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The Formation and Structure of Phosphomolybdic Acids in Aqueous Solutions

Taitiro FUJINAGA, Mutsuo KOYAMA and Toshitaka HORI

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The formation of phosphomolybdic acid has widely been utilized in the separation and the determination of phosphate ions. However, the optimum conditions presented so far, have been determined empirically and contradict one to the others, because of the lack of knowledges on the species of the acid formed in solutions. In the present paper, the authors demonstrate that the solution always contains a series of species of phosphomolybdic acids in equilibrium; especially noticeable at around pH 3 are the one which absorbs light at 255 nm and is predominantly found when [P]/[Mo]>1, and the other which absorbs light at 310 nm and becomes the major component when [P]/[Mo]<1/15.

The structure and the reaction mechanism of the formation of phosphomolybdic acids are discussed in comparison with heteropoly acids formed with phosphorous and pyrophosphoric acids.

INTRODUCTION

The fact that phosphate ions react with molybdate ions in acidic solutions to give yellow heteropoly acid has been utilized for the separation and determination of phosphate ions, especially for the spectrophotometric determination of traces of the ions.

However, as for the structure of phosphomolybdic acid in aqueous solutions is concerned, it has not fully been understood. The reason is mainly ascribed to the fact that the chemical and physical properties of phosphomolybdic acid are very close to those of reagent molybdic acids which always must be present in a large excess. The solution of each acid exhibits absorption spectra in the full ultra violet region, although they are different in shape. So, most of spectrochemical studies on phosphomolybdic acid have been confined to the visible region where the absorption on molybdic acid becomes less significant than that of phosphomolybdic acid.

On the other hand, it has been well known that the phosphomolybdic acid formed in aqueous solutions can be extracted quantitatively into ethers, alcohols or esters and the extract freed from molybdate ions shows the absorption maximum at 310 nm. The phosphomolybdic acid extracted with organic solvents has the molar ratio of P:Mo=1:12. As the result of x-ray analysis of the acid crystal, it is known that the compound has the so called "Keggin's structure.[1]"

In the present work, the authors have found the optimum conditions to study the phosphomolybdic acid without adding a large excess of the reagent. By the finding of the optimum experimental condition where pH of the solution was restricted between 2.8 and 4.0 and the concentration of molybdate ions between 10^{-3} and 10^{-4} M, it became possible to observe its absorption spectrum in the full ultra violet region. Through these observations, it is demonstrated that there must be

藤永太一郎，小山睦夫，堀智孝: Department of Chemistry, Faculty of Science, Kyoto University, Kyoto.

present at least two kinds of phosphomolybdic acid which are distinguishable spectroscopically and show absorption maxima at 255 nm and at 310 nm respectively. The natures and structures of the two species are also discussed in the present paper, together with heteropoly acid formed with pyrophosphate and phosphite ions.

REAGENTS AND APPARATUS

Reagents

Phosphate Ion Standard Solution: 1.361g of reagent grade potassium dihydrogen phosphate KH_2PO_4 was dissolved with water and diluted to 1 liter to prepare the 1.000×10^{-2}M stock solution. The solution was diluted properly for the use in the experiments. Its exact concentration was determined gravimetrically.[2]

Phosphite Ion Standard Solution: 2.237 g of reagent grade sodium hydrogen phosphite Na_2HPO_3 was dissolved with water and diluted to 1 liter to make the 1.000×10^{-2}M solution just before use. The exact concentration was checked by gravimetry in the form of phosphate ions after oxidizing it with hydrogen peroxide.

Pyrophosphate Ion Standard Solution: 4.277 g of sodium pyrophosphate $Na_4P_2O_7$ was dissolved and diluted with pure water to make the 1 liter solution of 1.000×10^{-2} M. The concentration was checked by gravimetric method after hydrolyzing pyrophosphate ions into phosphate ions with nitric acid.

Molybdate Standard Solution: 2.420 g of reagent grade sodium molybdate $Na_2MoO_4\cdot2H_2O$ was dissolved with water to make 1 liter of the 1.000×10^{-2} M stock solution.

Phosphomolybdic Acid Crystals: Phosphomolybdic acid $H_3P_2Mo_{24}O_{40}\cdot nH_2O$ was synthesized according to the method of Wu.[3]

Other Reagents and Chemicals: Reagent grade sodium hydroxide, perchloric acid *etc.* were used for the experiments. All the solutions were stored in the bottles made of polyethylene to avoid any possible contamination of silicate ions caused by the dissolution of glass.

Water: Deionized water was twice distilled with a pyrex glass distillation apparatus.

Apparatus

The pH of the solution was measured by a Hitachi-Horiba pH-meter type M–4. Absorption spectra were recorded with a Shimadzu Automatic Recording Spectrophotometer type SV–50A and a Manual Spectrophotometer QR–50.

