First Detection of a Silicic Acid Complex with a Catechol Derivative under Natural Conditions

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The formation of silicic acid–tiron complexes was predicted based on the increase in the solubility of amorphous silica in aqueous tiron solution near neutral pH compared with aqueous sodium chloride solutions of the same pH. A 6-coordinated silicic acid–tiron complex was detected by ^{29}Si NMR and the composition was determined to be 1:3 (Si:tiron) by ESI mass spectroscopy.

In recent years, the chemistry of silica nanostructures has been attractive. Diatoms and sponges utilize monomeric silicic acid [$Si(OH)_4$] dissolved in seawater to produce elaborate structures of amorphous silica.[1] In the case of diatoms, long chain polyamines which are covalently attached to polypeptides such as silaffins are thought to contribute to construction of the elegant structure of amorphous silica, however the reaction details remain uncertain. Some higher plants absorb monomeric silicic acid vigorously through the roots, considerably concentrate, transport, and finally precipitate as amorphous silica with beautiful geometric structures in tissue.[2] In the case of rice plants, the existence of a silicon transporter which monomeric silicic acid can specifically pass from root to xylem has been demonstrated.[3] However, the molecular mechanism responsible for the uptake of silicic acid through root and for accumulation of silica with specific geometries has been unknown. As a biomimetic investigation, nanostructured silicas with specific shapes such as rings, globes, and fibers were synthesized by template reaction between TEOS (tetraethylsilicon) and biomaterials such as DNA, protein, and sugars.[4]

From the viewpoint that silicic acid complexes with organic compounds may participate in uptake and transport of silicic acid by living things, silicic acid complexes with biomolecules have been vigorously explored, however, only a few silicic acid complexes with poly(hydroxy alcohols) have been detected in strong alkaline solutions by ^{29}Si NMR.[5] It is necessary to find silicic acid complexes with biomolecules under natural conditions. This paper describes the first detection of a silicic acid complex with a derivative of catechol that is a biomolecule. The detection was based on the increase in solubility of amorphous silica in the presence of tiron (disodium 4,5-dihydroxy-1,3-benzenedisulfonate), ^{29}Si NMR and ESI mass spectrometry.

First, in order to confirm the interaction between silicic acid and tiron, the solubility of amorphous silica was compared between a tiron solution and a NaCl solution as a control at pH 6. Sodium ion concentration in both solutions was the same ($0.2\,mol\,dm^{-3}$) to cancel the effect of sodium ions on the dissolution of amorphous silica. Sodium ions accelerate the initial dissolution rate of silica,[6] on the other hand, the solubility of amorphous silica decreases with increasing NaCl concentration.[7] Figure 1 shows the change in Si concentration with time determined by ICP-AES (same sodium ion concentration as tiron, it can cancel the effect of sodium ion on the solubility of amorphous silica). Judging from the variation of Si concentration, the dissolution equilibrium of amorphous silica in both solutions was reached after 250 h. The solubility of amorphous silica in the tiron solution was high compared with that in the NaCl solution, suggesting that the silicic acid interacts with tiron in aqueous solution to form silicon–tiron complexes. The solubility of amorphous silica is controlled by the sum of Si concentration as the complexes and the constant Si concentration as monosilicic acid.

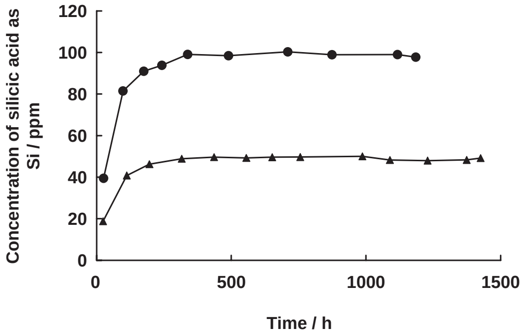

Figure 1. The change in silicic acid concentration with time; ●: solubility of amorphous silica in $0.1\,mol\,dm^{-3}$ tiron solution at pH 6.2; ▲: solubility of amorphous silica in $0.2\,mol\,dm^{-3}$ NaCl solution at pH 5.9.

