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Structures of Hydrated Titanium and Vanadium Ions in Aqueous Solutions Studied by X-Ray Absorption Spectroscopy

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The structures of titanium(III) and (IV), as well as vanadium(II), (III), and (IV) ions in aqueous solutions were investigated by the use of EXAFS (Extended X-ray Absorption Fine Structure) and XANES (X-ray Absorption Near Edge Structure). The Ti^{IV} ion in a sulfuric acid solution was found to form a -Ti^{IV}-O-Ti^{IV}- chain structure which is known to be present in the $TiOSO_4 \cdot 2H_2O$ crystal. The XANES spectrum of a mixed-valence complex, Ti^{III-IV}, in solution agrees with the sum of the individual XANES spectra of Ti^{III} and TI^{IV}, indicating a retention of individual oxidation states and coordination structures. While the peaks pertaining to Ti–Ti and V–V interactions were observed in the EXAFS Fourier transform spectra for Ti^{IV} in a sulfuric acid solution and for V^{III} in a hydrochloric acid solution, the mixed-valence complex, Ti^{III-IV}, did not show the Ti–Ti peak.

Titanium exhibits two oxidation states, Ti^{III} and Ti^{IV}, in an acidic solution. Information concerning the structure of Ti^{III} could be obtained by UV-visible absorption spectroscopy and ESR,[1] owing to its 3d electron. However, the means for studying Ti^{IV} is rather limited, since it has no d electron. The high charge-to-radius ratio of Ti^{IV} prevents the formation of simply hydrated Ti^{IV} ion like $[Ti(H_2O)_6]^{4+}$.[2] A simple structure of TiO^{2+} does not exist in the $TiOSO_4 \cdot H_2O$ crystal either, though zigzag -Ti-O-Ti- chains with SO_4^{2-} and H_2O coordinating to Ti have been found in the crystal phase.[3] It is not certain whether the chain structure remains in solution.

Mixing blue-violet Ti^{III} and colorless Ti^{IV} solutions produces a mixed-valence complex, Ti^{III-IV}, with a brown-violet color. The Ti^{III-IV} complex in concentrated HCl has been studied in some detail by Jørgensen.[4] From the formation constants of Ti^{III} and Ti^{IV} chloro complexes, he has suggested that the complex might be a dimer of the form of $[Ti^{III}Cl]^{2+} \cdot [Ti^{IV}Cl_6]^{2-}$. In a 20% sulfuric acid solution, the existence of a 1:1 Ti^{III}–Ti^{IV} complex has also been reported.[5] However, a structural model for it has never been proposed.

Vanadium ion exists in acidic solution with the oxidation states of (II) to (V). Their coordination structures in acidic solution can be quite different. For example, the V^{IV} ion is considered to have one double-bonding oxygen atom, and V^{II} and V^{III} ions form octahedral hexaaqua complexes. While the V^{III} ion exhibits a blue-green color in an H_2SO_4 solution (known to exist as a monomer),[6] it exhibits a brown color in an HCl solution. An analogous brown species was reported to appear as an intermediate species during a reaction between V^{II} and V^{IV} in an aqueous perchlorate solution and has been confirmed to be a dimeric species, such as VOV^{4+}, by means of UV-visible spectroscopy.[7] These Ti and V complexes mentioned above behave in a very complex manner in solutions. There remains much to be done in order to clarify the structures of these complexes in solutions. In recent years, EXAFS (the extended X-ray absorption fine structure) spectroscopy has proved to be a powerful tool for studies of metal complexes in solution.[8]

In this paper we report on the structural chemistry of Ti^{IV}, Ti^{III}, and their mixed valence complex, Ti^{III-IV}, by using EXAFS and XANES techniques. Furthermore, the structures of hydrated V^{IV}, V^{III}, and V^{II} ions in acidic solutions are discussed. UV-visible absorption spectra and Raman scattering spectra are included when necessary.

Experimental

Aqueous solutions of Ti^{IV} were prepared by dissolving $Ti(SO_4)_2 \cdot 4H_2O$ into 4M H_2SO_4 (M=mol dm^{-3}). A 0.75M Ti^{III} solution was prepared by two methods. One was the dissolution of 99.9% Ti metal into 4M H_2SO_4 in an atmosphere of nitrogen gas. The other was an electrolytic reduction of a Ti^{IV} solution. They were spectroscopically identical. The solution of a mixed-valence complex, Ti^{III-IV}, was prepared by mixing solutions of Ti^{III} and of Ti^{IV} under an atmosphere of nitrogen gas.

