3086 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3086—3090 (1973) [Vol. 46, No. 10

Thermometric Titration in the Investigation of the Formation of Polyanions of Molybdenum(VI), Tungsten(VI), Vanadium(V), and Chromium(VI). III. Titration of Molybdic Acid with Sodium Hydroxide Solution

Nobutoshi Kiba and Tsugio Takeuchi

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464

(Received December 21, 1972)

To define the properties of molybdenum-containing species which appear in the acidification of neutral molybdate solution with mineral acid, the reverse process, *i.e.* the titration of molybdic acid of acidified molybdate solution with sodium hydroxide, was examined and the titration curves were obtained thermometrically as well as potentiometrically. In the thermometric titration curves there are inflections not found on the pH-titration curves of the same systems. Titration curves of both methods change with molybdenum concentration, the reaction process being found to be responsible for the change. Polymolybdate anions were identified with the aid of the ultraviolet spectrophotometry of Punger *et al.* A neutral salt such as sodium perchlorate or lithium perchlorate was found to affect the shape of the thermometric titration curve, since in the presence of such salt octamolybdate ion was readily converted into heptamolybdate ion.

In a previous paper we reported on the formation of molybdenum-containing polyanions in the process of acidification of neutral molybdate solution,[1] the investigation being carried out by means of thermometric titration. The inflections on the titration curves gave useful information. The reverse reaction, *i.e.* neutralization of molybdic acid or acidified molybdate solution with alkali hydroxide, seems to be of interest in connection with the above process. We carried out the thermometric titration with a titrator of a new type.[2]

The reaction between molybdic acid and alkali hydroxide has been investigated mainly by pH-titration and conductometric titration. Cannon[3] reported two inflections at P-values 0.5 and 2.0 the alkali/Mo equivalent ratio, on the pH-titration curve of 0.310 M molybdic acid solution prepared by Auger's method.[4] He also reported that in the presence of 3 M sodium chloride the first inflection shifted to a larger P-value while the second remained unchanged. The shift was accounted for by the variation of the activity coefficient of hydrogen ion in the solution containing sodium chloride. Richardson[5] tried pH- and conductometric titrations with 2.2×10^{-1}—3.4×10^{-4} M molybdic acid prepared by an ion-exchange technique, and reported two inflections on the titration curves at P-values 0.5 and 2.0. The form of titration curve changes with the concentration of molybdic acid solution. Jain and Jain[6] carried out pH-titration with 0.018 M molybdic acid prepared by ion-exchange and also found two inflections on the titration curve at 0.5 and 2.0; in the presence of 4 M sodium chloride, the first shifted to 0.85 while the second remained constant. From the results they concluded that octamolybdate ($Mo_8O_{26}^{4-}$) exists in the initial molybdic acid solution and can be transformed into heptamolybdate($Mo_7O_{24}^{6-}$) in a medium with high ionic strength.

We observed four distinct inflections on the thermometric titration curve when acidified molybdate solution in the concentration range of molybdenum 2.29×10^{-1}—1.07×10^{-1} M was titrated with sodium hydroxide solution. The heat of the reaction of the four steps was estimated from each titration curve.[1] Richardson[5] and Heitner-Wirguin and Cohen[7] concluded that a similar equilibrium could be applied to an acidifed molybdate solution and a molybdic acid solution as a result of pH- and conductometric titrations[5] and ion-exchange technique.[7] We have examined the ionic equilibria by means of thermometric titration of acidified molybdate solution and molybdic acid solution in wide concentration ranges. The titration curves were compared with each other and also with the curve obtained by potentiometric titration. The effect of a neutral salt such as sodium perchlorate or lithium perchlorate on shape of the titration curve was also examined.

Experimental

Reagents. *Molybdic acid solution*[8]: Twenty grams of sodium molybdate dihydrate of reagent grade was dissolved in 200 ml of distilled water, and the solution was passed through a column of polystyrene cation-exchange resin (Amberlite IR-120, mesh 32—100). In order to remove sodium ion completely, the effluent was poured on the other column of the same cation-exchanger. The process was repeated till no sodium ion could be found in the effluent. 0.2 M molybdic acid solution was prepared by adjusting the volume of the solution to a definite volume. Standardization of the molybdenum content was made gravimetrically after precipitating molybdenum as 8-hydroxyquinolinate.[11]

---

1) N. Kiba and T. Takeuchi, *J. Inorg. Nucl. Chem.*, in press.

