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Studies on the Interaction of Molybdate Ion and Magnesium Ion Observed in the Raman Spectra of the Mixture Solutions

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When alkali metal or alkaline earth metal chloride, (except magnesium chloride) was added to a solution of sodium molybdate, similar Raman spectra were observed. When magnesium chloride was added to the molybdate solution, however, the intensity of the peak (ν_1) based on the symmetric stretching vibration of the tetrahedral molybdate decreased and a new peak (ν_x) appeared at a higher wavenumber than ν_1. The wavenumber of the new peak is almost equal to that observed for solid magnesium molybdate. This suggests that the new peak can be ascribed to the molybdates of the distorted octahedral structure, since the molybdate ion exists as an octahedral in the solid state of magnesium molybdate. The tetrahedral and the octahedral molybdates seem to be in equilibrium in the solution.

The molybdate ion is a typical oxoanion, having a tetrahedral structure in an alkaline or neutral solution.[1,2] The dissolved states of the molybdate ion have been studied under various experimental conditions, e.g., pH, ionic strength, coexisting salt etc.,[2-10] and their typical Raman peaks, based on the fundamental vibrations, have been assigned.[5] However, the number of studies regarding the effect of the coexisting salts on the Raman spectra of the solution have been few. In this study, a change in the Raman spectra was studied, especially when alkaline earth chloride was added to a solution of molybdates.

When magnesium ion was added to a molybdate ion solution, the appearance of a new peak was found in the Raman spectra. This peak seemed to be the result of interaction of these ions in solution.

Experimental

Reagents. Molybdate solutions were prepared using sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$). All reagents used were analytical reagent grade chemicals and were used without further purification.

Equipments. Raman spectra were measured with a laser Raman spectrometer with double monochromators (JASCO R800); the 514.5 nm line of an Ar^+ laser was used as the excitation light source. One ml of sample solution was used for each measurement. The slit widths of the spectrometer for the entrance, intermediate and exit were 300, 500, and 300 μm, respectively.

Results and Discussion

The Effect of Magnesium Ion. The Raman spectra of two 0.1M (1M=1 mol dm^{-3}) sodium molybdate solutions in which lithium chloride and magnesium chloride were added, respectively, are shown in Fig. 1. The Raman spectrum of a magnesium chloride solution is also shown for a reference. In the case of lithium chloride, only the peaks ascribed to the free molybdate were observed. The molybdate ion generally exists as a tetrahedral ion in alkaline or neutral solutions and four peaks characterizing tetrahedral structure have been observed at 900, 850, 310, and 270 cm^{-1} in the Raman spectra. The peak at 900 cm^{-1} (denoted by ν_1) has been assigned to the totally symmetric stretching vibration and the peaks at 850 cm^{-1} (ν_3) to an antisymmetric stretching vibration.[5] When magnesium chloride was added to the molybdate solution, a noticeable change was observed, namely the peak near 900 cm^{-1} decreased and the shape of the peak was deformed. A more detailed change in the shape is indicated by the dotted lines in Fig.2. As the magnesium concentration increased from 0.5 to 4.5M, the intensity of the peak at 900 cm^{-1} (ν_1) decreased, and a new peak (denoted by ν_x) appeared in the region 910 to 930 cm^{-1}. In order to separate the peaks, a nonlinear least-squares wave analysis was applied assuming Lorentz-Gauss sum functions. An algorithm of the calculation was taken from the work of Edgell et al.[11-13] Three peaks were obtained, as shown by the solid lines in Fig. 2. All spectra in Fig. 2 were normalized so that the highest peak in the spectrum had the same intensity. The dependence of the wavenumbers of each peak and that of the area fraction, $\nu_1/(\nu_1+\nu_x)$, upon magnesium concentration are shown in Fig. 3. The area fraction of ν_1 decreased against an increase in the magnesium concentration. This implies a decrease in the concentration of the free molybdate ion and an

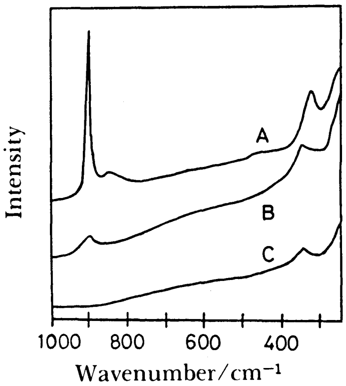

Fig. 1. Raman spectra of molybdate solutions, A: 0.1 M Na_2MoO_4, 1 M LiCl; B: 0.1 M Na_2MoO_4, 4 M $MgCl_2$ and C: 4 M $MgCl_2$.