Solutions of 1M V^{IV} ion were prepared by dissolving $VOSO_4 \cdot 5H_2O$ into 1M H_2SO_4 and $VOCl_2$ into 1M HCl aqueous solutions. The sample used as $VOSO_4 \cdot 5H_2O$ crystals was thermogravimetrically analyzed to have $5.7H_2O$. A solution of low-valence V^{II} was prepared by an electrolytic reduction of the V^{IV} solution. A solution of V^{III} was prepared by mixing equal amount of V^{II} and V^{IV} solutions. Since these low-valence state ions in solution are very sensitive to air, all of the procedures were performed under a nitrogen gas atmosphere. The solutions were placed in a polyethylene pouch for measurements of the X-ray absorption spectra. An X-ray path length of 0.5 mm was used in order to obtain optimum absorption at the Ti or V K-edge in the presence of interference absorption by coexisting $\mathrm{SO_4^{2-}}$ or $\mathrm{Cl^-}$ ions. Crystals were ground into fine powders and sandwiched between adhesive tape.

X-Ray absorption spectra measurements were performed at BL-7C of the Photon Factory in the National Laboratory for High Energy Physics. An Si(111) double-crystal monochromator was used. The electron storage ring was operated at 2.5 GeV with a beam current of 120—190 mA. In order to reduce the absorption of X-rays by air in the optical path, the exit window of the monochromator, I_0-detector, sample, and I-detector were placed as close as possible. The gas for the ionization chambers of the detectors was a mixture of 70% He and 30% $\mathrm{N_2}$. A short-path-length chamber of 5.5 cm was used for the I_0-detector. The measurements were performed at room temperature.

The EXAFS oscillation spectra, $\chi(k)$, were extracted from the raw absorption spectra and were Fourier transformed according to a procedure described elsewhere.[9] Here, k is the photoelectron wave number. Fourier transformations were performed over the range k=41.5—154 nm^{-1} (4.15—15.4 Å^{-1}). The window function was not used in order to gain the highest resolution possible, although this gave some side peaks due to a trancation effect. The values of back-scattering amplitude and phase shift, calculated and parameterized by Teo and Lee,[10] were used. The Fourier transformations were performed by using the parameters for the absorbing metal and the scattering oxygen atom. Therefore, the peak positions corresponding to metal–metal bonds in the Fourier transforms did not indicate the correct bond distances.

Results and Discussion

I. Titanium. UV-Visible Absorption Spectra. The UV-visible absorption spectra of (a) $\mathrm{Ti^{III}}$, (b) $\mathrm{Ti^{III-IV}}$, and (c) $\mathrm{Ti^{IV}}$ in sulfuric acid solution are shown in Fig. 1. The $\mathrm{Ti^{III}}$ solution exhibits a peak at 527 nm. If a colorless $\mathrm{Ti^{IV}}$ solution is added to the $\mathrm{Ti^{III}}$ solution, the peak shifts to 472 nm and its intensity increases significantly. Once the $\mathrm{Ti^{III-IV}}$ stoichiometry is attained, any further addition of $\mathrm{Ti^{IV}}$ gives no peak shift and reduces the peak height. The absorption at 472 nm by $\mathrm{Ti^{III-IV}}$ is due to an intervalence transition. The appearance of the intervalence peak indicates that the $\mathrm{Ti^{III}}$ and $\mathrm{Ti^{IV}}$ ions form either dimer or polymers.

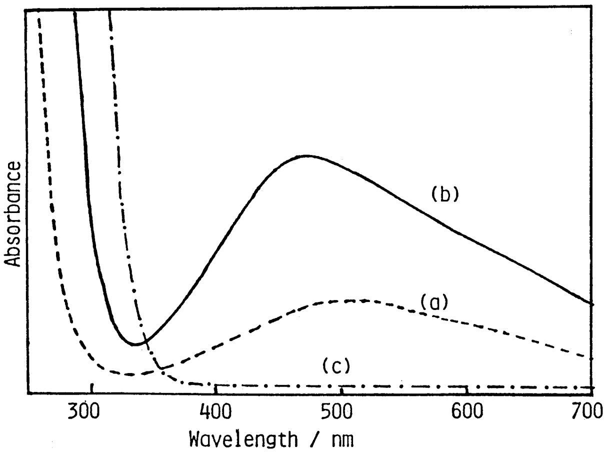

Fig. 1. UV-visible absorption spectra for 0.75 M Ti ions in 4M $\mathrm{H_2SO_4}$ solutions. (a) $\mathrm{Ti^{III}}$, (b) $\mathrm{Ti^{III-IV}}$, and (c) $\mathrm{Ti^{IV}}$.

