Interaction between Al$^{3+}$ and Acrylic Acid and Polyacrylic Acid in Acidic Aqueous Solution: A Model Experiment for the Behavior of Al$^{3+}$ in Acidified Soil Solution

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From the viewpoint of the phytotoxicity and mobility of Al$^{3+}$ released from soil minerals due to soil acidification, the interaction between Al$^{3+}$ and acrylic acid (AA) and polyacrylic acid (PAA) as a model compound of fulvic acid was investigated. The interaction was examined at pH 3 so as to avoid the hydrolysis of Al$^{3+}$. The interaction between Al$^{3+}$ and AA was weak. However, the interaction between Al$^{3+}$ and PAA was strong and depended on the initial (COOH in PAA)/Al molar ratio ($R_P$) of the solution. For the range of 1/$R_P$, the interaction between Al$^{3+}$ and PAA can be divided into three categories: (1) 1:1 Al-PAA-complex (an Al$^{3+}$ combines to a carboxyl group), (2) intermolecular Al-PAA-complex (an Al$^{3+}$ combines to more than 2 carboxyl groups of other Al-PAA-complexes) in addition to the 1:1 Al-PAA-complex and (3) precipitation of intermolecular complexes. In conclusion, $R_P$ is an important factor affecting the behavior of Al$^{3+}$ in acidic soil solution.

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concentration were prepared by dissolving solid polyacrylic acid 5000 (Molecular weight, 5000; Wako Pure Chemicals) in ultrapure water. All sample solutions were also prepared with ultrapure water. Mixed solutions of Al and AA or PAA with the desired molar ratio ((COOH in AA)/Al or (COOH in PAA)/Al molar ratio) were adjusted to pH 3 by dropping a sodium hydroxide solution. The Al concentration was varied from $2.00 \times 10^{-3}$ to $5.28 \times 10^{-1}$ mol dm$^{-3}$. When solid material precipitated, the suspension was filtered using a 0.45-$\mu$m membrane filter. The Al and dissolved carbon concentrations in the filtrate were determined by ICP-AES (Optima 5300DV, Perkin Elmer) and Total Organic Carbon Analyzer (TOC-VE, Shimadzu), respectively. The solid material was characterized by elemental analysis, FT-IR and $^{27}$Al MAS NMR.

**Measurement of $^{27}$Al NMR spectra for solution samples**

The $^{27}$Al NMR spectra for solution samples were recorded on a JNM-AL 400 FT NMR SYSTEM spectrometer operating at 104.05 MHz. The repetition period was 0.1 s. As an external standard for the chemical shift, a 0.1 mol dm$^{-3}$ Al(NO$_3$)$_3$ solution (in 0.1 mol dm$^{-3}$ HNO$_3$) was used. The peak separation for the $^{27}$Al NMR spectra was conducted using a software Origin Ver. 6.

**Measurement of $^{27}$Al magic angle spinning (MAS) NMR spectra for solid sample**

The $^{27}$Al MAS NMR spectra for solid samples were recorded on a JNM-CMX 300 NMR spectrometer operating at 78.1 MHz. The repetition period was 0.2 s. The spinning rate of the sample tube, which was made from ZrO$_2$, was 12 kHz. As an external standard for the chemical shift, a saturated Al(NO$_3$)$_3$ solution was used.

**Measurement of FT-IR spectra for solid sample**

The FT-IR spectra of solid samples were recorded on a JASCO FT/IR-420 FT IR spectrometer using a KBr pellet.

**Dynamic light scattering measurement**

The particle size in mixed solutions of Al and PAA were measured by dynamic light scattering (Zetasizer Nano ZS, Malvern).

**Results and Discussion**

### Al-AA complex in solution

As a preliminary experiment for the studying the interaction between aluminum ion, $[\text{Al(H}_2\text{O)}_6]^{3+}$, (Al$^{3+}$) and polyacrylic acid (PAA), the interaction between Al$^{3+}$ and acrylic acid (AA), which is a monomer unit of PAA, was investigated. For $(\text{carboxyl group in AA})/\text{Al}$ molar ratios ($R_A$) in the range of 1 to 20, no precipitation of solid material occurred. Therefore, we used $^{27}$Al NMR to determine whether the Al-AA complex formed under these conditions. Figure 1 shows the expanded $^{27}$Al NMR spectra of the mixed solutions of Al$^{3+}$ and AA with various $R_A$ values at pH 3. In all spectra, a sharp peak at 0 ppm due to $[\text{Al(H}_2\text{O)}_6]^{3+}$ (6-coordinated Al$^{3+}$) was observed. However, a small peak was observed around 1 ppm, as shown in Fig. 1, suggesting the formation of a 1:1 and monodentate complex between Al$^{3+}$ and AA because of the slight downfield shift. The $^{27}$Al NMR peaks could be separated into two peaks (Fig. 1(e)): the peak due to Al$^{3+}$ ($[\text{Al}^{3+}]_{\text{free}}$) and that due to the Al-AA complex ($[\text{Al}^{3+}]_{\text{complex}}$). As the formation of only 1:1 Al-AA monodentate complex is reasonably hypothesized, the conditional formation constant ($K$) for the 1:1 Al-AA monodentate complex was estimated.