2) N. Kiba and T. Takeuchi, *Talanta*, **20**, 875 (1973).

3) P. Cannon, *J. Inorg. Nucl. Chem.*, **9**, 252 (1959).

4) V. Auger, *C. R. Acad. Sci., Paris*, **206**, 913 (1938).

5) E. Richardson, *J. Inorg. Nucl. Chem.*, **9**, 267 (1959).

6) D. V. S. Jain and C. M. Jain, *Indian J. Chem.*, **7**, 821 (1969).

7) C. Heitner-Wirguin and R. Cohen, *J. Inorg. Nucl. Chem.*, **26**, 161 (1964).

8) Sasaki and Sillén[9] prepared 1 M molybdic acid solution by the use of cation exchanger (Dowex 50 X-8). The solution was found to show a strong Tyndall effect. After being left to stand for a few days a white precipitate appeared. However, the 0.2 M molybdic acid solution we prepared was very stable, the Tyndall effect being observed eventually after ten days and no precipitate appearing after one month. We prepared a fresh solution of molybdic acid every three days and the octamer was defined as the predominant species in the solution by the differential spectrophotometric method of Pungor and Halasz.[10]

9) Y. Sasaki and L. G. Sillén, *Arkiv Kemi*, **29**, 253 (1967).

10) E. Pungor and A. Halasz, *J. Inorg. Nucl. Chem.*, **32**, 1187 (1970).

11) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., Macmillan, New York, p. 89.

Preparation of Ion-exchanger Column: The cation exchanger should be free from reducing substance. 100 ml of powdered resin was suspended in acetone for about three hours to remove acetone-soluble substance. The resin was then poured into distilled water to let the resin particles settle, followed by repeated washing with water and decantation. The resin particles were put into 0.2% potassium dichromate solution and allowed to stand for a day. A slurry of the resin was poured into a glass tube 1.5×60 cm for chromatographic use, fitted with a sintered glass filter at one end. 500 ml of 3 M hydrochloric acid and 200 ml of 2 M sodium chloride solution were passed successively through the column. 200 ml of 3 M hydrochloric acid was then passed to make the hydrogen form of resin. Finally the column was washed with distilled water to remove chloride ion.

Acidified Molybdate Solution: A sodium molybdate solution was made acidic by adding perchloric acid of 2.00 times the molarity of the molybdate. The concentration of molybdenum was determined gravimetrically in a similar manner to that described above.[11)]

All the other reagents were of guaranteed reagent grade (Wako Chemicals Co.) unless otherwise stated, and used without further purification.

Apparatus. *Thermometric titrator*: A thermometric titrator (TOA Electric Co.) was used. Construction has been described in detail.[2)]

All pH measurements were made using a Metrohm potentiograph E 336 with a glass-calomel electrode system calibrated with buffer solutions complying with accepted standards.

All spectrophotometric measurements were carried out with an automatic Shimadzu ultraviolet spectrophotometer. Silica microcuvettes of path lengths 1.0—0.02 mm were used.

Procedure. The procedure was just the same as before.[1,2)] Titration was carried out for molybdic acid in the concentration range 0.2—0.004 M. Following Richardson's prescription, the molybdic acid solution was left to stand for about twelve hours after preparation to attain homogeneity.[5)] Titration with sodium hydroxide was performed under conditions where the volume of the titrant to be required was not to exceed 10% of the total volume of the final solution in the titration cell.

The spectra of the solutions examined were measured against distilled water and neutral monomeric molybdate solution according to the method by Pungor and Halasz.[10)] All experiments were conducted at 25 °C.