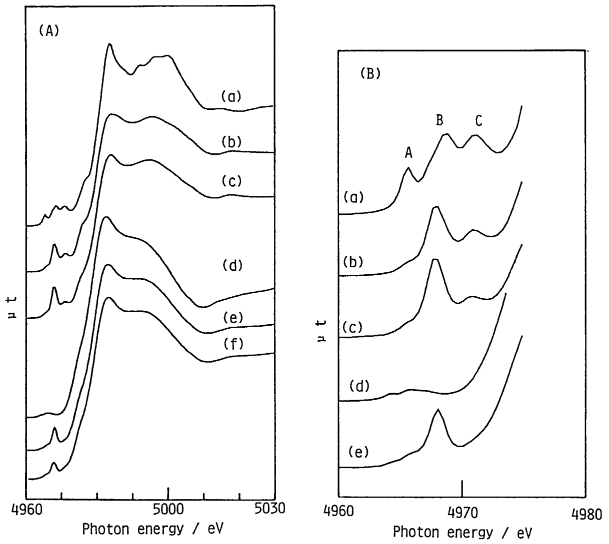

Fig. 2. XANES (A) and pre-edge (B) spectra of Ti K-edge for (a) $\mathrm{TiO_2}$ (anatase), (b) $\mathrm{TiOSO_4{\cdot}2H_2O}$, and 0.75 M solutions of (c) $\mathrm{Ti^{IV}}$, (d) $\mathrm{Ti^{III}}$, and (e) $\mathrm{Ti^{III-IV}}$, all in 4 M $\mathrm{H_2SO_4}$ solutions, (f) is the sum (average) of the spectra of (c) and (d).

XANES. XANES spectra of Ti K-edge are shown in Fig. 2 for powdered crystals of (a) $\mathrm{TiO_2}$ (anatase) and (b) $\mathrm{TiOSO_4{\cdot}2H_2O}$, and solutions of (c) $\mathrm{Ti^{IV}}$, (d) $\mathrm{Ti^{III}}$, and (e) $\mathrm{Ti^{III-IV}}$. Figure 2(B) shows only the pre-edge regions. Three pre-edge peaks for $\mathrm{TiO_2}$ (a) have been assigned to (A) a Frenkel exciton peak, and transitions from 1s (B) to 3d($\mathrm{t_{2g}}$) and (C) to 3d($\mathrm{e_g}$).[11] In the spectra for (b) and (c), the latter two peaks (1s–3d transitions) are strong. In spetrum (c) peak A appears, though it is weak; this indicates the presence of Frenkel exciton, even in solution, since it localizes on a Ti atom. Now, one may compare the XANES spectra in order to obtain information about the structure of $\mathrm{Ti^{IV}}$ in solution. It is obvious that spectra (b) and (c) in both Figs. 2(A) and 2(B) are perfectly identical. This means that the coordination structure of $\mathrm{Ti^{IV}}$ in a sulfuric acid solution must be similar to that in the $\mathrm{TiOSO_4{\cdot}2H_2O}$ crystal. The structures are further discussed later in the EXAFS section.

In spectrum (d) for the $\mathrm{Ti^{III}}$ solution the pre-edge peaks corresponding to 1s–3d transitions are very small. As observed in vanadium compounds by Wong et al.,[12] the existence of a center of inversion in $\mathrm{O_h}$ symmetry does not allow the 1s–3d type transitions. Thus, the XANES spectra for Ti ions in solution indicate that the shape of the $\mathrm{Ti^{III}}$ ion is closer to $\mathrm{O_h}$ symmetry than that of $\mathrm{Ti^{IV}}$.