$$\text{Al}^{3+} + \text{AA} = \text{Al-AA}, \quad (1)$$

$$K = \frac{[\text{Al-AA}]_{\text{complex}}}{[\text{Al}^{3+}]_{\text{free}}[\text{AA}]_{\text{free}}}, \quad (2)$$

$$[\text{Al}^{3+}]_{\text{total}} = [\text{Al}^{3+}]_{\text{free}} + [\text{Al}^{3+}]_{\text{complex}}, \quad (3)$$

$$[\text{AA}]_{\text{free}} = [\text{AA}]_{\text{total}} - [\text{AA}]_{\text{complex}}, \quad (4)$$

$$[\text{AA}]_{\text{complex}} = [\text{Al}^{3+}]_{\text{complex}} = [\text{Al-AA}]_{\text{complex}}. \quad (5)$$

From the peak separation, the $[\text{Al-AA}]_{\text{free}}/[\text{Al}^{3+}]_{\text{free}}$ molar ratio was estimated as shown in Fig. 1. The obtained $K$ value was approximately 3.5. As a result, a weak interaction occurred between Al$^{3+}$ and AA in aqueous solution at pH 3. Additionally, it was demonstrated that the monodentate complex between the COO$^-$ group and Al$^{3+}$ had a 1-ppm downfield shift relative to the Al$^{3+}$ in the $^{27}$Al NMR spectra.
Titration curve for addition of Al\textsuperscript{3+} solution to PAA solution

To elucidate the interaction between Al\textsuperscript{3+} and PAA in aqueous solution, a PAA solution (10\textsuperscript{–2} mol dm\textsuperscript{–3} as COOH in PAA, pH 3, 100 cm\textsuperscript{3}) was titrated with an Al\textsuperscript{3+} solution (10\textsuperscript{–2} mol dm\textsuperscript{–3} aluminum nitrate solution, pH 3) and a NaCl solution (0.1 mol dm\textsuperscript{–3}, pH 3). The NaCl was used as a supporting electrolyte, and the concentration of NaCl in Al and PAA solutions was 0.1 mol dm\textsuperscript{–3}. Figure 2a shows the titration curve. At first, when NaCl solution was added to the PAA solution, no pH change was observed (in Fig. 2a, ˘). Since the pK\textsubscript{a} of PAA is 4.5, the degree of dissociation of the carboxylic group was equal to 0.03 at pH 3.16 The pH was lowered by increasing the volume of the Al\textsuperscript{3+} solution added (in Fig. 2a, ˚). As the ionic strength was maintained throughout this titration, a decrease in the pH was caused only by the interaction between Al\textsuperscript{3+} and PAA due to the release of H\textsuperscript{+}, which resulted in the coordination of Al\textsuperscript{3+} to the carboxyl groups. Figure 2b shows the relationship between the amount of Al\textsuperscript{3+} added and the amount of H\textsuperscript{+} released from PAA.

Mixing Al\textsuperscript{3+} and PAA solutions at various (COOH in PAA)/Al molar ratios

When PAA and Al\textsuperscript{3+} solutions were mixed at various molar ratios, the mixtures were fixed to pH 3. In this case, precipitation occurred in some solutions. For molar ratios from 1 to 20 ((COOH in PAA)/Al molar ratio; R\textsubscript{P}), a white material precipitated immediately after mixing the Al\textsuperscript{3+} and PAA solutions. From measurements of dissolved carbon and aluminum in the filtrates, we determined that most of the PAA and Al\textsuperscript{3+} were precipitated. Because the hydrolysis of Al\textsuperscript{3+} can be neglected at pH 3, it can be reasonably deduced that the precipitation occurred as a result of the interaction between Al\textsuperscript{3+} and PAA at pH 3.

Increase in the size of Al-PAA complex with increasing (COOH in PAA)/Al molar ratios

For sample solutions with the R\textsubscript{P} value above 44, no precipitation occurred. Figure 3 shows the average particle size in a mixed solution with 1/R\textsubscript{P} measured by DLS. R\textsubscript{C} (COOH in PAA)/Al molar ratio.