Results and Discussion

Thermometric Titration Curves of Molybdic Acid and Acidified Molybdate Solution with Sodium Hydroxide. The titration curves of molybdic acid in 2.29×10^{-1} M and 4.58×10^{-3} M are shown in Figs. 1 and 2, respectively. We see four inflections in the former and two in the latter. The P-values are listed in Table 1. In consequence of the titration of acidified molybdate solution in 2.14×10^{-1} to 5.35×10^{-3} M with sodium hydroxide solution, similar titration curves to those as in the case of molybdic acid were obtained. The P-values of each titration curve are listed in Table 2. It is evident that the shape of the titration curve depends upon the initial concentration of molybdenum. A variation of the P-value could be observed in a wide range of concentration of molybdic acid rather than in that of acidified molybdate. This may be

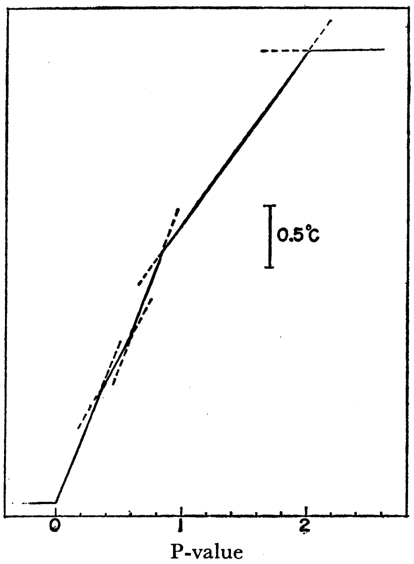

Fig. 1. Thermometric titration of 2.29×10^{-1} M molybdic acid with sodium hydroxide.
P-value=number of moles of base added per mole of molybdenum and the ordinate is relative heat change during the titration.

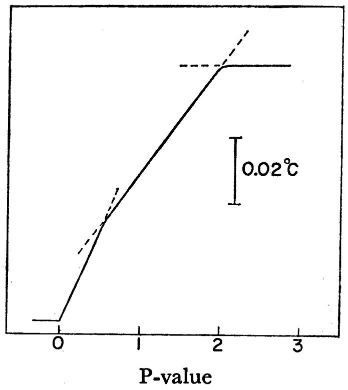

Fig. 2. Thermometric titration of 4.58×10^{-3} M molybdic acid with sodium hydroxide.

Table 1. Results of thermometric titration of molybdic acid in various concentrations with sodium hydroxide

Molybdic acid taken (mol/l)	P-value[a)] inflections 1st	2nd	3rd	4th
2.29×10^{-1}	0.375	0.571	0.857	2.00
1.14×10^{-1}	0.315	0.519	0.722	2.00
9.16×10^{-2}	0.264	0.400	0.687	2.00
6.87×10^{-2}	—	0.312	0.664	2.00
4.58×10^{-2}	—	0.304	0.658	2.00
2.29×10^{-2}	—	—	0.558	2.00
1.14×10^{-2}	—	—	0.511	2.00
9.16×10^{-3}	—	—	0.509	2.00
6.87×10^{-3}	—	—	0.503	2.00
4.58×10^{-3}	—	—	0.501	2.00

a) P-value=number of moles of base added per mole of molybenum.

Table 2. Results of thermometric titration of acidified molybdate solution[a] in various concentrations with sodium hydroxide

Molybdate taken (mol/l)	P-value inflections 1st	2nd	3rd	4th
2.14×10^{-1}	0.375	0.571	0.857	2.00
1.50×10^{-1}	0.375	0.570	0.857	2.00
1.07×10^{-1}	0.373	0.570	0.857	2.00
8.56×10^{-2}	0.366	0·549	0.850	2.00
6.56×10^{-2}	0.305	0.500	0.827	2.00
4.28×10^{-2}	—	0.463	0.689	2.00
1.07×10^{-2}	—	0.311	0.543	2.00
8.56×10^{-3}	—	—	0.527	2.00
5.35×10^{-3}	—	—	0.508	2.00

a) The ratio of acid added to molybdate in an acidified molybdate solution is 2.00.

attributed to the variation of ionic strength during the titration of molybdic acid solution, since in the latter case sodium ion is initially present in the solution and the change of ionic strength is relatively small. Thus, the shape of the titration curve seems to be determined not only by the concentration of molybdic acid taken initially but by the variation of the ionic strength in the solution during titration.

pH-Titration Curves of Molybdic Acid and Acidified Molybdate Solution with Sodium Hydroxide. The pH-titration curves of molybdic acid in the range 2.10×10^{-1}—4.20×10^{-3} M are shown in Fig. 3. Two inflections can be seen in all of them. The P-values of the inflections estimated by secondary differentiation of the curve are shown in Table 3. In the pH-titration of acidified molybdate solution in the range 2.14×10^{-1}—5.35×10^{-3} M with sodium hydroxide, similar titration curves were obtained. The P-values of the inflections are listed in Table 4.