As already mentioned, the mixed-valence complex

Ti$^{\mathrm{III-IV}}$ exhibits a new absorption peak in the visible region. The new peak does not have any components in either the spectrum of Ti$^{\mathrm{III}}$ or Ti$^{\mathrm{IV}}$. On the other hand, the XANES (e) of Ti$^{\mathrm{III-IV}}$ in Fig. 2 is quite similar to the sum of the spectra of (c) Ti$^{\mathrm{IV}}$ and (d) Ti$^{\mathrm{III}}$. For the sake of convenience, the sum spectrum (f), [(c)+(d)], is included in Fig. 2(A). It thus becomes clear that the spectra of (e) and (f) are in perfect agreement over the entire energy region of XANES. This suggests that the individual coordination structures of Ti$^{\mathrm{III}}$ and Ti$^{\mathrm{IV}}$ remain unchanged in the Ti$^{\mathrm{III-IV}}$ complex in solution. Further, the 1s-3d(t_{2g}) peak of Ti$^{\mathrm{IV}}$ appears in the spectrum of Ti$^{\mathrm{III-IV}}$ at the same energy. This is in contrast with the result regarding vanadium[12] in which the 1s-3d peak shifts, depending on the valence states of (III), (III-IV), and (IV). In the present case of the Ti$^{\mathrm{III-IV}}$ complex, the valences of Ti$^{\mathrm{III}}$ and Ti$^{\mathrm{IV}}$ are distinguishable and a 3d electron is localized at the Ti$^{\mathrm{III}}$ site in Ti$^{\mathrm{III-IV}}$. The Ti$^{\mathrm{III-IV}}$ mixed-valence complex in sulfuric acid is therefore regarded as being class II according to a classification scheme by Robin and Day.[13]

EXAFS. Figure 3 shows the Fourier transforms of EXAFS of the Ti K-edge for (a) $\mathrm{TiOSO_4{\cdot}2H_2O}$ crystals, and solutions of (b) Ti$^{\mathrm{IV}}$, (c) Ti$^{\mathrm{III}}$, and (d) Ti$^{\mathrm{III-IV}}$. A crystallographic study[3] indicated that the $\mathrm{TiOSO_4{\cdot}H_2O}$ takes a zigzag chain structure, $\mathrm{Ti}{\diagup}\mathrm{O}{\diagup}\mathrm{Ti}{\diagdown}\mathrm{O}{\diagdown}\mathrm{Ti}$, in which the Ti–O–Ti unit is linear. The distances of Ti–O and Ti–Ti in the -Ti–O–Ti- chain have been reported to be 180 and 360 pm, respectively.[3] The other four oxygen atoms coordinate to a Ti atom whose Ti–O distances are 193—201 pm.[3]

The peaks shown in Fig. 3(a) at 200 and 349 pm are regarded as corresponding to the Ti–O bonds, including bridging oxygens and others, and to the Ti–Ti bond, respectively.

It is remarkable that the peak corresponding to the Ti–Ti distance is present at 351 pm in spectrum (b) of Ti$^{\mathrm{IV}}$ in solution as well. The peak for Ti–O bonds appears at the same position, 200 pm, as that for $\mathrm{TiOSO_4{\cdot}2H_2O}$ crystals. The XANES spectra for $\mathrm{TiOSO_4{\cdot}2H_2O}$ and Ti$^{\mathrm{IV}}$ solutions also support the idea that the Ti$^{\mathrm{IV}}$ coordination structures in these media must be quite similar, as already mentioned. The detection of the long Ti–Ti bond is possibly due to an enhanced forward-scattering effect of an intervening oxygen atom.

In Fourier transform (c) of the Ti$^{\mathrm{III}}$ solution, the Ti–O peak appears at 212 pm; there is no peak corresponding to a Ti–Ti interaction.

It has been estimated from the UV-visible absorption spectra that dimeric or polymeric species must exist in a Ti$^{\mathrm{III-IV}}$ solution. Similar mixed-valence complexes have been known to exist in the cases of $[\mathrm{V{-}O{-}V}]^{4+}$[7] and $[\mathrm{Cr{-}O{-}CrO_3}]^{+}$.[14] If the Ti–Ti interaction exists in a Ti$^{\mathrm{III-IV}}$ solution, in the form of Ti–O–Ti, analogous to the structure in the Ti$^{\mathrm{IV}}$ solution, the distance of Ti–Ti should be about 360 pm. In Fourier transform (d) of the Ti$^{\mathrm{III-IV}}$ solution, however, no peak corresponding to the Ti–Ti interaction was observed. The Ti–O bonds in the mixed-valence complex gave a peak at 207 pm, which is the average of those for Ti$^{\mathrm{III}}$ and Ti$^{\mathrm{IV}}$.