In order to directly detect the formation of the silicon–tiron complexes, ^{29}Si NMR spectra for the mixed solutions of monosilicic acid and tiron were recorded on a JEOL JNM-AL 400 FT NMR spectrometer as shown in Figure 2. The mixed solutions (tiron/Si mole ratio was in the range from 0 to 30) were prepared

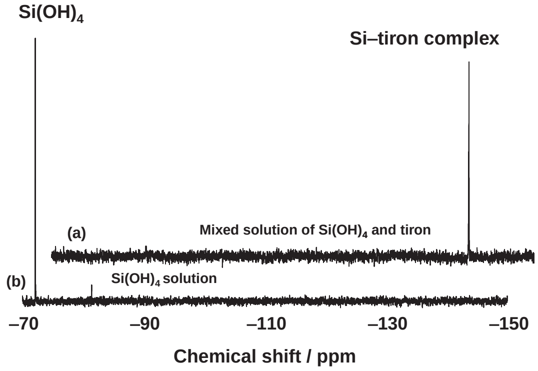

Figure 2. ^{29}Si NMR spectrum (a) for mixed solution of 3.4 $mmol\,dm^{-3}$ sodium silicate and $0.1\,mol\,dm^{-3}$ tiron at pH 6.6. Spectrum (b) for only sodium silicate solution of pH 6.6 was also shown. (resonance frequency: 79.30 MHz, acquisition time: 4.4 s, repetition time: 30 s, D_2O: 50%).

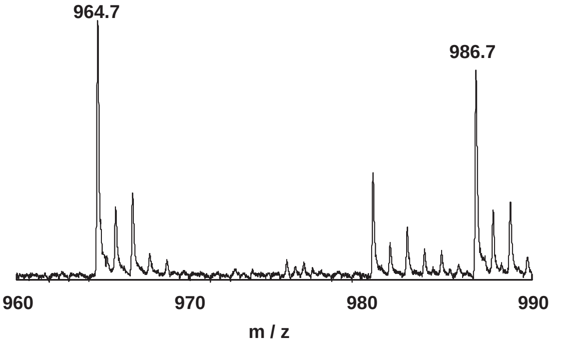

Figure 3. ESI mass spectrum for mixed solution of 1.8 mmol dm^{-3} sodium silicate and 0.1 mol dm^{-3} tiron (tiron/$Si(OH)_4$: 30) at pH 6.8 by cation mode.

using sodium silicate solution prepared from ^{29}Si-enriched silica gel. The chemical shifts are relative to external tetramethylsilane (TMS) for ^{29}Si nuclei. The chemical shift value of monosilicic acid was around -72.2 ppm [tiron/$Si(OH)_4$ mole ratio $= 0$]. In the case of silicic acid solution, the peak due to disilicic acid was observed at -82 ppm, but in the case of mixed solutions, the peak disappeared. For the mixed solutions, when the tiron/Si mole ratio exceeded 3, only one sharp peak was observed around -140 ppm in addition to a peak for monosilicic acid. Above the tiron/Si mole ratio of 25, only the peak due to the complex was observed. The appearance of the peak around -140 ppm suggests the formation of a 6-coordinated silicic acid complex with a composition of 1:3 with three tirons coordinated to a monosilicic acid as a bidentate ligand.[5,8]

To precisely determine the composition of the silicon–tiron complex, ESI positive mode mass spectra for the mixed solutions were measured by a JEOL JMS-T 100CS mass spectrometer. Figure 3 shows the mass spectrum. The peaks at m/z 964.7 and 986.7 correspond to the 1:3 silicon–tiron complex associated with a proton or a sodium ion ($[Si(C_6H_2O_8S_2Na_2)_3]H^+$ or Na^+). For the two peaks, the observed spectra coincided with the simulated spectra considering the existence of isotopes. A peak at m/z of 980 could not be assigned.

Evans and Wong synthesized a catecholato–silicon complex in organic solvent and derived crystals, however, these complexes were unstable in aqueous solution because of rapid hydrolysis.[9] The silicic acid–tiron complex derived from this study is very stable in neutral aqueous solution at room temperature.

A lot of organic compounds (from simple organic compounds with low molecular weight to polymer with high molecular weight) are also present in natural waters. In oil fields, groundwater with higher Si concentration than the solubility of quartz was found and the Si concentration increased with increasing total organic carbon in the groundwater, suggesting that organic compounds may accelerate the dissolution of quartz.[10] A phenolic hydroxy group and carboxyl group are often contained in main functional groups in natural organic compounds such as humic acid, therefore humic acid–silicic acid complexes may be formed under natural conditions.

A silicic acid–β-isopropyltropolon complex has been isolated from a plant (Thujaplicate).[11] Sjöberg et al.[12] reported that only a 1:3 silicon–troponate complex was detected in acidic aqueous solution by ^{29}Si NMR. In Figure 2, the 1:1 and 1:2 silicon–tiron complexes were not detected but only a 1:3 silicon–tiron complex was observed, strongly suggesting that only the 1:3 complex is formed stably. Probably, it may be stabilized due to the sp^3d^2 hybrid orbital resulting from π electrons in tiron coupling with 3d orbitals in silicon atom. The result of theoretical calculation for the silicon–tiron complexes will be published elsewhere in the near future. This 6-coordinated silicon complex may be essential to understand the behavior of silicon in life.

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