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Raman Studies on the Identification of Isopolymolybdates in Aqueous Solution

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Molybdenum(VI) solutions were investigated in detail by Raman spectroscopy with a view to establishing the speciation of the predominant polynuclear species (isopolymolybdates) formed in aqueous solution. The most intense Raman frequencies due to asymmetric stretching vibration of Mo=O were very sensitive to even small changes of the structure of the isopolymolybdates. As the pH was lowered, the major Raman line showed no gradual shift but exhibited a discrete change. Evidence was obtained for the existence of $Mo_7O_{24}^{6-}$ (pH 4—6), $Mo_3O_{10}^{2-}$ (pH 3.5—5), α-$Mo_8O_{26}^{4-}$ (pH 2—5), β-$Mo_8O_{26}^{4-}$ (pH 1.5—4), and $Mo_{36}O_{112}^{8-}$ (pH 0.5—1.5). On the other hand, neither of $Mo_6O_{19}^{2-}$ and γ-$Mo_8O_{26}^{4-}$ existed in any appreciable amount in aqueous solution.

The speciation of isopolymolybdates in aqueous solution is the basis for the formation processes and the solution chemistry of heteropolymolybdates. Since most of the heteropolymolybdates have been prepared from aqueous solution, considerable effort has been directed to identify isopolymolybdate species formed on acidification of aqueous molybdenum(VI) solutions.

There is general agreement that the first polymeric species is $Mo_7O_{24}^{6-}$ or its protonated forms at pH values of 3.5—5.8, while tetrahedral MoO_4^{2-} is stable above pH 7. The octamolybdate, β-$Mo_8O_{26}^{4-}$ is formed at greater acidities.[1—14] Further acidification leads to the formation of the biggest isopolyanion known so far around pH 0.9 ($H^+/MoO_4^{2-} \approx 1.8$); from such solutions $Mo_{36}O_{112}^{8-}$ is precipitated as alkali metal and ammonium salts,[15] and the crystallographic structure has been determined.[15,16]

Although the formation of isopolymolybdates is thus pH-dependent, it is also known that the nature of the counterions can affect the crystallization process of $Mo_8O_{26}^{4-}$. From aqueous solution of pH 3—4,[17,18] β-$Mo_8O_{26}^{4-}$ is precipitated in the presence of smaller counterions and its existence in solution is confirmed,[9] while large organic countercations such as $(n\text{-}C_4H_9)_4N^+$ favor the precipitation of α-$Mo_8O_{26}^{4-}$. The crystallographic structure of the α-$Mo_8O_{26}^{4-}$ isomer was determined,[19] and the isomerization mechanism was proposed.[20] In contrast to β-$Mo_8O_{26}^{4-}$, however, the existence of α-$Mo_8O_{26}^{4-}$ in aqueous solution is still uncertain. Niven et al. isolated the salt of γ-$Mo_8O_{26}^{4-}$ proposed to be an intermediate in the α–β isomerization of $Mo_8O_{26}^{4-}$ in CH_3CN.[21] However, the existence of γ-$Mo_8O_{26}^{4-}$ in solution is unclear, because the γ-isomer is precipitated only by acidification of an aqueous solution containing both Mo(VI) and $[(CH_3)_3N(CH_2)_6N(CH_3)_3]^{2+}$ to a relatively high pH (pH about 6). Fuchs prepared the $(n\text{-}C_4H_9)_4N^+$ salt of $Mo_6O_{19}^{2-}$ from aqueous solution of $H^+/MoO_4^{2-} \approx 1.5$;[22,23] later, the $Mo_6O_{19}^{2-}$ anion was proved to be stabilized in the presence of organic solvents.[24—26] In addition, the so-called trimolybdate, $Mo_3O_{10}^{2-}$ was prepared from acidified Mo(VI) solutions as the Rb^+ and alkylammonium salts,[27,28] although its existence in solution remains to be confirmed. The anhydrous salt of $Mo_3O_{10}^{2-}$ was also obtained from the melt.[29,30]

The formation of isopolymolybdates is essentially pH-dependent. In general, the isopolymolybdate species coexist in equilibrium and the dominant species are not necessarily precipitated. On the basis of preparative studies, therefore, it is very difficult to identify isopolymolybdates in aqueous solution. Raman spectroscopy has been used to characterize isopolymolybdates occurring in acidified aqueous solution.[8,9,12—14] Although discrete changes in the Raman spectra were observed with the change of the acidities, their interpretations were sometimes contradictory. In view of the consideration that a good knowledge of the structural and Raman properties of isopolymolybdates in the solid states is required for a better understanding of the observed Raman spectral change in solution, isopolymolybdates were prepared as the salts of common countercations (NH_4^+, $(NH_2)_3C^+$, $(CH_3)_4N^+$, and $(n\text{-}C_4H_9)_4N^+$) from Mo(VI) solutions in the pH range of 0.5—6.5 (at pH intervals of 0.5). On the basis of their characterization by elemental analysis, and IR and Raman spectroscopies, the isopolymolybdates were used as reference compounds. Comparison of the major Raman frequencies (1000—900 cm^{-1}) for the reference compounds with those for the mother Mo(VI) solutions made it possible to identify the isopolymolybdates existing in aqueous solution.