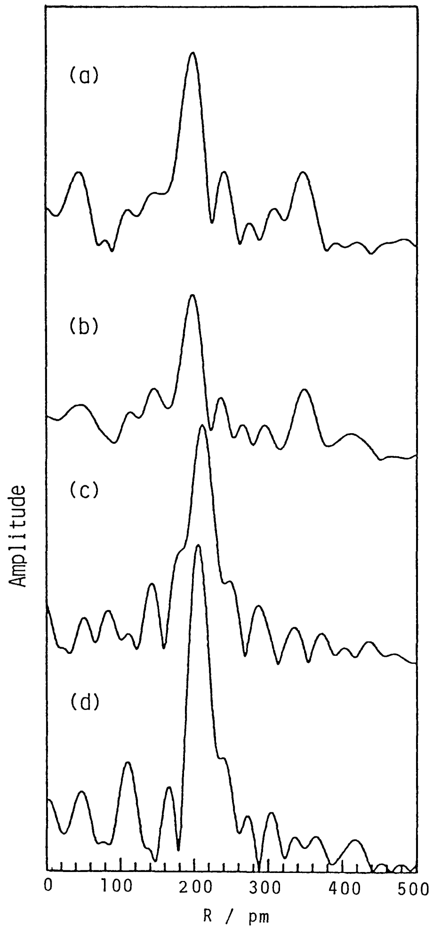

Fig. 3. Fourier transforms of Ti K-edge EXAFS for (a) $\mathrm{TiOSO_4{\cdot}2H_2O}$, and 0.75M solutions of (b) Ti$^{\mathrm{IV}}$, (c) Ti$^{\mathrm{III}}$, and (d) Ti$^{\mathrm{III-IV}}$, all in 4M $\mathrm{H_2SO_4}$ solutions.

II. Vanadium. XANES. The XANES spectra for various oxidation states of vanadium ion in solutions are shown in Fig. 4. Since the 1s-3d transition is dipole-forbidden, the intensity of the pre-edge peak must be weak in an octahedral $\mathrm{VO_6}$ system. This is the case for (b) V$^{\mathrm{III}}$ or (c) V$^{\mathrm{II}}$ in solution. On the other hand, the pre-edge peak of (a) for V$^{\mathrm{IV}}$ is significantly strong. This must be the result of a deformed structure of the V$^{\mathrm{IV}}$ ion from O_h symmetry. It has been reported that the V$^{\mathrm{IV}}$ ion in a $\mathrm{VOSO_4{\cdot}5H_2O}$ crystal coordinates four $\mathrm{H_2O}$ molecules in a plane (the V–O lengths are distributed between 203—231 pm), one double-bonding oxygen at 167 pm and one oxygen atom of $\mathrm{SO_4}^{2-}$ ion at 185 pm by X-ray diffraction analysis.[15] Therefore, the structure is not of O_h symmetry and the pre-edge absorption becomes dipole-allowed due to a combination of strong 3d-4p mixing and overlap of

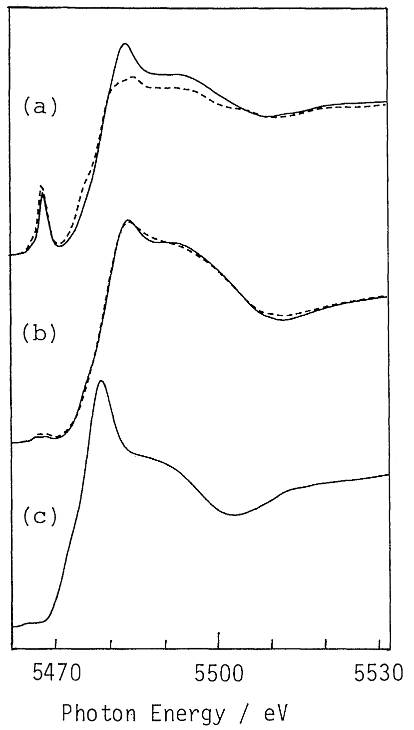

Fig. 4. XANES spectra for 1 M solutions of (a) V^{IV}, (b) V^{III}, and (c) V^{II} in 1 M H_2SO_4 solutions. Dashed line in (a) is for $VOSO_4\cdot 5H_2O$. Dashed line in (b) denotes that in 1 M HCl solution.