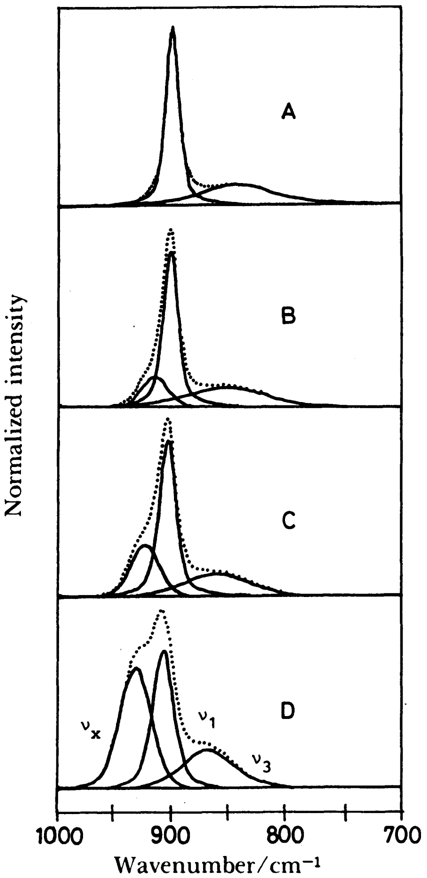

Fig. 2. Effect of $MgCl_2$ concentration on Raman spectra of 0.1 M Na_2MoO_4 solution. A: 0.5; B: 2.5; C: 3.5 and D: 4.5 M $MgCl_2$.

increase in a new species (ν_x). The peak ν_x appeared at a higher wavenumber than ν_1 and its wavenumber moved to a higher value, accompaning an increase in the magnesium concentration.

In acidic molybdate solutions, the presence of such isopolymolybdates as heptamer and octamer had been known.[14–16] The pH of the solution studied in this work changed from 7.0 (0.1M Na_2MoO_4) to 5.0 (0.1M Na_2MoO_4, 4M $MgCl_2$). Thus, the possibility that the new species might be the isopolymolybdate, was suspected. A study concerning the dissolved states of the isopolymolybdate ions, however, has shown that the peak wavenumbers of the isopolymolybdates are not consistent with ν_x : ν_x=910-930, cf. $\nu(Mo_7O_{24}{}^{6-})=945$, $\nu(HMo_7O_{24}{}^{5-})=957$, and $\nu(Mo_8O_{26}{}^{4-})=970$ cm^{-1}.[17] The new species observed here is not the isopolymolybdate ion, but other species.

The Raman spectra of the solutions in which the concentration of the sodium molybdate was varied and that of magnesium chloride was kept 3M, were shown in Fig. 4. Almost the same spectra were obtained independently of the molybdate concentration, i.e., the peak wavenumbers of each spectra were almost the same and the fraction of the peak areas was nearly constant.

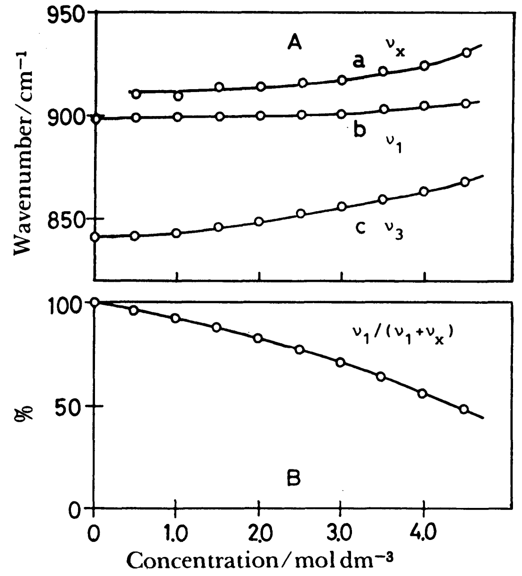

Fig. 3. Effect of $MgCl_2$ concentration on changes of maximum wavenumber of the peaks (A. a: ν_x, b: ν_1, c: ν_3) and B: area fraction, $\nu_1/(\nu_1+\nu_x)$ in 0.1 M Na_2MoO_4 solution.