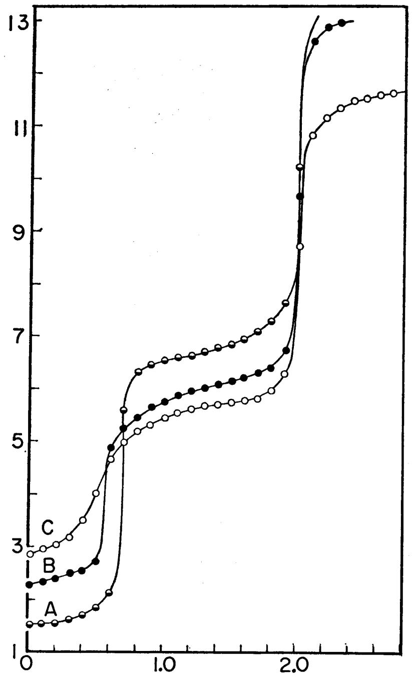

Fig. 3. pH-titration of
A: 100 ml 0.210 M molybdic acid with 2.14 M NaOH
B: 100 ml 0.0420 M molybdic acid with 0.42 M NaOH
C: 100 ml 0.00420 M molybdic acid with 0.042 M NaOH

Table 3. Results of pH-titration of molybdic acid in various concentrations with sodium hydroxide

Molybdic acid taken (mol/l)	P-value 1st inflection	2nd inflection
2.10×10^{-1}	0.66	2.0
1.05×10^{-1}	0.63	2.0
9.03×10^{-2}	0.63	2.0
6.45×10^{-2}	0.61	2.0
4.20×10^{-2}	0.59	2.0
2.10×10^{-2}	0.54	2.0
1.05×10^{-2}	0.52	2.0
6.45×10^{-3}	0.51	2.0
4.20×10^{-3}	0.50	2.0

Table 4. Results of pH-titration of acidified molybdate solution in various concentrations with sodium hydroxide

Molybdate taken (mol/l)	P-value 1st inflection	2nd inflection
2.14×10^{-1}	0.64	2.0
1.50×10^{-1}	0.63	2.0
1.07×10^{-1}	0.63	2.0
8.56×10^{-2}	0.61	2.0
6.56×10^{-2}	0.60	2.0
4.28×10^{-2}	0.57	2.0
1.07×10^{-2}	0.52	2.0
8.56×10^{-3}	0.52	2.0
5.35×10^{-3}	0.51	2.0

We see that the P-value of the second inflection was held constant at about 2.0, while that of the first inflection was 0.6 in higher and 0.5 in lower concentration of molybdic acid. Previous investigations[3] showed that the first inflection does not depend on the concentration of molybdic acid, its P-value being held constant at 0.5, potentiometrically and conductometrically. However, Heitner-Wirguin and Cohen reported variations of the P-values of both the first and second inflections with the concentration of molybdic acid from their results on the pH-titration of molybdic acid with sodium hydroxide solution.[7] This discrepancy is difficult to interpret because of the lack of understanding of the chemical species existing in the solution or appearing during the course of titration.

Richardson[5] pointed out that the variety of titration curves might result to some extent from the hydrolysis of the salt formed in a dilute solution. He assumed the hydrolysis from the results of his conductometric titration of molybdic acid with sodium hydroxide solution, in which a variation of titration curves was found in every case. We proposed a different assumption from his, since the variation of titration curves, either potentiometric and thermometric, depends upon the initial concentration of molybdic acid or acidified molybdate. The variation should show a difference in the reaction process in each case. The chemical species existing in the solution before titration was identified by spectrophotometry as octamolybdate ion and that after titration monomeric molybate ion.[9)]