Experimental

Apparatus and Materials. Raman spectra were recorded with a Jobin Yvon Model Ramanor U-1000 spectrophotometer. The argon line at 488 nm was used for excitation. In order to measure quantitatively the Raman intensities, 0.1 M (M=mol dm^{-3}) $NaNO_3$ was added to each Mo(VI) solution to provide an internal intensity standard. The NO_3^- line observed at 1048 cm^{-1} was also used as a standard for the Raman frequencies in solution. The Raman measurements were made at 20 °C. The reproducibility and resolution of the Raman spectra were found to be better than 2 cm^{-1}. IR spectra were obtained on a Hitachi Model 270-30 spectrophotometer by the KBr pellet method. The TG-DTA measurements were made with a Rigaku Denki Model TAS-100 thermal analyzer.

Molybdenum was determined with a Shimadzu Model ICPS-5000 inductively coupled argon plasma emission spectrometer. Countercations were determined with a Hitachi high-performance liquid chromatography. For the determination of NH_4^+ and $(NH_2)_3C^+$, the separation was made with a Hitachi #2720-SK-IC column. The eluents were 1.6 mM HNO_3. A Tosoh TSKgel-IC-Cation-SW column was used to determine $(CH_3)_4N^+$ and $(n\text{-}C_4H_9)_4N^+$; the eluent was comprised of 3.2 mM HNO_3 and 35% CH_3CN.

All stock solutions were prepared from reagent grade chemicals; $Na_2MoO_4\cdot 2H_2O$ was used to prepare Mo(VI) stock solutions.

Preparation of Isopolymolybdates. Detailed knowledge of the Raman properties of the isopolymolybdates in the solid state is required for analysis of the observed Raman spectral change in solution. Therefore, isopolymolybdates were isolated with the following procedures. The pH of a solution of 2.42 g $Na_2MoO_4\cdot 2H_2O$ in 100 ml of water was adjusted to 0.5—6.5 at ambient temperature. Then, four kinds of counterions (NH_4^+, $(NH_2)_3C^+$, $(CH_3)_4N^+$, and $(n\text{-}C_4H_9)_4N^+$) were added to the respective solutions to precipitate the corresponding salts of isopolymolybdates. The precipitates were washed with water and ethanol, and air-dried. The isopolymolybdates thus obtained were characterized by elemental analysis, and IR and Raman spectroscopies; then they were used as reference compounds.

$((NH_2)_3C)_6Mo_7O_{24}\cdot 2H_2O$: The heptamolybdate anion was easily obtained as the NH_4^+ and $(NH_2)_3C^+$ salts from the solution of pH 5—6 and as the $(CH_3)_4N^+$ salt from the solution of pH 6. It must be noted that the addition of $(n\text{-}C_4H_9)_4N^+$ leads to the precipitation of $\alpha\text{-}[(n\text{-}C_4H_9)_4N]_4Mo_8O_{26}$ even in the solution of pH 6 (Table 1). Anal. Calcd for $((NH_2)_3C)_6Mo_7O_{24}\cdot 2H_2O$: Mo, 46.25; $(NH_2)_3C$, 24.82; H_2O, 2.5%. Found: Mo, 46.21; $(NH_2)_3C$, 24.34; H_2O, 1.9%. IR (1000—400 cm^{-1}): 924, 896, 880, 834, 642, 574, 534 cm^{-1} (Fig. 1a). Raman (1000—800 cm^{-1}): 939 cm^{-1} (Fig. 2a).

$NaNH_4Mo_3O_{10}\cdot H_2O$: This compound was simply isolated by the addition of NH_4^+ to the solution in the narrow pH range of 4—4.5. It should be stressed that this compound is precipitated only by the addition of NH_4^+. Anal. Calcd for $NaNH_4Mo_3O_{10}\cdot H_2O$: Mo, 56.79; Na, 4.54; NH_4, 3.56; H_2O, 3.6%. Found: Mo, 56.29; Na, 4.68; NH_4, 3.54; H_2O, 3.6%. IR (1000—400 cm^{-1}): 946, 930, 910, 650, 560, 502, 428 cm^{-1} (Fig. 1b). Raman (1000—800 cm^{-1}): 950, 918, 901, 874 cm^{-1} (Fig. 2b). According to Schwing-Weill and Arnaud-Neu,[30] the IR spectra of $Mo_3O_{10}^{2-}$ were slightly changed in shape with the change of countercations. The IR spectrum shown in Fig. 1b is analogous to those given in the literature.[27,30]

$(NH_4)_8Mo_{36}O_{112}\cdot 48H_2O$: The $Mo_{36}O_{112}^{8-}$ salt was obtained by the addition of smaller counterions such as NH_4^+ and $(CH_3)_4N^+$ to the same solution from which the $Mo_6O_{19}^{2-}$ salt was precipitated. Anal. Calcd for $(NH_4)_8Mo_{36}O_{112}\cdot 48H_2O$: Mo, 55.22; NH_4, 2.31; H_2O, 13.8%. Found: Mo, 55.15; NH_4, 2.35; H_2O, 13.5%. IR (1000—400 cm^{-1}): 952, 882, 790, 694, 626, 574 cm^{-1} (Fig. 1c). Raman (1000—800 cm^{-1}): 983, 957, 899 cm^{-1} (Fig. 2c).