EXPERIMENTALS

General Experimental Procedures

Measured quantities of the solutions of phosphoric acid, phosphorous acid, pyrophosphoric acid and/or molybdic acid were pipetted out into a 100 ml polypropylene beaker. The solution was diluted with pure water to a volume of approximate 90 ml. The pH of the solution was adjusted with 1N-$HClO_4$ or 1N-NaOH to a definite value using the pH-meter. The solution was then transferred to a 100 ml measuring flask and diluted exactly to the mark with pure water. The absoption

spectrum was obtained with an aliquot of the solution. The temperature of the solution was maintained exactly at 25±1°C by flowing water of the constant temperature through the holder of the optical cell. Qualtz cells of 50.0 mm, 10.0 mm or 2.0 mm were used according to the concentration of the sample. In the measurement of difference spectra or in the analysis of continuous variation methods, appropriate reference solutions were used. However, water was the reference in the measurement of most of absorption spectra unless otherwise stated.

RESULTS AND DISCUSSION

1) Reversibility of formation and decomposition of phosphomolybdic acid.

40 mg of synthesized phosphomolybidc acid was dissolved and diluted to 500 ml with water, whose pH was measured to be 3.8. The pH of the solution was changed between 12 and 1 by the use of 5N-NaOH and 5N–$HClO_4$. The absorption spectra measured are shown in Fig. 1: As is seen in the Figure, the spectrum changes from curve *a* to *d* which correspond to those of the solutions kept at pH values 3.8, 4.5, 5.6 and 1.9 respectively. Above pH 5.6 the phosphomolybdic acid seems to decompose into simple molybdate ions and phosphate ions, because all the spectra conform to the curve *c* which is due to the absorption of molybdate anion MoO_4^{2-}. The shapes of the spectra are only dependent upon the pH value of the solution at the fixed concentration of phosphomolybdic acid dissolved, even when the pH of

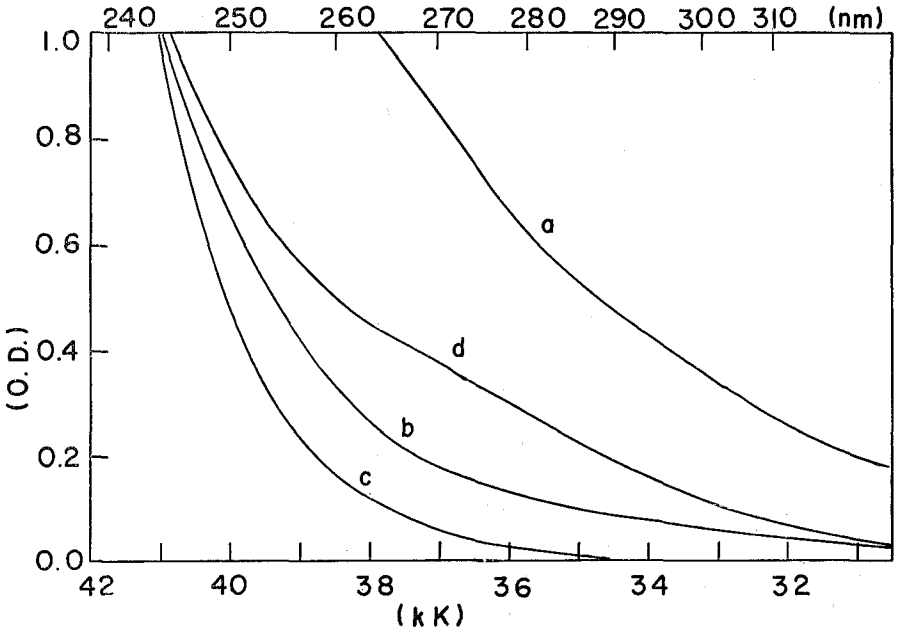

Fig. 1. Spectra of phosphomolybdic acid dissolved in aqueous solutions.
concn. of phosphomolybdic acid: 40 mg/500 ml, light pass: 10.0 mm
a: pH 3.8 **b**: 4.5 **c**: pH above 5.6 **d**: 1.9

the solution was changed in a cyclic manner, for example, from acidic to alkaline and vice versa. The fact indicates that the formation and decomposition of the phosphomolybdic acid is reversible without showing any hysteresis. So far as phosphomolybdic acid is concerned, the solution in which corresponding amounts of molybdate and phosphate ions are added separately exhibits the same spectrum as the solution prepared by dissolving phosphomolybdic acid crystals. In the following experiments, the acidified mixture of molybdate and phosphate ion solution was used instead of the solution of phosphomolybdic acid crystal. In contrast to phosphomolybdic acid, Strickland[4] reported that silicomolybdic acid solution prepared by dissolving the crystal showed different spectra from those prepared by mixing silicate and molybdate solutions.

2) **Absorption spectra of phosphomolybdic acid formed in solutions.**

Absorption spectra of the solutions of molybdic acid (5×10^{-4} M) and those of the mixture of phosphoric acid (5×10^{-5} M) and molybdic acid (5×10^{-4} M) were shown in Fig. 2. The difference spectrum shows more clearly the difference between molybdic and phosphomolybdic acid which has the characteristic absorption maxima at 310 nm and 255 nm.