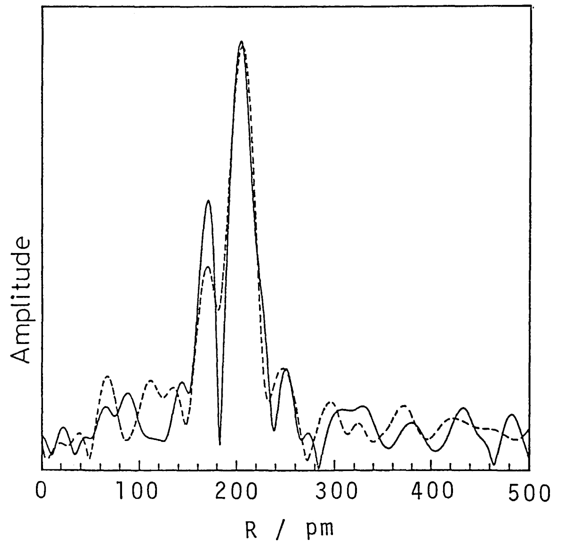

Fig. 5. Fourier transforms of V K-edge EXAFS for $VOSO_4\cdot 5H_2O$ (solid line) and 1 M V^{IV} in 1 M H_2SO_4 solution (dashed line).

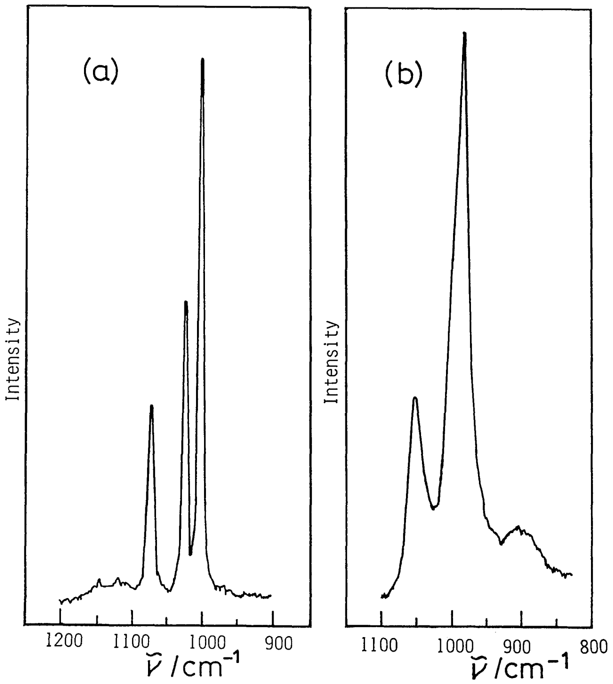

Fig. 6. Raman spectra for (a) $VOSO_4\cdot 5H_2O$ and (b) 1 M V^{IV} in 1 M H_2SO_4 solution.

the metal 3d orbitals with the 2p orbitals of the double-bonding oxygen atom. The XANES spectra of V^{IV} in a H_2SO_4 solution (solid line in Fig. 4(a)) and $VOSO_4\cdot 5H_2O$ crystals (dashed line) are different. The EXAFS spectra of V^{IV} in solution and crystals are also different and are treated in the next section.

The XANES spectra of V^{III} in an H_2SO_4 solution (solid line) and in an HCl solution (dashed line) in Fig. 4(b) are slightly different. There is a shoulder at 5476 eV only in the spectrum for an H_2SO_4 solution; the H_2SO_4 solution displays a stronger oscillation in the region of 5483—5520 eV. This must be due to a difference in structures of V^{III} in these solutions, as is discussed in the next section.

EXAFS. The Fourier transforms of the EXAFS for the V^{IV} ion in solid and in solution are shown in Fig. 5. The peaks at 170 pm and 201 pm correspond to the distances from V^{IV} to a double-bonding oxygen atom and to five other oxygen atoms, respectively. The reported length of the V=O bond in a crystal is 167 pm and the others 185—231 pm.[15] It is noted that the intensity of the V=O peak at 170 pm for a solution is less than that for a solid. Since the peak positions or the bond lengths are the same for both samples, the Debye–Waller factor for the V=O bond in solution should be larger than in solid. This would arise either from the hydrogen-bond formation at the double-bonding oxygen in an aqueous solution or from a trans effect. The bond directed to the trans position with respect to the V=O bond may influence the strength of the V=O bond. The trans site is occupied by different oxygens, i.e. by an H_2O molecule in solution and by an oxygen atom of SO_4^{2-} in a solid. The behavior of the EXAFS peak intensity is in good accordance with the results of a Raman study. Figure 6 shows the Raman spectra over the range of the V=O bond stretching vibration for (a) a solid and (b) a solution. The peak at 1070 cm^{-1} in (a) and at