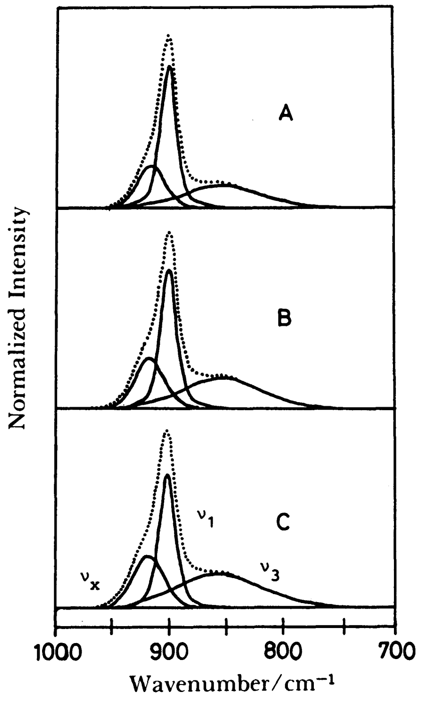

Fig. 4. Effect of Na_2MoO_4 concentration on Raman spectra of 3 M $MgCl_2$ solution. A: 0.05; B: 0.3 and C: 0.5 M Na_2MoO_4.

Raman Spectra of Powdered Alkaline Earth Salts of Molybdate. The solubility of calcium, strontium, and barium molybdates are very small, but that of magnesium molybdate is fairly large in water. A precipitate of magnesium molybdate was obtained by concentrating a mixed solution of sodium molybdate and magnesium chloride. The compositions of these freshly prepared precipitates were all 1 : 1 as for the ratio of the alkaline earth metal ion against the molybdate as a result of a quantitative analysis. After drying them in a desiccator with concentrated sulfuric acid, their Raman spectra were measured. The obtained spectra are shown in Fig. 5. Calcium, strontium, and barium molybdates gave similar Raman spectra. Only magnesium salt gave a different spectrum from the others. From this fact, it is supposed that these alkaline earth salts, except magnesium salt, have a similar crystal structure. In Fig. 6, the X-ray diffraction pattern of these salts are shown. The same analogy was observed among the calcium, strontium and barium molybdates. However, only the pattern of the magnesium molybdate was complex and was different from the others. The crystal salts were divided to two groups. The crystals, except magnesium salt, are all ascribed to Scheelite and only magnesium salt is ascribed to Wolframite.[18–20)]

If the salt of molybdate is expressed as XYO_4, the Y atom in Scheelite is surrounded by four oxygen atoms in a tetrahedral structure. On the other hand, the Y atom of XYO_4 in Wolframite type lies in the center of a distorted octahedral structure and is surrounded by six oxygen atoms.[19,21)] This suggests that the peak, which is observed in the Raman spectra of magnesium molybdate in solid state, should be ascribed to the molybdate species in a distorted octahedral structure. Even in a such isopolymolybdate ions as heptamer and octamer, it has been reported that each molybdenum atom lies in a center of the octahedral unit.[22,23)] The octahedral structure might be a stable structure for molybdate. Figure 3 shows that the wavenumber of the new peak ν_x observed in a mixed solution approaches the peak (930 cm^{-1}) of the solid state magnesium molybdate (Fig. 5) upon increasing the concentration of magnesium chloride. From these facts, it is suggested that both peaks, one for the solid and the other for the solution, must be based on a similar structure; the distorted octahedral structure. Thus, tetrahedral and distorted octahedral ions must be in equilibrium in the solutions.

On the other hand, if the new species formed in the mixture solution is a stoichiometric compound and its shape is constant, then its concentration only depends upon the magnesium concentration and its wavenumber will not shift. However, a shift of ν_x was observed with an increase in the magnesium concentration. This fact implies that the structure of the new species, itself, depends upon the composition. Thus, the formation reaction equation can not be strictly expressed.