In order to determine the optimum pH for the formation of phosphomolybdic acid, the absorbance at 310 nm against the pH of the solution is plotted as in Fig. 3. Fig. 4 shows the plot of the absorbance at 255 nm. In these Figures, the differences

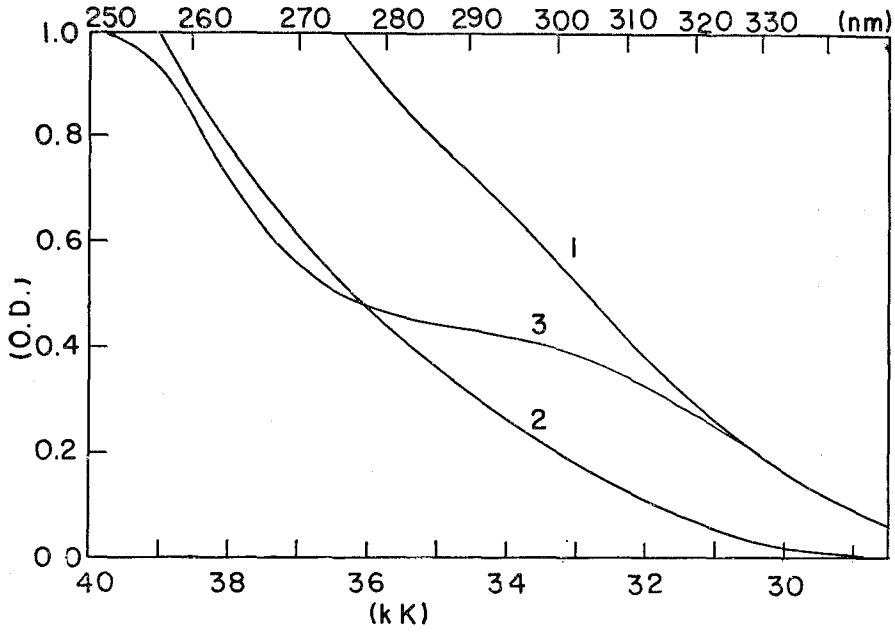

Fig. 2. Spectra of molybdic acid and phosphomolybdic acid formed in aqueous solutions. light pass: 10.0 mm, pH: 3.0
1: 5×10^{-4}M $[MoO_4^{2-}]+5\times10^{-5}$M $[PO_4^{3-}]$
2: 5×10^{-4}M $[MoO_4^{2-}]$
3: difference spectrum of *1* against *2*

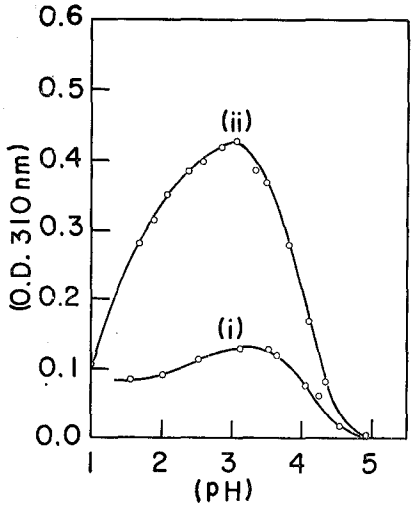

Fig. 3. Variation of absorbance of molybdic acid and phosphomolybdic acid at 310 nm.
light pass: 10.0 mm
(i) 5×10^{-4}M $[MoO_4^{2-}]$
(ii) 5×10^{-4}M $[MoO_4^{2-}]+5\times10^{-5}$M $[PO_4^{3-}]$

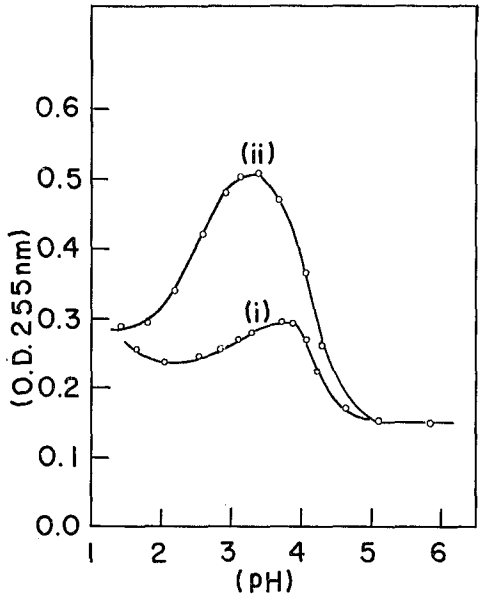

Fig. 4. Variation of absorbance of molybdic acid and phosphomolybdic acid at 255 nm.
light pass: 10.0 mm
(i) 2×10^{-4}M $[MoO_4^{2-}]$
(ii) 2×10^{-4}M $[MoO_4^{2-}]+2\times10^{-5}$M $[PO_4^{3-}]$

of the two curves (i) and (ii) correspond to the amount of phosphomolybdic acid formed at the corresponding pH. It is shown that in both wave lenghs the amount of the phosphomolybdic acid formed reaches to the maximum at the pH ranging form 3.0 to 3.5.

3) **Species of phosphomolybdic acids formed in aqueous solutions.**

In order to determine whether two maxima at 310 nm and 255 nm belong to the same species or to different ones, relations between the shape of the spectrum and the [P]:[Mo] ratios of the solutions were examined at pH 3.0. The [P]:[Mo] ratio was changed from 40:1 to 1:40. Representative spectra are shown in Fig. 5 and Fig. 6.