From Tables 1—4 and spectrophotometric measurements, we conclude that the titration of about 2×10^{-1} M molybdic acid or acidified molybdate solution with sodium hydroxide solution might proceed through the following four reaction process:

$$H_4Mo_8O_{26} + 3OH^- = HMo_8O_{26}{}^{3-} + 3H_2O \quad (P=0-0.375) \qquad (1)$$

$$7HMo_8O_{26}{}^{3-} + 11OH^- = 8H_2Mo_7O_{24}{}^{4-} + H_2O \quad (P=0.375-0.571) \qquad (2)$$

$$H_2Mo_7O_{24}{}^{4-} + 2OH^- = Mo_7O_{24}{}^{6-} + 2H_2O \quad (P=0.571-0.857) \qquad (3)$$

$$Mo_7O_{24}{}^{6-} + 8OH^- = 7MoO_4{}^{2-} + 4H_2O \quad (P=0.857-2.00) \qquad (4)$$

On the other hand, in the titration of *ca.* 5×10^{-3} M molybdic acid or acidified molybdate solution, P-values of the inflections seem to prove the existence of two reaction processes:

$$H_4Mo_8O_{26} + 4OH^- = Mo_8O_{26}{}^{4-} + 4H_2O \quad (P=0-0.500) \qquad (5)$$

$$Mo_8O_{26}{}^{4-} + 12OH^- = 8MoO_4{}^{2-} + 6H_2O \quad (P=0.500-2.00) \qquad (6)$$

It is supposed that in the range above 4×10^{-2} M reactions (1)—(4) are predominant and (5) and (6) subdominant, while below that concentration reactions (5) and (6) become predominant and (1)—(4) subdominant.

Titration of Molybdic Acid with Sodium Hydroxide Solution in the Presence of Sodium Perchlorate or Lithium Perchlorate. Molybdic acid of concentrations 2.00×10^{-1}—2.00×10^{-2} M in 4 M sodium perchlorate solution was titrated with sodium hydroxide solution and thermometric titration curves were obtained; the curve of 2.00×10^{-1} molybdic acid is shown in Fig. 4 and that of 2.00×10^{-2} M molybdic acid in Fig. 5. P-values of the inflections of titration curves for molybdic acid in various concentrations are given in Table 5. Three inflections were observed in the case of 2.00×10^{-1} M molybdic acid. In the case of 2.00×10^{-2} M, the P-value of the first inflection was 0.856, but 0.542 in absence of sodium perchlorate. The pH-titration curves were also obtained under the same conditions for 2.00×10^{-1}—2.00×10^{-2} M molybdic acid in 4 M sodium perchlorate solution. Each titration curve was similar to the corresponding one of the pH-titration curves (Fig. 3). The P-values of the inflections of the curves are given in Table 6. The influence of sodium perchlorate on the P-values of the first inflections seems to be important in various concentrations of molybdic acid.

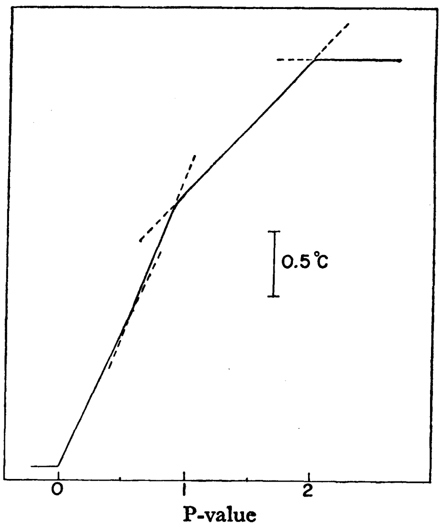

Fig. 4. Thermometric titration of 2.00×10^{-1} M molybdic acid with sodium hydroxide in the presence of 4.0 M sodium perchlorate.

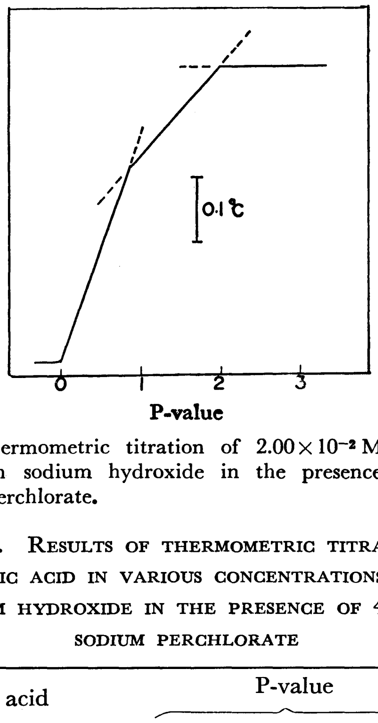

Fig. 5. Thermometric titration of 2.00×10^{-2} M molybdic acid with sodium hydroxide in the presence of 4.0 M sodium perchlorate.