$[(n\text{-}C_4H_9)_4N]_2Mo_6O_{19}$: As described above, the addition of $(n\text{-}C_4H_9)_4N^+$ to the solution of pH 0.5—1.0 failed to precipitate the $Mo_{36}O_{112}^{8-}$ salt. Instead, the hexamolybdate ion, $Mo_6O_{19}^{2-}$ was produced. Although the $Mo_6O_{19}^{2-}$ anion is originally precipitated from aqueous solution,[22] the anion is extracted into organic solvents,[24,25] and is stabilized by the presence of organic solvents such as acetonitrile.[26] IR (1000—400 cm^{-1}): 954, 798, 600, 434 cm^{-1} (Fig. 1d). Raman (1000—800 cm^{-1}): 985, 958 cm^{-1} (Fig. 2d).

$\alpha\text{-}[(n\text{-}C_4H_9)_4N]_4Mo_8O_{26}$: The α-isomer of octamolybdate was obtained as the $(n\text{-}C_4H_9)_4N^+$ salt from the solution of pH 2—6. IR (1000—400 cm^{-1}): 950, 922, 912, 854, 808, 664, 562, 502 cm^{-1} (Fig. 1e). Raman (1000—800 cm^{-1}): 959, 918 cm^{-1} (Fig. 2e). Anal. Calcd for $[(n\text{-}C_4H_9)_4N]_4Mo_8O_{26}$: Mo, 35.64; $(n\text{-}C_4H_9)_4N$, 45.04%. Found: Mo, 35.59; $(n\text{-}C_4H_9)_4N$, 44.97%.

$\beta\text{-}[(CH_3)_4N]_{3.75}Na_{0.25}Mo_8O_{26}\cdot H_2O$: This compound was obtained by the addition of 9 g of $(CH_3)_4NBr$ to the solution of pH 2—5; the compositional ratio of $(CH_3)_4N^+/Na^+$ was changed with the variation of the added amount of $(CH_3)_4NBr$. As shown in Table 1, the $\beta\text{-}Mo_8O_{26}^{4-}$ was obtained only as the $(CH_3)_4N^+$ salt from the solution of pH 2—5. Anal. Calcd for

Table 1. Isolated Isopolymolybdates as Functions of Counterion and pH

pH / COUNTERION	1.0	2.0	3.0	4.0	5.0	6.0
$(n\text{-}C_4H_9)_4N^+$	$Mo_6O_{19}^{2-}$	$\alpha\text{-}Mo_8O_{26}^{4-}$	$\alpha\text{-}Mo_8O_{26}^{4-}$	$\alpha\text{-}Mo_8O_{26}^{4-}$	$\alpha\text{-}Mo_8O_{26}^{4-}$	$\alpha\text{-}Mo_8O_{26}^{4-}$
$(CH_3)_4N^+$	$Mo_{36}O_{112}^{8-}$	$\beta\text{-}Mo_8O_{26}^{4-}$	$\beta\text{-}Mo_8O_{26}^{4-}$	$\beta\text{-}Mo_8O_{26}^{4-}$	$\beta\text{-}Mo_8O_{26}^{4-}$	$Mo_7O_{24}^{6-}$
$(NH_2)_3C^+$	▨	▨	▨	▨	$Mo_7O_{24}^{6-}$	$Mo_7O_{24}^{6-}$
NH_4^+	$Mo_{36}O_{112}^{8-}$	▨	▨	$Mo_3O_{10}^{2-}$	$Mo_7O_{24}^{6-}$	$Mo_7O_{24}^{6-}$

Blank spaces represent the region where mixtures are precipitated.

$[(CH_3)_4N]_{3.75}Na_{0.25}Mo_8O_{26}\cdot H_2O$: Mo, 51.67; Na, 0.39; $(CH_3)_4N$, 18.72; H_2O, 1.2%. Found: Mo, 51.84; Na, 0.48; $(CH_3)_4N$, 18.78; H_2O, 1.4%. IR (1000—400 cm^{-1}): 946, 910, 844, 712, 666, 556, 512, 454 cm^{-1} (Fig. 1f). Raman (1000—800 cm^{-1}): 971, 943, 915, 904 cm^{-1} (Fig. 2f).