In Fig. 5, spectra of molybdic acid and of the mixture of molybdic acid (5×10^{-4}M) and phosphoric acid (1.2×10^{-3}M) are shown; Curve 2 represents the spectrum of molybdic acid, curve 1 that of mixture and 3 the difference spectrum of 1 against 2. Although the difference spectra may not show the exact spectra of phosphomolybdic acid because of the over-subtraction of absorption caused by molybdic acid at shorter wave length, they are useful in examining the difference between phosphomolybdic acid and molybdic acid. The mixture having the ratio ([P]:[Mo]=2.4:1) shows one absorption maximum at 255 nm. When the [P]:[Mo] ratio was varied to 1:20 or 1:40, another absorption maximum appeared at 310 nm as is shown in Fig. 6. It was observed that the maximum at 310 nm becomes larger while the one at 255 nm becomes smaller, on increasing the concentration of

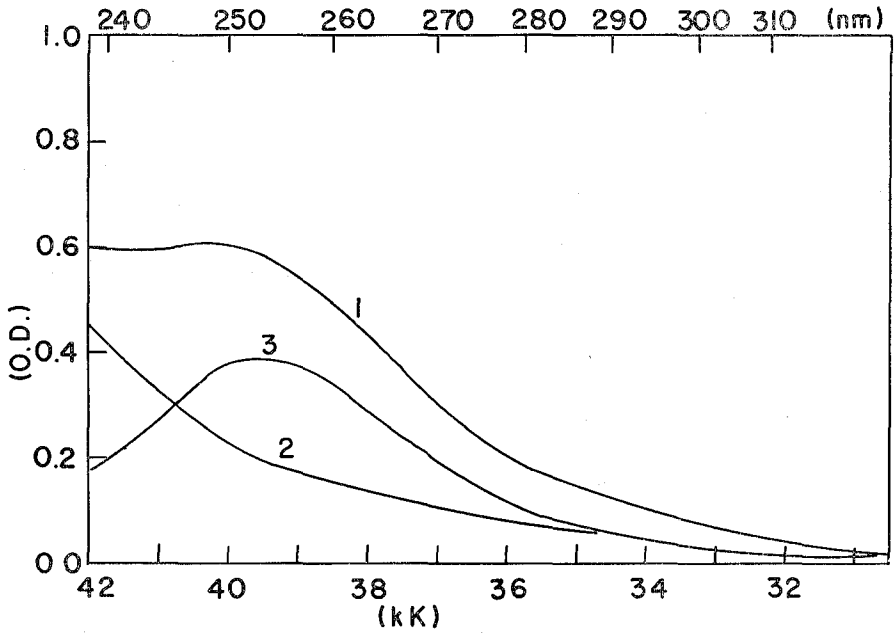

Fig. 5. Spectra of molybdic acid and phosphomolybdic acid formed in aqueous solutions ($[PO_4^{3-}]:[MoO_4^{2-}]=2.4:1$)
light pass: 2.0 mm, pH 3.0
1: 5×10^{-4}M $[MoO_4^{2-}]+1.2\times10^{-3}$M $[PO_4^{3-}]$ *2*: 5×10^{-4}M $[MoO_4^{2-}]$
3: difference spectrum of *1* against *2*