However, suppose the stoichiometry and assume the following reaction for the qualitative explanation of the experimental results:

$$Mg^{2+} + Mo(T) = Mg\text{-}Mo(O), \qquad (1)$$

where Mo(T) is the free tetrahedral molybdate, and Mg-Mo(O) the distorted octahedral molybdate inte-

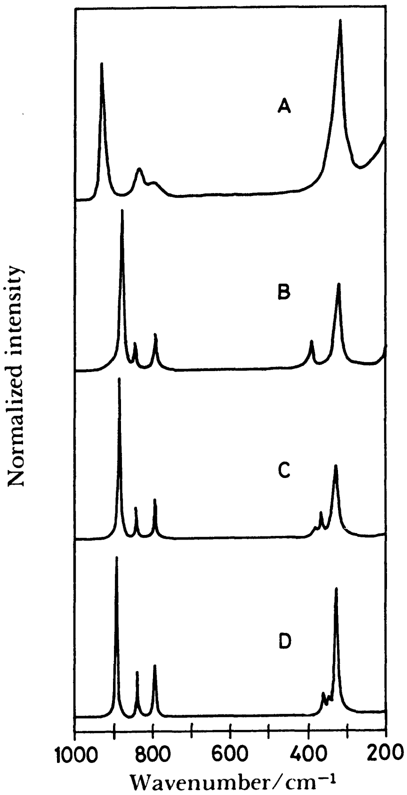

Fig. 5. Raman spectra of solid samples; A: $MgMoO_4$; B: $CaMoO_4$; C: $SrMoO_4$ and D: $BaMoO_4$.

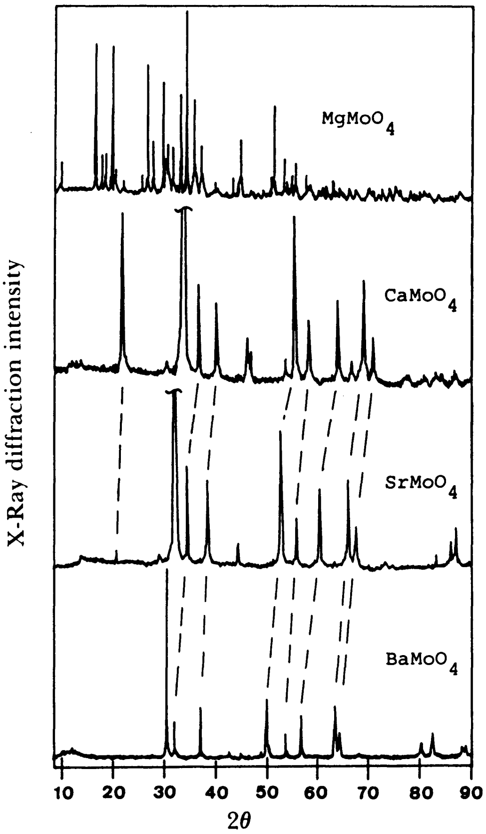

Fig. 6. Comparison of X-ray powder diffraction spectra of A: $MgMoO_4$; B: $CaMoO_4$; C: $SrMoO_4$ and D: $BaMoO_4$.

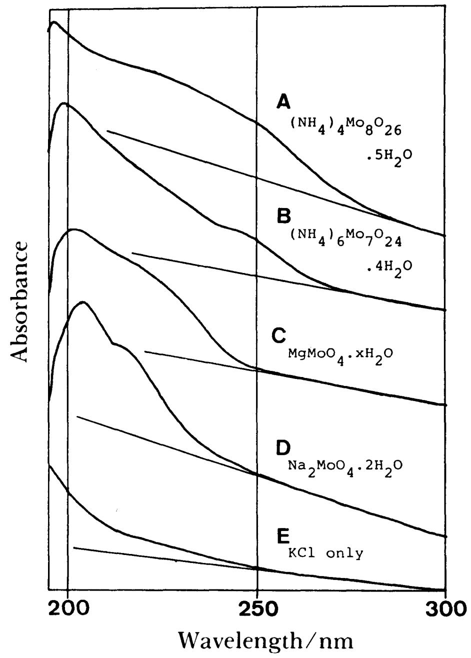

Fig. 7. Comparison of ultraviolet absorption spectra of powder disks containing A: ammonium tetramolybdate; B: ammonium paramolybdate; C: magnesium molybdate and D: sodium molybdate, diluted by KCl powder and E: pure KCl disk.

