIGURE 4 - Reverse titrations of paramolybdate (M/80 $Na_6Mo_7O_{24}$ vs. M/300 $(CH_3COO)_2UO_2$). (1) pH, (2) dpH/dV, and (3) conductometric.

In direct titrations, when uranyl acetate solution (pH 3.6) was added from the microburette to $Na_6Mo_7O_{24}$ solution (pH 5.5), 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 (Figure 3, curve 1) and maxima in dpH/df (Figure 3, curve 2) was noted corresponding to the molar ratio of $UO_2^{2+}$: $Mo_7O_{24}^{6-}$ as 3:1, suggesting the formation of uranyl paramolybdate $3UO_2O.7MoO_3$ in the vicinity of pH 4.6. In the case of reverse titrations (Figure 4, curves 1 and 2) 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 and a sharp maxima in dpH/dV was observed, suggesting the formation of the same compound. The reaction can be represented as follows:

$3(CH_3COO)_2UO_2 + Na_6Mo_7O_{24} = (3UO_2O.7MoO_3) + 6CH_3COONa$.

Employing similar concentrations of the reactants a series of direct (Figure 3, curve 3) and reverse (Figure 4, curve 3) conductometric titrations was performed between the solutions of uranyl acetate and sodium paramolybdate. The titration curves provide well-defined breaks at a point (see Table 1), where the molar ratio of $UO_2^{2+}$:$Mo_7O_{24}^{6-}$ is at 3:1, confirming the formation of uranyl paramolybdate as suggested by the pH study.

### Uranyl octamolybdate

Figure 5 illustrates the changes occurring in the conductance values during the conductometric titrations between the solutions of uranyl acetate and $Na_4Mo_8O_{26}$. The direct (curve 1) and reverse (curve 2) titration curves show well-defined breaks at the point where the molar ratio of $UO_2^{2+}$:$Mo_8O_{26}^{4-}$ is 2:1 which corresponds to the stoichiometry for the formation of uranyl octamolybdate $2UO_2O.8MoO_3$, in the neighbourhood of pH 3.8. The reaction can be represented by the following equation:

$$2(CH_3COO)_2UO_2 + Na_4Mo_8O_{26} = (2UO_2O.8MoO_3) + 4CH_3COONa.$$

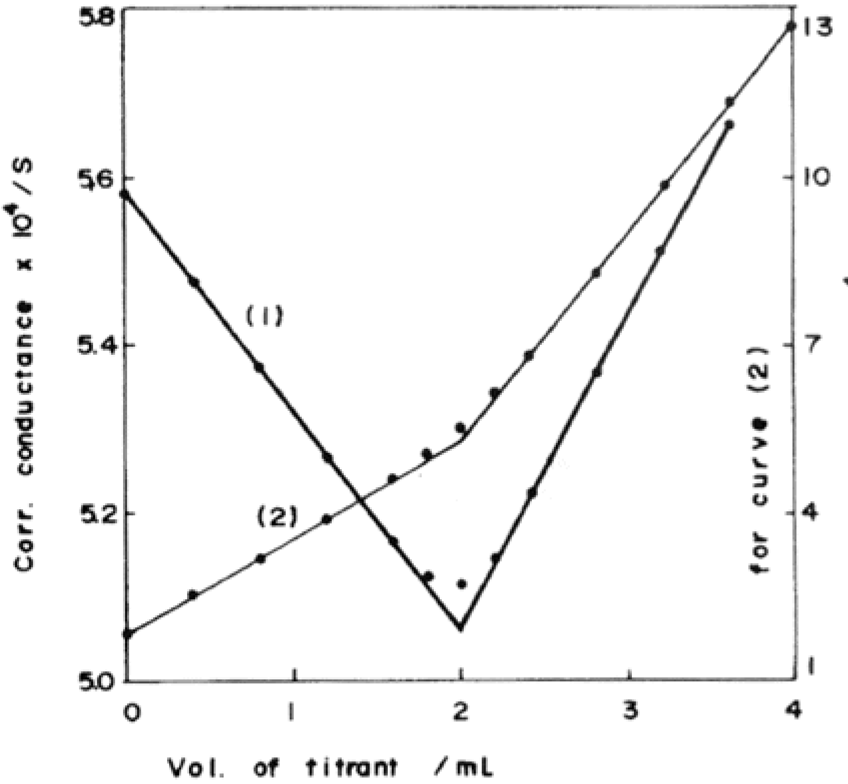


FIGURE 5 - Conductometric titrations of octamolybdate. (1) M/20 $(CH_3COO)_2UO_2$ added to 25 of M/500 $Na_4Mo_8O_{26}$. (2) M/20 $Na_4Mo_8O_{26}$added to 25 ml of M/125 $(CH_3COO)_2UO_2$.

pH titrations between the solutions of uranyl acetate and sodium octamolybdate did not give dependable results which may be ascribed to the very close values of pH of the two solutions.

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 presence 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.

The precipitates obtained at the end-points of the titrations of uranyl acetate with sodium molybdate at different pH levels were also analyzed by the classical methods for uranium and molybdenum. The results obtained (Table 2) confirm those obtained by the electrometric study. The analytical results obtained were also confirmed by atomic absorption spectroscopy.

The present electrometric and analytical study confirm the formation and precipitation of uranyl normal molybdate $UO_2O.MoO_3$, paramolybdate $3UO_2O.7MoO_3$ and octamolybdate $2UO_2.8MoO_3$ in the vicinity of pH 5.7, 4.6 and 3.8, respectively. As the structure of these molecules is not known, they are represented as double compounds, the way usually adopted for such compounds.[2,17]

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PRASAD, S., BARROS, J.V. Estudos Eletrométricos sobre a Formação de Molibdatos de Uranila em Função do pH. *Ecl. Quím. (São Paulo)*, v.23, p.59-70, 1998.

**RESUMO:** A formação e composição de molibdatos de uranila obtidos a partir de interação de uranila e molibdato de sódio a específicos níveis de pH 7,6; 5,5 e 4,1 foi investigada por meio de técnicas eletrométricas envolvendo titulações condutométricas e potenciométricas entre os reagentes. Os resultados obtidos fornecem evidências convincentes sobre a formação de três molibdatos de uranila com fómulas moleculares $UO_2O.MoO_3$ , $3UO_2O.7MoO_3$ e $2UO_2O.8MoO_3$ nas vizinhanças de pH 5,7 ; 4,6 e 3,8, respectivamente. Também foram realizadas investigações analíticas sobre os precipitados obtidos, que comprovam os resultados dos estudos eletrométricos.
**PALAVRAS-CHAVE:** Molibdatos; uranila; estudos eletrométricos.

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