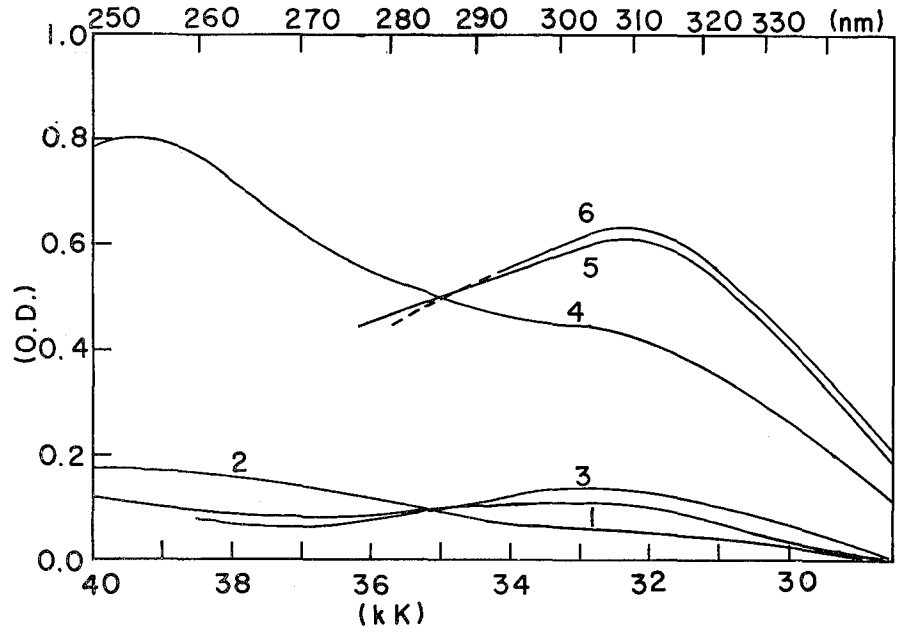

Fig. 6. Difference spectra of phosphomolybdic acid formed in aqueous solution ($[PO_4^{3-}]:[MoO_4^{2-}]=1:10$, $1:20$ and $1:40$)
light pass: 2.0 mm, pH 3.0
1: 5×10^{-5}M $[PO_4^{3-}]+5\times10^{-4}$M $[MoO_4^{2-}]$ *2*: 5×10^{-5}M $[PO_4^{3-}]+1\times10^{-3}$M $[MoO_4^{2-}]$
3: 5×10^{-5}M $[PO_4^{3-}]+2\times10^{-3}$M $[MoO_4^{2-}]$ *4*: 2.5×10^{-4}M $[PO_4^{3-}]+2.5\times10^{-3}$M $[MoO_4^{2-}]$
5: 2.5×10^{-4}M $[PO_4^{3-}]+5\times10^{-3}$M $[MoO_4^{2-}]$ *6*: 2.5×10^{-4}M $[PO_4^{3-}]+1\times10^{-2}$M $[MoO_4^{2-}]$

molybdate ions relative to that of phosphate ions. The fact means that the two maxima belong to the different species; one which shows the maximum at 310 nm combines with more molybdate ions and the other combines with fewer molybdate ions, respectively.

The continuous variation method and the molar ratio method were applied to the solution of the acid in order to determine the compositions of complexes. The complex showing the maximum at 310 nm (abbreviate as PO_4-Mo(II)) has the composition P:Mo=1:12 as is shown in Fig. 7 and Fig. 8. It seems probable that

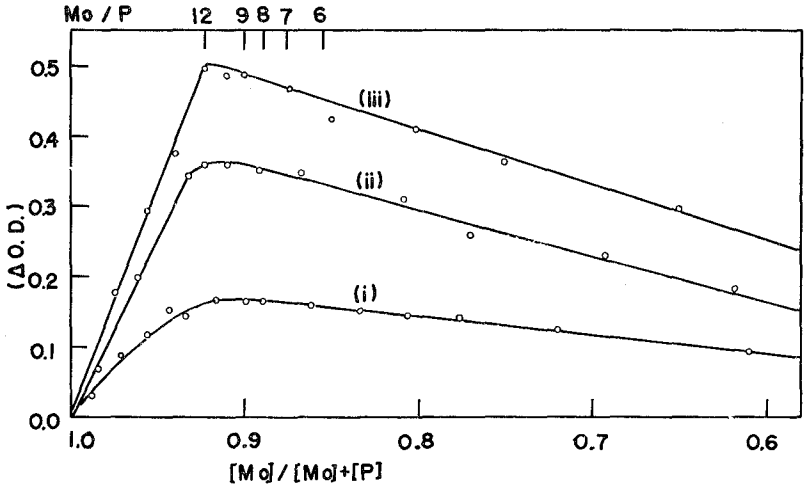

Fig. 7. Determination of composition of PO_4-Mo (II) by continuous variation method at 310 nm or at 290 nm.
light pass: 10.0 mm pH 3.0
(i) $[PO_4^{3-}]+[MoO_4^{2-}]=3.6\times10^{-4}$M, 310 nm
(ii) $[PO_4^{3-}]+[MoO_4^{2-}]=5.2\times10^{-4}$M, 290 nm
(iii) $[PO_4^{3-}]+[MoO_4^{2-}]=8.0\times10^{-4}$M, 310 nm

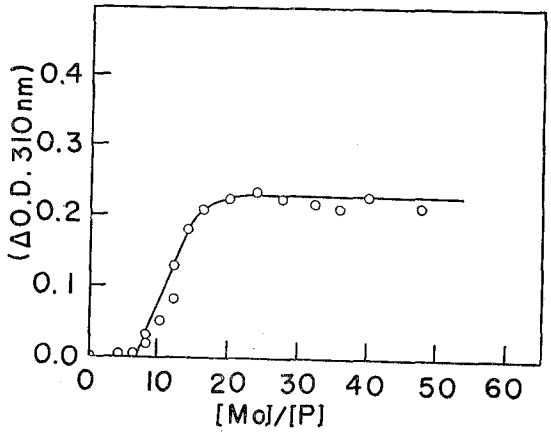

Fig. 8. Determination of composition of PO_4-Mo (II) by molar ratio method at 310 nm.
ligh pass: 2.0 mm, pH 3.0
concn. of PO_4^{3-} : 2×10^{-5}M (constant)