γ-$[(CH_3)_3N(CH_2)_6N(CH_3)_3]_2Mo_8O_{26}\cdot 2H_2O$: This compound was prepared according to the method of Niven et al.[21] This method is unique in that the precipitation occurs by the addition of HCl to an aqueous solution containing equimolar amounts of Mo(VI) and $[(CH_3)_3N(CH_2)_6N(CH_3)_3]^{2+}$. In contrast to the α- and β-isomers, the γ-isomer was precipitated only from the solution of pH about 6. IR (1000—400 cm^{-1}): 946, 918, 904, 858, 790, 735, 662, 512, 476 cm^{-1} (Fig. 1g). Raman (1000—800 cm^{-1}): 963, 943, 922, 912, 840 cm^{-1} (Fig. 2g). Comparison of the IR spectrum is impossible owing to the lack of a corresponding spectrum in the literature.[21]

In addition to the isopolymolybdate species described above, Day et al. prepared $[(n\text{-}C_4H_9)_4N]_2Mo_2O_7$ by stoichiometric addition of $(n\text{-}C_4H_9)_4NOH$ to α-$[(n\text{-}C_4H_9)_4N]_4Mo_8O_{26}$ in CH_3CN.[31] Furthermore, they found that the addition of water to the CH_3CN solution of $Mo_2O_7^{2-}$ produced the pentamolybdate $Mo_5O_{17}H^{3-}$

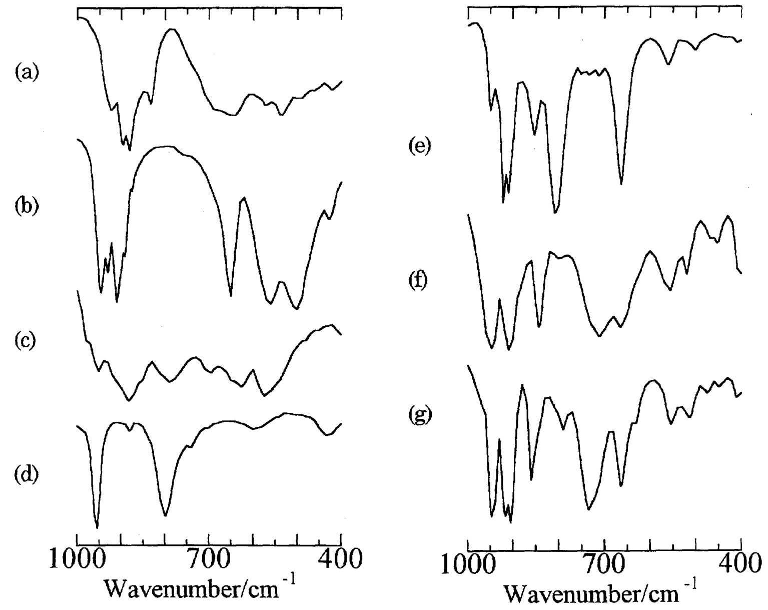

Fig. 1. IR spectra of (a) $((NH_2)_3C)_6Mo_7O_{24}\cdot 2H_2O$, (b) $NaNH_4Mo_3O_{10}\cdot H_2O$, (c) $(NH_4)_8Mo_{36}O_{112}\cdot 48H_2O$, (d) $[(n\text{-}C_4H_9)_4N]_2Mo_6O_{19}$, (e) α-$[(n\text{-}C_4H_9)_4N]_4Mo_8O_{26}$, (f) β-$[(CH_3)_4N]_{3.75}Na_{0.25}Mo_8O_{26}\cdot H_2O$, and (g) γ-$[(CH_3)_3N(CH_2)_6N(CH_3)_3]_2Mo_8O_{26}\cdot 2H_2O$ as the KBr pellets.

