



Complexation Between Aluminum Ion and Glycolic Acid Under Acidic Condition

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Abstract

The complexation between Al^{3+} ($[\text{Al}(\text{H}_2\text{O})_6]^{3+}$) and glycolic acid (GA, $\text{C}_2\text{H}_4\text{O}_3$) which has a carboxyl group and a hydroxyl group in a molecule was investigated under acidic condition using ^{27}Al NMR, ^{13}C NMR and ESI–MS techniques. The five peaks including a peak due to Al^{3+} were observed in ^{27}Al NMR spectra for the mixed solution of Al^{3+} and GA, suggesting the existence of at least four Al–GA complexes. The results of NMR and ESI–MS measurements revealed that GA and Al^{3+} can form one monodentate complex (AlGA^{2+}) and three bidentate complexes (AlGA^+ , AlGA_2^- , and AlGA_3^{3-}) complexes. From the deconvolution of ^{27}Al NMR spectra and pK_a value of GA, the conditional formation constants ($\log_{10} K$) of each complex (GA/Al molar ratio of 25 in mixed solution) can be determined to be 0.94 (AlGA^{2+}), -0.96 (AlGA^+), -0.77 (AlGA_2^-) and -2.21 (AlGA_3^{3-}), respectively. In addition, the overall formation constant of three bidentate complex at pH 3 was also calculated to be -1.65 .

Keywords Aluminum ion · Complexation · Glycolic acid · Acidic condition

1 Introduction

Aluminum (Al) is the most abundant metal ion (approximately 7%) in earth's crust. Under ordinary conditions, Al is fixed as Al^{3+} in natural solids such as rocks and soils. However, in acidified environments, Al is released as hexaaqua aluminum ion ($[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, Al^{3+}) and its hydrolytic species (AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, and the tridecameric Al polymer (the Keggin-type Al_{13} polycation)) into the soil solution due to decomposition of soil minerals by attack of H^+ . As a result, it can easily mobilize in aquatic environments [1]. In addition,

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these dissolved Al^{3+} species exhibit significant toxicity towards plants and animals. For example, several studies have reported that even micromolar concentrations of Al^{3+} can inhibit plant growth and production [2–7], while this toxicity disappeared upon the formation of organic and inorganic Al^{3+} complexes [2, 4, 7–11].

Many Al-tolerant plants release organic acids, especially carboxylic acids, that can complex Al^{3+} , consequently reducing the toxicity of Al^{3+} [2–7]. Therefore, the interactions between Al^{3+} and such simple organic acids have been intensively investigated [12–18]. In addition, humic substances (HS) which are abundant natural organic compounds are also able to form Al-HS complexes in the environment. The complexation between Al^{3+} and HS plays an important role in reducing the toxicity and mobility of Al^{3+} in natural waters [19–22]. The structure of HS is very complicated and the main functional groups are carboxylic group and hydroxyl group [23–27]. Although the complexation between Al^{3+} and HS is very important, it is difficult to determine the functional groups in HS that are behind this complexation [28]. Therefore, a model compound with the local structure of HS has been used to study its interaction with Al^{3+} [28–30]. In previous investigations, we investigated the interactions between Al^{3+} and salicylic acid (SA), an aromatic compound with one carboxylic group and one hydroxyl group, and synthesized 2,3-dihydroxyterephthalic acid (DHTPA), an aromatic compound with two carboxylic and two hydroxyl groups, as a model compound with the functional groups of fulvic acids which is a soluble HS in water both under acid and alkaline conditions [28, 30]. The average conditional stability constant of the Al-SA and Al-DHTPA complex was successfully calculated by nuclear magnetic resonance (NMR) and potentiometric titration. The use of such model compound is useful to determine the interaction between Al^{3+} and local structure of fulvic acid.