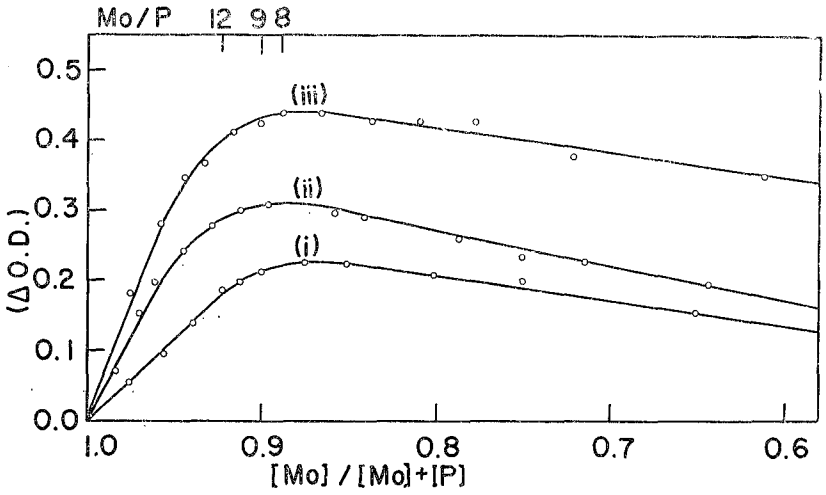

Fig. 9. Determination of composition of PO_4-Mo (I) by continuous variation method at 255 nm.
pH 3.0
(i) $[PO_4^{3-}]+[MoO_4^{2-}]=8.0\times10^{-4}$M, 2.0 mm
(ii) $[PO_4^{3-}]+[MoO_4^{2-}]=2.8\times10^{-4}$M, 10.0 mm
(iii) $[PO_4^{3-}]+[MoO_4^{2-}]=3.6\times10^{-4}$M, 10.0 mm

the complex is similar to the phosphomolybdic acid which is well known as "Keggin's structure[1]", because its absorption spectra is very alike to that of the complex extracted into organic solvents such as ethers or alcohols.

On the other hand, the complex showing the maximum at 255 nm (abbreviate as PO_4-Mo(I)) has a composition of smaller number of molybdate ions per one phosphate ion. The Mo/P ratio is less than 12/1 or, probably 9/1 or 8/1 according to Fig. 9. The assumption mentioned above is supported by the experiments with phosphorous acid and pyrophosphoric acid, both of which are not able to form the complex of Keggin's structure as is described later.

4) Heteropoly acid formed with phosphorous acid and pyrophosphoric acid

Similar experiments to those of orthophosphate ions were performed on phosphite and pyrophosphate ions. Figure 10 shows the absorption spectra of molybdic acid (2×10^{-4}M) and the mixture of molybdic acid (2×10^{-4}M) and phosphorous acid (1.0×10^{-4}M). The spectra exhibits one absorption maximum at 255 nm irrespective of the composition and the concentration of the solution. Therefore in the case of phosphorous acid (abbreviated as PO_3-Mo), differing from the case of phosphomolybdic acid where two species always exist, the formation of only one sort of complex is possible. The continuous variation method was applied again to determine the composition of PO_3-Mo and the part of the results is represented in Figure 11, which demonstrates that the ratio (PO_3/Mo) is in between 1/7 and 1/6. This means that phosphite ion requires six molybdate ions, while phosphate ion combines with eight (PO_4-Mo(I)) or twelve (PO_4-Mo(II)) molybdate ions.

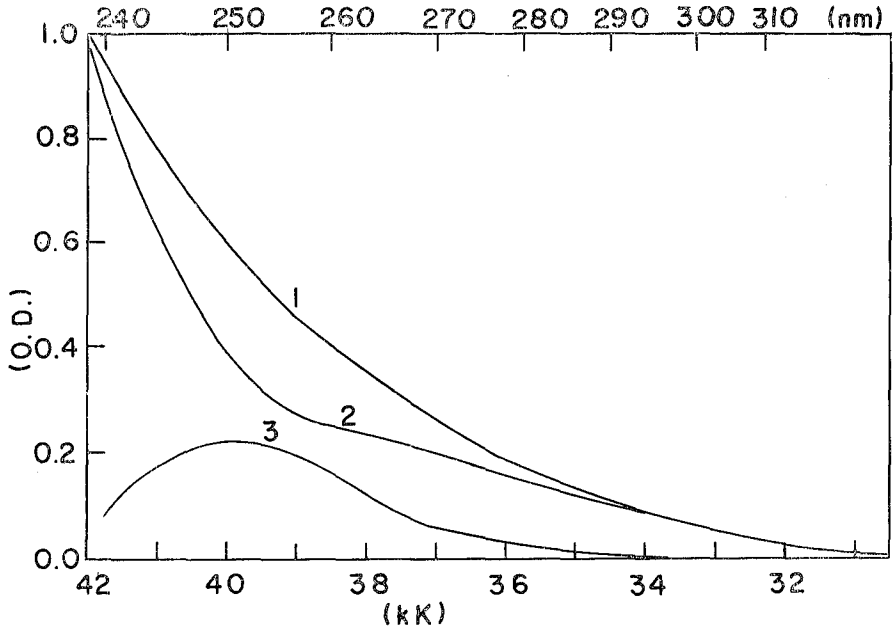

Fig. 10. Spectra of molybdic acid and a complex formed between phosphite and molybdate ions (PO_3-Mo).
pH 3.0, light pass: 10.0 mm
1: 1.0×10^{-4}M $[HPO_3^{2-}]+2.0\times10^{-4}$M $[MoO_4^{2-}]$
2: 2.0×10^{-4}M $[MoO_4^{2-}]$
3: difference spectrum of *1* against *2*