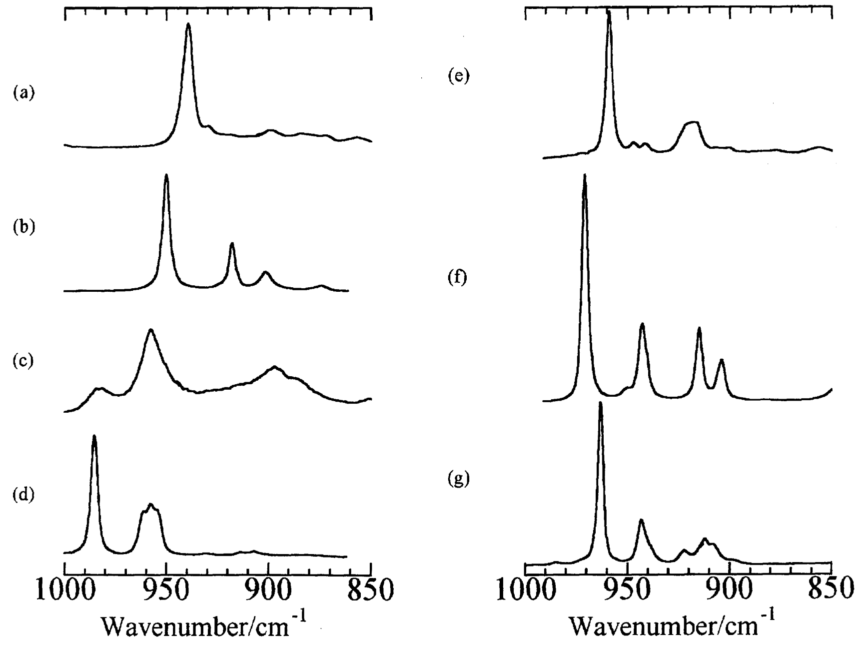

Fig. 2. Raman spectra of (a) $((NH_2)_3C)_6Mo_7O_{24}\cdot 2H_2O$, (b) $NaNH_4Mo_3O_{10}\cdot H_2O$, (c) $(NH_4)_8Mo_{36}O_{112}\cdot 48H_2O$, (d) $[(n\text{-}C_4H_9)_4N]_2Mo_6O_{19}$, (e) α-$[(n\text{-}C_4H_9)_4N]_4Mo_8O_{26}$, (f) β-$[(CH_3)_4N]_{3.75}Na_{0.25}Mo_8O_{26}\cdot H_2O$, and (g) γ-$[(CH_3)_3N(CH_2)_6N$-$(CH_3)_3]_2Mo_8O_{26}\cdot 2H_2O$.

ion.[32] Besides, the decamolybdate anion, $Mo_{10}O_{34}{}^{8-}$ was first prepared by thermal decomposition of $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ at 110 °C and the crystallographic structures of the thallium and octakis(methylammonium) salts were determined.[33—36] However, these polymolybdate species were not precipitated from aqueous solution.

Results and Discussion

Raman Spectra of Isopolymolybdates in the Solid States. The present study has demonstrated that the choice of counterions plays a decisive role in the isolation of isopolymolybdates from aqueous solution. The cation-dependent isomerization of α- and β-$Mo_8O_{26}{}^{4-}$ was already reported by Klemperer et al.[17,18] Besides α- and β-$Mo_8O_{26}{}^{4-}$, however, different kinds of isopolymolybdates were precipitated from the solution of the same pH, depending on the nature of counterions. The seven isopolymolybdates thus obtained are summarized as functions of pH (at pH intervals of 1.0) and countercation in Table 1.

As shown in Fig. 2, each isopolymolybdate possesses an inherent major Raman line, assigned to the asymmetric stretch of Mo=O, at the specific wavenumber: $Mo_7O_{24}{}^{6-}$, 939 cm^{-1}; $Mo_3O_{10}{}^{2-}$, 950 cm^{-1}; α-$Mo_8O_{26}{}^{4-}$, 959 cm^{-1}; β-$Mo_8O_{26}{}^{4-}$, 971 cm^{-1}; γ-$Mo_8O_{26}{}^{4-}$, 963 cm^{-1}; $Mo_{36}O_{112}{}^{8-}$, 983 cm^{-1}; $Mo_6O_{19}{}^{2-}$, 985 cm^{-1}. The $Mo_6O_{19}{}^{2-}$ and $Mo_{36}O_{112}{}^{8-}$ anions exhibit the Raman lines at nearly the same wavenumber. As discussed later, however, the Raman line due to $Mo_{36}O_{112}{}^{8-}$ is accompanied by a Raman line at 899 cm^{-1}, so that the Raman line at 983—985 cm^{-1} can be distinguished between $Mo_{36}O_{112}{}^{8-}$ and $Mo_6O_{19}{}^{2-}$. It should be noted that the Raman frequencies for $Mo_7O_{24}{}^{6-}$, $Mo_3O_{10}{}^{2-}$, β-$Mo_8O_{26}{}^{4-}$, $Mo_{36}O_{112}{}^{8-}$, and $Mo_6O_{19}{}^{2-}$ are in good agreement with the literature values. We did not find the Raman spectra for α- and γ-$Mo_8O_{26}{}^{4-}$ in the literature.

As discussed above, preparative studies give little information about the existence of isopolyanions in solution because the predominant species is not necessarily precipitated. In order to obtain direct information on the isopolymolybdate species in solution, therefore, Raman spectra in the 1000—850 cm^{-1} range were recorded for 100 mM Mo(VI) solutions at various acidities. The spectral changes were analyzed in detail on the basis of the major Raman frequencies of the reference compounds. It must be added that the Raman spectra contain lines below 800 cm^{-1} about which no discussion is made, because they are too weak in intensities to study the solution chemistry of isopolymolybdates.