Al-PAA complexes in solution

Figure 4 shows \textsuperscript{27}Al NMR spectra of the mixed solutions of Al\textsuperscript{3+} and PAA with various R\textsubscript{P} values (44 to 560, (b) – (g)) in addition to the spectrum for an aluminum nitrate solution of pH 3 as a reference ((a)). If a part of the Al was present as free [Al(H\textsubscript{2}O\textsubscript{6})\textsuperscript{3+}} in solutions, a sharp peak, such as (a), should be observed at 0 ppm because the hydrolysis of Al\textsuperscript{3+} can be ignored at pH 3. In the spectra (b) – (g), however, broad spectra were observed independent of R\textsubscript{P}, suggesting that all of the Al\textsuperscript{3+} interacted with carboxyl groups in PAA molecules. These sample solutions with various R\textsubscript{P} values were prepared using a constant PAA concentration and varying the Al concentrations. In all cases of the Al-PAA system, the peak around 1 ppm was clearly observed. Judging from the results in Figs. 1 and 3, the peak at 1 ppm can be assigned to a 1:1 and monodentate complex. As the proportion of Al increased (the spectra of (b) and (c)), an additional peak at around –4 to –7 ppm was observed. This peak can be assigned to a higher coordination complex because of the upfield shift caused by an increase in the number of ligands (i.e., increase in the electron density). Considering the
result of the DLS measurement (Fig. 3) in addition to the appearance of the peak around –4 to –7 ppm, as shown in Fig. 4, it appears with increasing $1/R_P$ in the mixed solution, that intermolecular multidentate complex (higher coordination complexes for Al$^{3+}$) are formed and the particle size could become large.

**Al-PAA complex in precipitate**

Below an $R_P$ of 20 in mixed solutions, precipitation occurred. According to the results of an elemental analysis for the precipitate ($R_P = 5$), for which inorganic ash can be assumed to be Al$_2$O$_3$, the $R_P$ of the precipitates, which corresponds to the mean coordination number for Al$^{3+}$, was estimated to be 4.3, suggesting the occurrence of intermolecular complexation due to the formation of higher coordination complexes, as described above.

Figure 5 shows IR spectra for PAA as a reference and of the precipitate ($R_P = 5$). $R_P$: (COOH in PAA)/Al molar ratio.

**Interaction between Al$^{3+}$ and PAA at pH 3**

For the solution with $R_P$ values of solutions, the interaction between Al$^{3+}$ and PAA at pH 3 can be interpreted as shown in Scheme 1. At $R_P = 0$ (in the absence of Al$^{3+}$), the PAA molecule shrunk because of hydrogen bonds between carboxyl groups at pH 3 (see Scheme 1). Increasing the $1/R_P$ from 0.0017 to 0.0135 (increasing the amount of Al$^{3+}$ relative to that of PAA), resulted in the formation of a 1:1 and monodentate Al-PAA complex, which was assigned to the peak at 1 ppm, as shown in Fig. 4, and the formation proceeds. With increases in the $1/R_P$ value, the size of Al-PAA complex increased. As a result, the PAA molecule of the Al-PAA complex may gradually expand as a result of electrostatic repulsion between Al$^{3+}$ ions in the Al-PAA complex. In parallel with the formation of Al-PAA complexes and their expansion, the formation of intermolecular complexes among the expanded Al-PAA complexes, which were assigned to the peak around –4 to –7 ppm in Fig. 4, may proceed successively. Above a $1/R_P$ value of 0.05, the intermolecular Al-PAA complexes precipitate as a result of neutralization of the negative charges on the carboxyl groups by the coordination of Al$^{3+}$, and this complex was assigned to the peak at –4.4 ppm in Fig. 6. Consequently, the interaction
between Al\[^{3+}\] and PAA in an aqueous solution of pH 3 strongly depends on \(R_P\).

A viewpoint of environmental chemistry

Various organic carboxylic acids, from monocarboxylic acids, such as acetic acid and acrylic acid, to polycarboxylic acids such as polyacrylic acid, are present in soil solutions. In this study, we found that monocarboxylic acids are weak ligands for phytotoxic Al\[^{3+}\], while polycarboxylic acids with many carboxyl groups as the functional group are strong ligands, that is, most of the Al\[^{3+}\] can combine with polycarboxylic acids to form Al-polycarboxylic acid complexes in the presence of excess polycarboxylic acid, even at pH 3, which is considered to be the limiting pH for soil acidification. The complexation reaction depends on \(R_P\). If the \(R_P\) value is larger than a certain limit, the complex can be dissolved, whereas if it is lower (indicating an increase in the amount of Al\[^{3+}\]), the complex precipitates as intermolecular complexes. In conclusion, an excess of polycarboxylic acid can decrease the phytotoxicity of Al\[^{3+}\].

In addition, the mobility of the complex is also greatly affected by \(R_P\). The environmental chemistry of aluminum after soil acidification can be controlled by change in the relative amount of organic polymer containing carboxyl groups as functional group in the soil against that of Al\[^{3+}\].

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