Since the SA and DHTPA are aromatic compounds with one carboxyl group and one hydroxyl group and with two carboxyl groups and two hydroxyl groups in the molecule, in this work, glycolic acid (hydroxyacetic acid, $\text{C}_2\text{H}_4\text{O}_3$) (GA) which is an aliphatic compound with one carboxyl group and one hydroxyl group was selected to examine the interaction between Al^{3+} and a local structure of fulvic acid. As the GA is a natural organic compound found especially in sugar-related plants and has one carboxyl group and one hydroxyl group in the molecule, it is reasonable to use GA as the model compound of local structure of HS. In addition, the GA is the smallest molecule having a carboxylic group and a hydroxyl group within a molecule. The interaction with metal ions is interesting both for complex chemistry and for environmental chemistry. In this study, the complexation between Al^{3+} and GA was investigated using ^{27}Al and ^{13}C NMR and ESI-MS techniques. All experiments were conducted at pH 3, which is a limiting pH of acidified soil so as to avoid the hydrolysis of Al^{3+} . From a viewpoint of the Al^{3+} toxicity in hydrosphere, it is essential to examine whether Al^{3+} ion can interact with organic compounds in aqueous solution under the pH 3 or not.

2 Experimental

2.1 Reagents and Solutions

Aluminum (Al) stock solution ($0.1 \text{ mol}\cdot\text{dm}^{-3}$) was prepared by dissolving crystalline aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, FUJIFILM Wako Pure Chemical Corporation) in $0.1 \text{ mol}\cdot\text{dm}^{-3}$ nitric acid. The Al concentration was determined by EDTA titration. Glycolic acid (GA) (pK_a : 3.83) solution with the desired concentrations was prepared

by dissolving the GA (Tokyo Chemical Industry Co., Ltd.) in water. All sample solutions were prepared with ultrapure water (18.0 M Ω cm) (Milli-Q SP system, Millipore). Sample solutions were prepared by mixing the Al stock solution with the GA stock solution in the desired molar ratio (GA/Al ratio). Mixed solutions of Al and GA with desired GA/Al molar ratio were adjusted to pH 3 by dropping a sodium hydroxide solution and nitric acid. ^{27}Al and ^{13}C NMR spectra and ESI–MS spectra of the mixed solutions were measured.

2.2 Measurement of ^{27}Al and ^{13}C NMR Spectra

The ^{27}Al NMR spectra were recorded on a JEOL ECA-600 spectrometer operating at 156.39 MHz. (repetition period: 0.37 s, acquisition time: 0.262 s). Each sample solution was placed in a 5 mm quartz tube. A sodium aluminate dissolved in D_2O enclosed in quartz tube with a diameter of 2 mm was placed into 5 mm quartz tube as an external standard. Chemical shifts were referenced to the signal of $0.02 \text{ mol}\cdot\text{dm}^{-3} [\text{Al}(\text{OD})_4]^-$ solution (80 ppm from $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$). The ^{13}C NMR spectra were also recorded on a JEOL ECA-600 spectrometer operating at 150.91 MHz (repetition time: 1.19 s, acquisition time: 0.693 s). Chemical shift was referenced to the signal of TMS.

The peak separation of each spectrum was conducted using Origin Pro (Light Stone). The function used for fitting was the Voigt function.

2.3 Measurement of ESI- MS Spectra

ESI–MS measurement of mixed solution of Al^{3+} and GA was performed using a Waters ESI–MS spectrometer, Quattromicro API in the positive ionization mode. The solutions were introduced into the spectrometer at a flow rate of $2 \mu\text{L}\cdot\text{min}^{-1}$. The operation conditions were as follows: capillary voltage 3.0 kV, sample cone voltage 50 V, RF lens 0 V, source temperature 120 $^\circ\text{C}$, desolvation temperature 150 $^\circ\text{C}$, cone gas flow rate $50 \text{ L}\cdot\text{h}^{-1}$ and desolvation gas flow rate $600 \text{ L}\cdot\text{h}^{-1}$.