Raman Spectra of Isopolymolybdates in Aqueous Solution. Figure 3 shows Raman spectra at pH values of 8.4—5.1. Above pH 6.3, only a Raman line assigned to $MoO_4{}^{2-}$ was observed at 896 cm^{-1}.[13,37] Below pH 6.1, a new Raman line appeared at 940 cm^{-1}, and increased in intensity with a decrease in the intensity of the 896 cm^{-1} line. The new Raman line at 940 cm^{-1} is due to the formation of $Mo_7O_{24}{}^{6-}$ in solution.[8,12] In the narrow pH range of 6.1—5.6, the intensity change of the two Raman lines at 896 and 940 cm^{-1} occurred with a constant Raman intensity at 908 cm^{-1} like an isosbestic point in UV-vis. absorption spectroscopy, indicating that there were no intermediate species between $MoO_4{}^{2-}$ and $Mo_7O_{24}{}^{6-}$. This result is in accord with earlier observations by Raman spectroscopy.[8,13,14] Below pH 5.8, the 940 cm^{-1} line increased in intensity with lowering of pH. The absence of the Raman line at 963 cm^{-1} excludes the presence of major amounts of γ-$Mo_8O_{26}{}^{4-}$ in solution of pH ca. 6 where the γ-isomer is precipitated. As Niven et al. discussed in their paper,[21] the γ-isomer may be formed as the counterion effect in the course of the crystallization process.

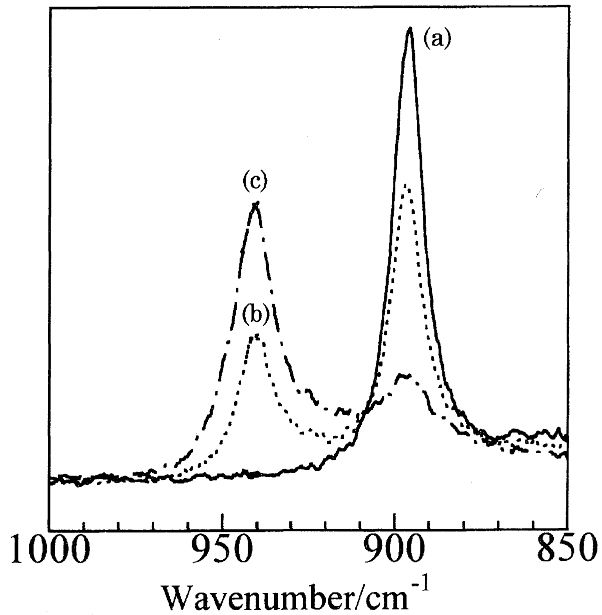

Fig. 3. Raman spectral change with acidities. (a) pH 8.38; (b) pH 5.81; (c) pH 5.08.

The polynuclear species formed on further acidification have not been definitely established so far. As shown in Fig. 4, the 940 cm^{-1} line became asymmetric below pH 4.4, showing the presence of the unresolved line on the higher frequency side. In fact, a new Raman line appeared like a shoulder around 950 cm^{-1} (Fig. 4b), and grew as a peak at pH 3.9. On the basis of the Raman frequencies for the reference compounds of $NaNH_4Mo_3O_{10}\cdot H_2O$ and $Rb_2Mo_3O_{10}\cdot H_2O$,[28] the 950 cm^{-1} line can be assigned to the so-called trimolybdate anion. The existence of the trimolybdate anion as a soluble polymeric species such as $([Mo_3O_{10}]^{2-})_\infty$ may be suggested because the structures of $Rb_2Mo_3O_{10}\cdot H_2O$ and $K_2Mo_3O_{10}$ are polymeric.[28,29] The structure of the trimolybdate anion in aqueous solution seems worthy of further study. The 950 cm^{-1} line can be distinguished from the $Mo_7O_{24}{}^{6-}$ line at 940 cm^{-1} which decreases in height as pH is lowered. The $Mo_7O_{24}{}^{6-}$ line disappeared completely at pH 3.5, although the peak height was not determined accurately because of overlaps. As pH was lowered to 3.5 or below, as shown in Fig. 5, there appeared two new Raman lines at 959 and 971 cm^{-1} which, by comparison with the solid samples, were due to α-$Mo_8O_{26}{}^{4-}$ and β-$Mo_8O_{26}{}^{4-}$ respectively. In the pH range of 2.8—1.9, there are only two major Raman lines at

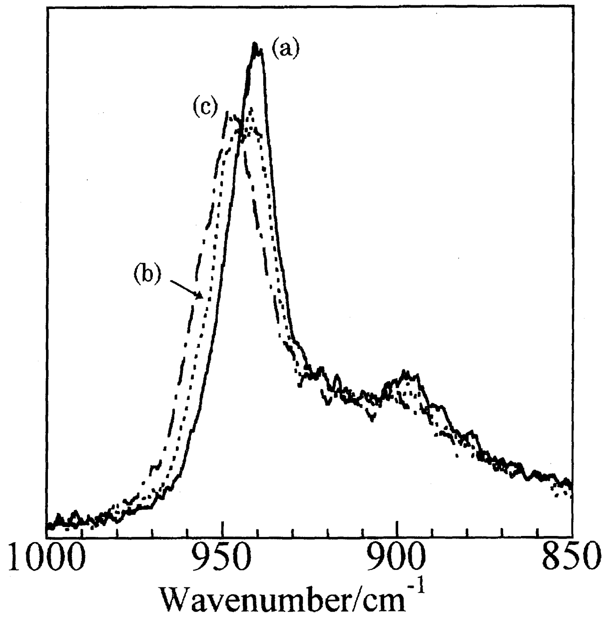

Fig. 4. Raman spectral change with acidities. (a) pH 4.64; (b) pH 4.25; (c) pH 3.79.