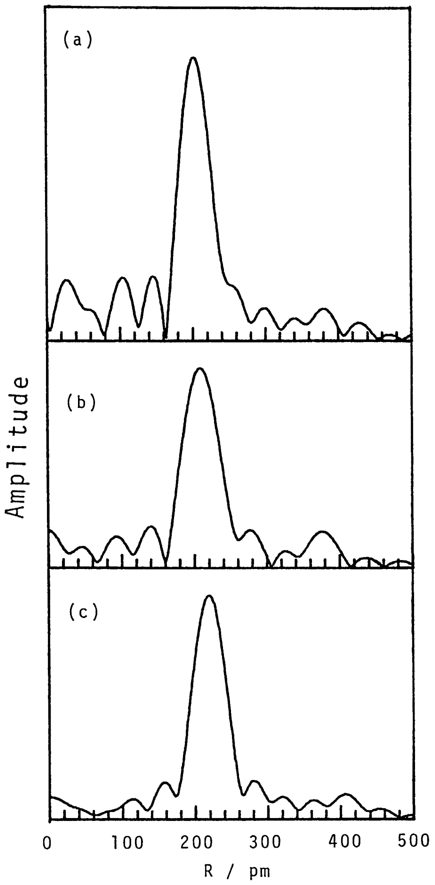

Fig. 7. Fourier transforms of V K-edge EXAFS for (a) 1 M V^{III} in 1 M H_2SO_4 solution, (b) 1 M V^{III} in 1 M HCl solution, and (c) 1 M V^{II} in H_2SO_4 solution.

$1050 cm^{-1}$ in (b) has been assigned to the vibration of the SO_4 group and the peaks at 1000 and $1020 cm^{-1}$ in (a) and the unresolved peak at $980 cm^{-1}$ in (b) to the V=O vibration.[16] The most significant difference between these two spectra exists regarding the peak widths. The peaks corresponding to the V=O vibration for solution are far broader than those for a solid. The correlation of the peak width in the Raman spectrum with the Debye–Waller factor in EXAFS has been well established.[17,18] Though the mechanism which causes the larger Debye–Waller factor is not known in the present case, these is no doubt about the fact that the EXAFS results indicate a different environment around the V^{IV} ion in a soluion from that in a solid.

Fourier transforms for the V^{III} ion in (a) H_2SO_4 and (b) HCl solutions are shown in Fig. 7. Both solutions were obtained by mixing V^{II} and V^{IV} solutions. The peaks at 203 pm in an H_2SO_4 solution and 210 pm in an HCl solution correspond to V–O bonds. The intensity of the peak in an HCl solution is obviously smaller than that in H_2SO_4. It should be noted that a characteristic peak is observed at 377 pm in the spectrum for an HCl soloution but not that for an H_2SO_4 solution. This peak might be due to a V–V interaction in the HCl solution. The VOV^{4+} dimer was reported to exist as a brown intermediate species during the reaction of V^{II} with V^{IV} in an aqueous perchlorate solution by means of a UV-visible spectroscopic technique,[7] which shows the characteristic absorption band at 427 nm. Since the species in the HCl solution also exhibits the absorption band at 427 nm (cf. in an H_2SO_4 solution, no band exists at 427 nm), both brown species in $HClO_4$ and HCl solutions are regarded as having a linear VOV^{4+} structure; thus, the V–V interaction could be detected by EXAFS. The present study concludes that the mixing of V^{II} and V^{IV} gives the V^{III} monomer in an H_2SO_4 solution, but the V^{III} dimer in an HCl solution. No coordination of the Cl^- ion to V^{III} in an HCl solution was detected in the present EXAFS study.

As shown in Fig. 7(c), the V–O bond length for the V^{II} ion is 218 pm. The difference in the bond length from that of the V^{III} complex (203 pm) is 15 pm, which is the same as that reported by Sutin.[19]

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