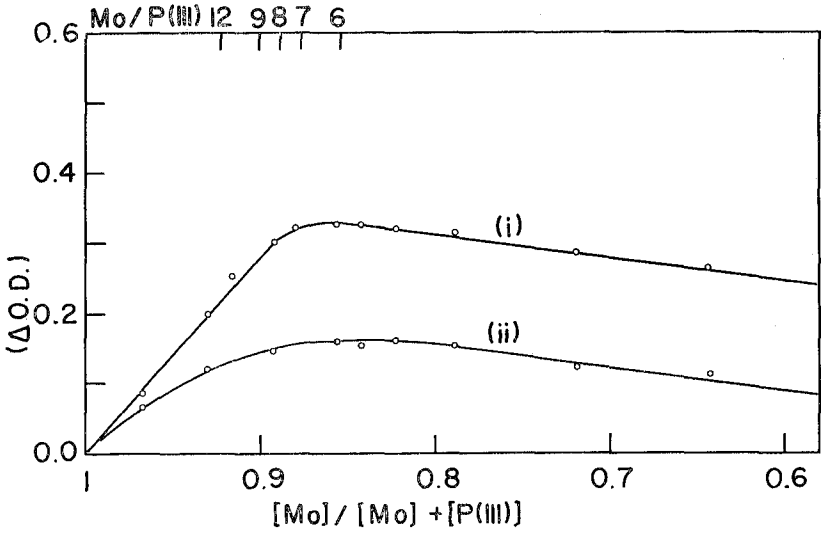

Fig. 11. Determination of composition of PO_3-Mo by continuous variation method at 255 nm. pH 3.0
(i) $[HPO_3^{2-}]+[MoO_4^{2-}]=1.4\times10^{-3}$M, 2.0 mm
(ii) $[HPO_3^{2-}]+[MoO_4^{2-}]=2.8\times10^{-4}$M, 10.0 mm

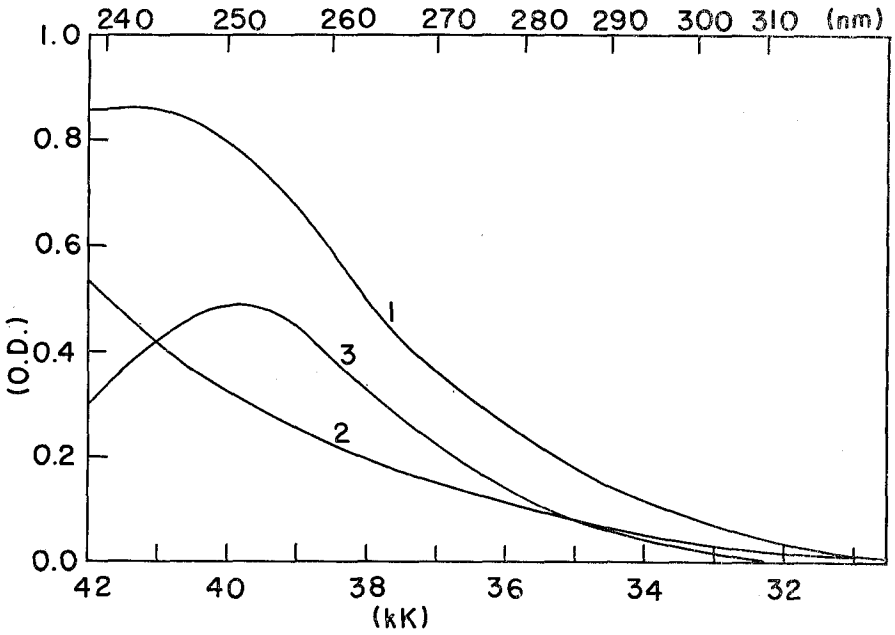

Fig. 12. Spectra of molybdic acid and a complex formed between pyrophosphate and molybdate ions (P_2O_7-Mo).
light pass: 2.0 mm, pH 3.0
1: 2×10^{-4}M $[P_2O_7^{4-}]+6.0\times10^{-4}$M $[MoO_4^{2-}]$
2: 6.0×10^{-4}M $[MoO_4^{2-}]$
3: difference spectrum of *1* against *2*

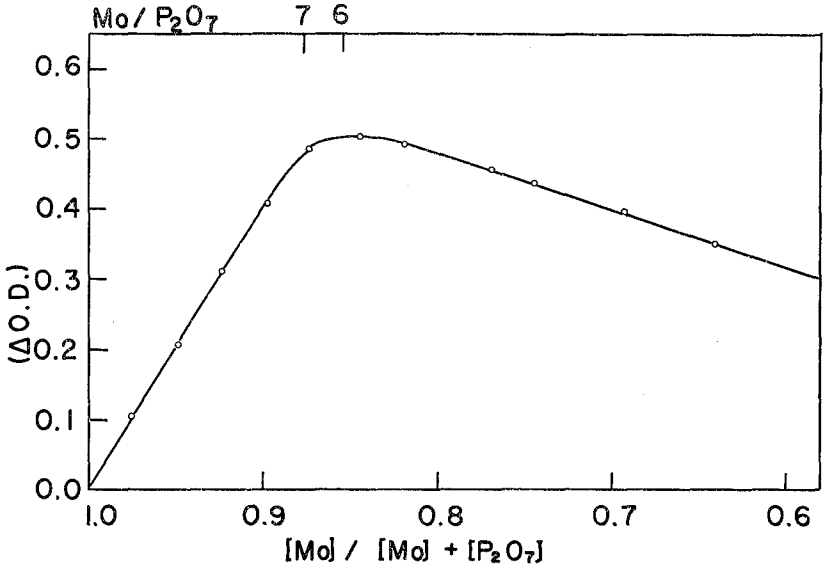

Fig. 13. Determination of composition of P_2O_7-Mo by continuous variation method at 255 nm.
light pass: 2.0 mm, pH 3.0,
$[P_2O_7^{4-}]+[MoO_4^{2-}]=7.8\times10^{-4}$M