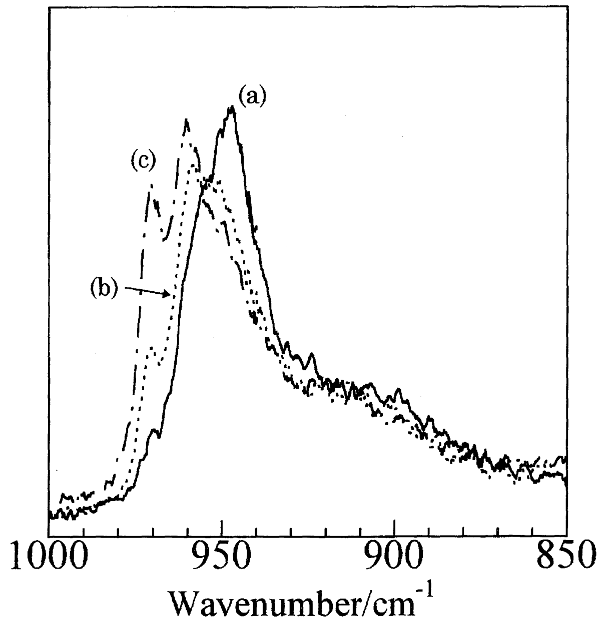

Fig. 5. Raman spectral change with acidities. (a) pH 3.53; (b) pH 3.08; (c) pH 1.95.

959 and 971 cm^{-1} (Fig. 5c). As pH was lowered further, the Raman line at 959 cm^{-1} merged into a new line at 955 cm^{-1}. Simultaneously, the 971 cm^{-1} line decreased in height with an increase of a Raman line at 982 cm^{-1}. In parallel with the increase of the 982 cm^{-1} line, a Raman line at 901 cm^{-1} grew (Fig. 6c). On this basis, the presence of $Mo_6O_{19}{}^{2-}$ as a predominant species is excluded. At pH values of 1.2—0.6, the Raman spectra show only three Raman lines at 982, 955, and 901 cm^{-1}, indicating that the dominant species is $Mo_{36}O_{112}{}^{8-}$. During the pH change of 1.8—1.4, another "isosbestic point" at 976 cm^{-1} was obtained between the

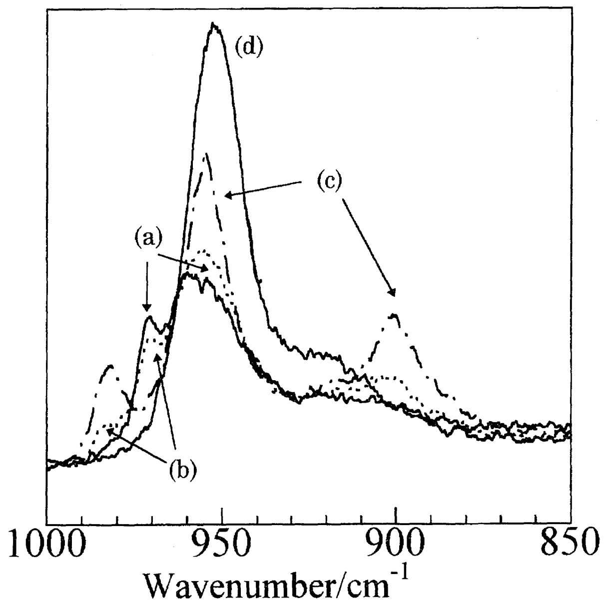

Fig. 6. Raman spectral change with acidities. (a) pH 1.77; (b) pH 1.62; (c) pH 1.03; (d) pH 0.25 (1 M HCl).

971 and 982 cm^{-1} lines. This result shows that two species, β-$Mo_8O_{26}{}^{4-}$ and $Mo_{36}O_{112}{}^{8-}$ coexist with no intermediate species.