TABLE 5. RESULTS OF THERMOMETRIC TITRATION OF MOLYBDIC ACID IN VARIOUS CONCENTRATIONS WITH SODIUM HYDROXIDE IN THE PRESENCE OF 4.0 M SODIUM PERCHLORATE

Molybdic acid taken (mol/l)	P-value		
	1st inflection	2nd inflection	3rd inflection
2.00×10^{-1}	0.602	0.857	2.00
1.00×10^{-1}	0.670	0.857	2.00
3.00×10^{-2}	0.735	0.857	2.00
6.00×10^{-2}	0.814	0.858	2.00
4.00 ± 10^{-2}	0.835	0.857	2.00
2.00 ± 10^{-2}	—	0.856	2.00

We examined exclusively the first inflections of the thermometric titration curves for 2.00×10^{-2} M molybdic acid in the presence of the perchlorate in varying concentrations. The results are shown in Table 7. The second inflection remained constant at the P-value of 2.00 in all runs. We see that the amount of neutral salt necessary to change the P-value of the first inflection from 0.542 to 0.856 differs for sodium and lithium salts, *i.e.*, above 3.0 M of sodium

Table 6. Results of pH-titration of molybdic acid in various concentrations with sodium hydroxide in the presence of 4.0 M sodium perchlorate

Molybdic acid taken (mol/l)	*P*-value	
	1st inflection	2nd inflection
2.00×10^{-1}	0.81	2.0
1.00×10^{-1}	0.82	2.0
8.00×10^{-2}	0.82	2.0
6.00×10^{-2}	0.82	2.0
4.00×10^{-2}	0.84	2.0
2.00×10^{-2}	0.84	2.0

Table 7. Salt-effect of sodium perchlorate and lithium perchlorate on P-value of the first inflection of the thermometric titration curve
Molybdic acid: 2.00×10^{-2} M

Perchlorate taken (mol/l)	P-value of the first inflection
none	0.542
Sodium perchlorate	
0.5	0.747
1.0	0.765
1.5	0.783
2.0	0.843
2.5	0.850
3.0	0.858
3.5	0.857
4.0	0.858
4.5	0.858
Lithium perchlorate	
1.1	0.702
1.7	0.730
2.2	0.768
2.8	0.779
3.3	0.788
3.9	0.831
4.4	0.857
5.0	0.857

perchlorate and above 4.4 M of lithium perchlorate. The difference of salt concentration between sodium perchlorate and lithium perchlorate required to display the salt effect sufficiently seems therefore to be in conflict with Cannon's interpretation of the salt effect, for which discussion was given only from the data in the presence of sodium chloride. The difference might be caused by the extent of protonation of molybdate owing to the difference in hydration of cations and anions of the salt added.[7] We have obtained the spectrum with only a well defined maximum at 258 mμ in the absorption of 2.00×10^{-2} M molybdic acid in 4 M sodium perchlorate solution against sodium monomeric molybdate in the region 210—330 mμ.[11] The molybdenum-containing species in this solution was revealed as being heptamolybdate ion and not octamolybdate ion. This shows the validity of the assumption on salt effect described by Jain and Jain.[6] Thus, we concluded that the reactions proceeding in the titration of 2.00×10^{-2} M molybdic acid in 3 M sodium perchlorate or in 4.4 M lithium perchlorate with sodium hydroxide solution might consist of the following two steps:

$$H_6Mo_7O_{24} + 6OH^- = Mo_7O_{24}^{6-} + 6H_2O \quad (P=0-0.857)$$

$$Mo_7O_{24}^{6-} + 8OH^- = 7MoO_4^{2-} + 4H_2O \quad (P=0.857-2.00)$$