racting with magnesium ions. Then, the equilibrium constant K is

$$K=[\text{Mg-Mo(O)}]/[\text{Mg}^{2+}][\text{Mo(T)}]. \qquad (2)$$

This equation can be rewritten as

$$[\text{Mg-Mo(O)}]/[\text{Mo(T)}]=K[\text{Mg}^{2+}]. \qquad (3)$$

This equation indicates that the ratio of the concentration of the new species Mg-Mo(O) against that of free molybdate Mo(T) is in proportion to the total concentration of the magnesium ions, since the latter concentration is in large excess against that of molybdate and is almost identical to the free magnesium ion concentration. If the amount of magnesium is constant and that of molybdate is varied, the fraction of Eq. 3 remains constant. Thus, the results shown in Figs. 2 to 4 are well explained qualitatively by Eq. 3.

Spectroscopic Analysis of the Interaction at Low Concentration Solution. It was expected that the ultraviolet absorption spectra of the molybdate solution would change by the formation of molybdate octahedral species. The absorption spectra of 0.1 mM sodium molybdate solutions in which various concentrations of magnesium chloride were added, were measured; no noticeable change was observed. On the other hand, 3 mg of four kinds of molybdate compounds (sodium molybdate: Na_2MoO_4, magnesium molybdate: $MgMoO_4$, ammonium paramolybdate: $(NH_4)_6Mo_7O_{24}$, and ammonium tetramolybdate: $(NH_4)_4Mo_8O_{26}$), were each mixed with the 0.3 g KCl ground powder, respectively, and their sample disks were prepared by pressing each mixture powders into the disks (1 cm diameter and 1mm thickness) in a vacuum chamber. The measured ultraviolet absorption spectra of these disks are shown in Fig. 7. Two kinds of isopolymolybdates gave different spectra from that of sodium molybdate disk: The former had a definite absorption intensity at 250 nm, but the latter had no absorption there. However, the spectrum of a disk of magnesium molybdate was almost the same as that of sodium molybdate. This indicates that a noticeable difference will not be observed between the absorption spectra of the molybdate tetrahedral ion and that of the octahedral deformed ion. Namely, the fact that the ultraviolet spectra observed in the mixture solutions were almost same as that of free molybdate, does not rule out the presence of the octahedral molybdate species. On the other hand, the fact that the ultraviolet absorption spectra of any isopolymolybdates were shifted to the longer wavelength region, suggests the possibility that the new species is essentially a monomer and, thus, has no direct bonding between each molybdenum atom.

Conclusion

When magnesium chloride is added in greater concentrations than 4.5 M to a 0.1 M sodium molybdate solution, magnesium molybdate precipitates. In the Raman spectra of the mixture solution, a ν_x peak similar to that of a precipitate crystal was already observed, even in a solution of 0.5M $MgCl_2$. This peak shifted to a higher wavenumber. These facts suggest that a crystal-like structure is already formed in a mixture solution of such low concentrations and grows. The new peak was ascribed to the molybdates in the distorted octahedral structure, resulting in the interaction of molybdate and magnesium ions.

We believe that in a precipitation reaction, the ions are all present as free ions before saturation and that they change in structure when the composition reaches a saturated state. Namely, the transformation of the structure occurrs at a saturated composition. However this model is not adequate for explaining the system studied above. This study suggests that before saturation (even in the low concentration solutions) there exists an ion having a structure similar to that of the precipitate crystal. Also, not the free tetrahedral molybdate but, rather, the distorted octahedral molybdates precipitates through a formation reaction of the latter species. This phenomenon was observed for the first time, since the structure of the free molybdate ion in solution happened to be different from that of molybdate ion of magnesium molybdate precipitate. We expect that this is not a unique case but that a similar phenomenon will also be found in the other systems.

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