Further acidification brings about changes of Raman spectra as shown in Fig. 6d. Below pH 0.4, both Raman lines at 982 and 901 cm^{-1} disappeared, leaving the Raman line at 953 cm^{-1} with a shoulder around 920 cm^{-1}. With further addition of acid, the Raman spectra remained essentially unchanged. As reported previously,[38)] the appearance of the 953 and 920 cm^{-1} lines indicates the formation of $Mo_2O_5{}^{2+}$ in which each Mo atom contains two terminal oxygens; the former Raman line is assigned to the symmetric stretching vibrational mode of the MoO_2 group, and the latter to the asymmetric stretching vibrational mode.[39)] Later, Yokoi et al. determined the Mo–O–Mo angle to be ca. 125° on the basis of XANES and EXAFS.[40)] It should be noted that monomeric $MoO_2{}^{2+}$ species predominate at Mo(VI) concentrations less than 1×10^{-4} M.[41—44)]

In order to illustrate the distribution curves of the molybdate species, the Raman intensities at 896, 940, 950, 959, 971, and 982 cm^{-1} were shown in Fig. 7 as a function of pH. Monomeric $MoO_4{}^{2-}$ is the main species above pH 6.3, and it persists until pH 4.5. At pH 5.2, $Mo_7O_{24}{}^{6-}$ is predominant in the solution. As illustrated in Fig. 7e, the formation of β-$Mo_8O_{26}{}^{4-}$ becomes maximum at pH 2.0, and with further acidification, $Mo_{36}O_{112}{}^{8-}$ predominates at pH 1.0. These observations are in good agreement with the previous results.[12,15)]

The existence of the remaining isopolymolybdates in solution is still uncertain; but the present study has demonstrated the presence of $Mo_3O_{10}{}^{2-}$ and α-$Mo_8O_{26}{}^{4-}$ as major components in aqueous solution. The presence of α-$Mo_8O_{26}{}^{4-}$ in aqueous solution has been excluded so far in the literature.[13,17)] The cation-dependent α–β isomerization

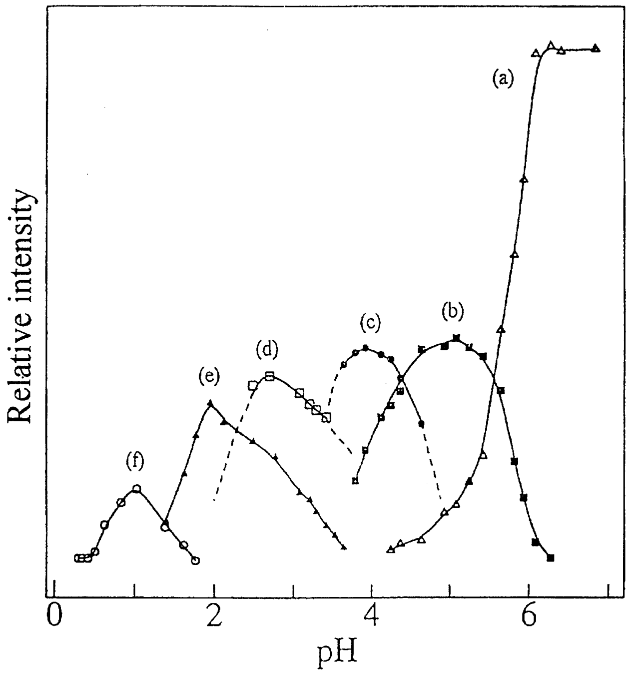

Fig. 7. Relative Raman intensities at (a) 896, (b) 940, (c) 950, (d) 959, (e) 971, and (f) 982 cm^{-1} as a function of pH.

of $Mo_8O_{26}{}^{4-}$ may occur as a result of the difference in solubility between the salts of α- and β-$Mo_8O_{26}{}^{4-}$, because both isomers coexist at pH 3—4. On the other hand, neither of $Mo_6O_{19}{}^{2-}$ and γ-$Mo_8O_{26}{}^{4-}$ is present at any appreciable concentration.

In conclusion, the following molybdates species exist as the predominant species in aqueous solution:

$$\underset{(\mathrm{pH}>6.3)}{MoO_4{}^{2-}} \rightarrow \underset{(\mathrm{pH}5.0)}{Mo_7O_{24}{}^{6-}} \rightarrow \underset{(\mathrm{pH}4.0)}{Mo_3O_{10}{}^{2-}} \rightarrow \underset{(\mathrm{pH}2.7)}{\alpha\text{-}Mo_8O_{26}{}^{4-}}$$

$$\rightarrow \underset{(\mathrm{pH}2.0)}{\beta\text{-}Mo_8O_{26}{}^{4-}} \rightarrow \underset{(\mathrm{pH}1.0)}{Mo_{36}O_{112}{}^{8-}}$$

It is well known that protonation of $MoO_4{}^{2-}$ causes the coordination number of the molybdenum to expand, and thus condensed molybdate species are formed.[1] As the pH of the solution is lowered, the negative charge per molybdenum decreases from -2 for $MoO_4{}^{2-}$ to $-2/9$ for $Mo_{36}O_{112}{}^{8-}$. Further acidification leads to the formation of cationic species such as $Mo_2O_5{}^{2+}$ via neutral species.

As given in Fig. 7, the distribution curves show considerable overlapping of equilibria, indicating that several isopolymolybdates coexist at comparable amounts. The counterion-effect shown in Table 1 can be accounted for in terms of the difference in solubility, in analogy with the case of α- and β-$Mo_8O_{26}{}^{4-}$. It must be added that the relative Raman intensities vs. pH curves are independent of the Mo(VI) concentrations in the range of 100—200 mM.

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