As is shown in Fig. 12, pyrophosphate ions also combines with molybdate ions to form a sort of complex of which absorption spectrum is similar to that of PO_3-Mo. The continuous variation method was performed on pyrophosphoric acid, and the result is shown in Fig. 13, which demonstrates that the ratio P_2O_7/Mo in pyrophosphomolybdic acid (abbreviate as P_2O_7-Mo) is 1/6. The formation constant is much larger than that of PO_4-Mo(I) and PO_3-Mo.

5) Structures of PO_4-Mo(I), PO_4-Mo(II), PO_3-Mo and P_2O_7-Mo

As is disscussed in the chapter 3, PO_4-Mo(II) corresponds to the compound of Keggin's structure. However, the structural analysis of other species PO_4-Mo(I) is not easily possible. The similarity of the spectrochemical nature of three phosphomolybdic acids *i.e.* PO_4-Mo(I), PO_3-Mo and P_2O_7-Mo suggests the possibility of the following deduction.

As the difference of phosphoric acid and phosphorous acid is ascribed to the number of P-O bonding *i.e.* four bondings in the former and three in the latter. Experimental facts indicate that one P-O bonding requires two molybdenum atoms, in other words, one oxygen in phosphate group combines with one molybdic acid dimer, whose characteristic absorption maximum appears at 255 nm. In the case of phosphoric acid, PO_4-Mo(I) can combine with two more molybdic dimer per one molecule to complete the symmetric Keggin's structure (PO_4-Mo(II)) which absorbs light at longer wave length (310 nm). On the other hand, phosphorous and pyrophosphoric acids can not combine with more molybdic acid owing to the presence of P-H and P-O-P bondings respectively, which inhibit the formation of symmetric structure.

In conclusion, the most probable structure for these heteropoly acids are illustrated in Fig. 14.

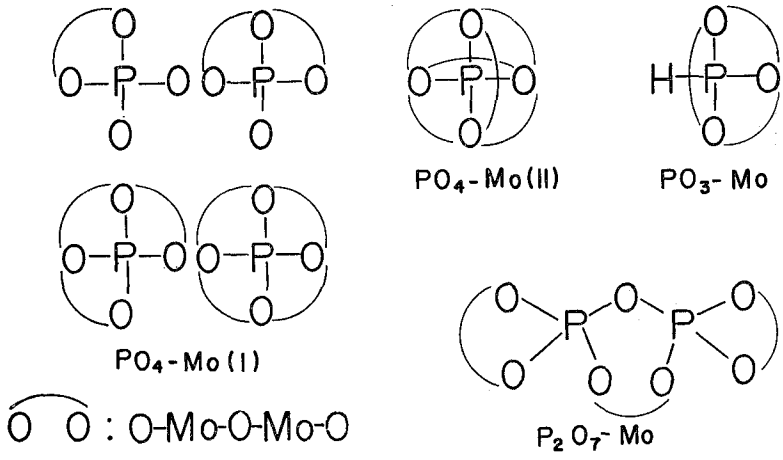

Fig. 14. Illustrations of probable structures of PO_4-Mo (I), PO_4-Mo (II), PO_3-Mo and P_2O_7-Mo.

CONCLUSION

As shown in Fig. 3 and Fig. 4, absorbances of molybdic acid and phosphomolybdic acid solutions at 310 nm and 255 nm change markedly with decreasing pH of the solution. The formation of PO_4-Mo(I) and PO_4-Mo(II) seems to be related to the spectral change of molybdic acid solution, in other words, a kind of species of molybdic acid being formed. Phosphate ion combine with the molybdate species to give a series of phosphomolybdic acids (PO_4-Mo(I)) stepwisely and finally reache to PO_4-Mo(II). The former compound is analogous to PO_3-Mo or P_2O_7-Mo in the structure and in the spectral nature.

Under the constant pH value 3.0, both PO_4-Mo(I) and PO_4-Mo(II) coexist in equilibrium, and the equilibrium shifts a little to the formation of PO_4-Mo(II) by adding excess molybdic acid. As is shown in Fig. 6, PO_4-Mo(II) which absorbs light at 310 nm with the molar absorption coefficient 23,000 $M^{-1}L^{-2}$ was not formed fully, even in the presence of a large excess molybdic acid, so far as the pH is kept 3.0. The fact means the formation of phosphomolybdic acids depends on the formation of a unique molybdic acid species. Actually, when pH was decreased in the presence of a large excess of molybdic acid, PO_4-Mo(II) is formed nearly fully.

Although the existence of a unique molybdic acid species was assumed as described above, the structure and the composition of the acid were left unresolved.

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