3 Results and Discussion

3.1 Interaction Between Al^{3+} and GA in Solution at pH 3

Figure 1 shows the ^{27}Al NMR spectra of Al^{3+} and GA mixed solutions at various GA/Al molar ratio at pH 3. The total Al concentration in sample solutions was $0.02 \text{ mol}\cdot\text{dm}^{-3}$. The sharp peak at 0 ppm (* in Fig. 1) is due to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, and at least four new broad peaks were observed by the peak separation (shown in Fig. 2). The chemical shift values of the peaks from the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ were 0.28, 9.8, 17.8, and 26.2 ppm, respectively. Consequently, these new peaks are attributed to the Al-GA complexes. Based on the chemical shift values, the Al^{3+} in the Al-GA complex is 6-coordinated. From the peak intensities of the ^{27}Al NMR spectra, the distribution of each Al^{3+} as a function of the GA/Al molar ratio was calculated (Fig. 3). When the GA/Al ratio was < 5 , the dominant form of Al was free $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. On the other hands, in the GA/Al ratio of ≥ 5 , the Al-GA complexes became dominant, and at a molar ratio of 25, almost all Al^{3+} species were under the form of the Al-GA complex. In the new peaks present due to the Al-GA complexes, the first peak at 0.28 ppm has a slight downfield shift from the peak at 0 ppm due to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. Etou

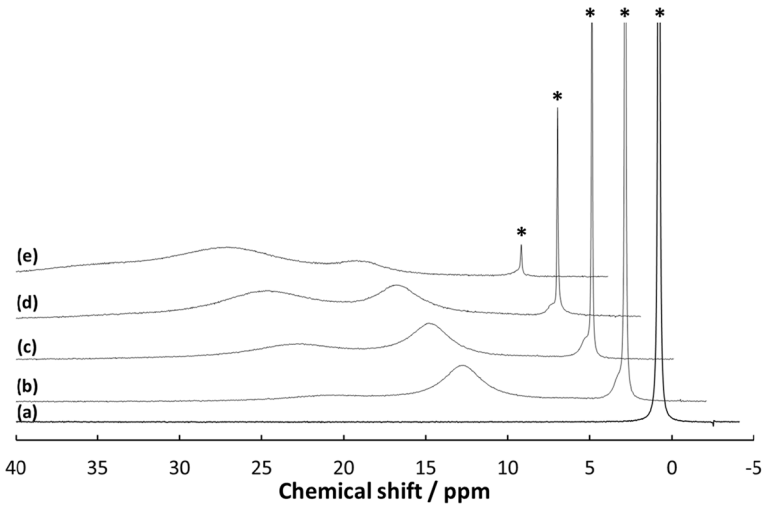


Fig. 1. ^{27}Al NMR spectra of the mixed solutions of Al^{3+} and GA at pH 3 with various GA/Al molar ratios. **a** $\text{Al}(\text{NO}_3)_3$ solution at pH 3. GA/Al = **b** 2, **c** 5, **d** 10, and **e** 25

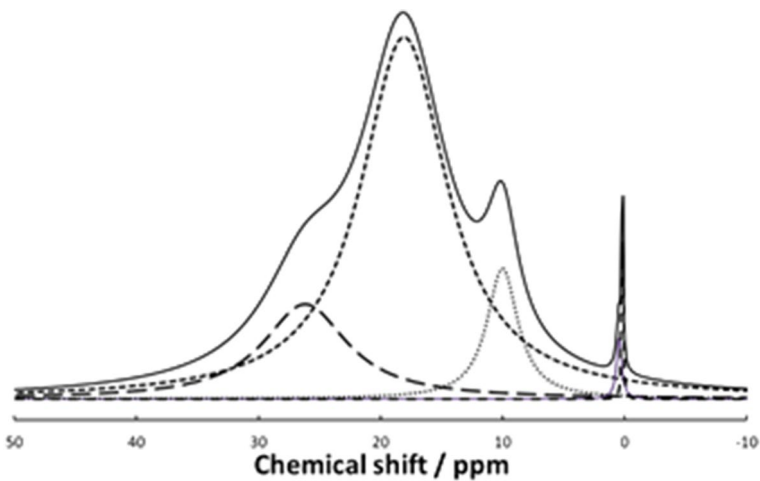
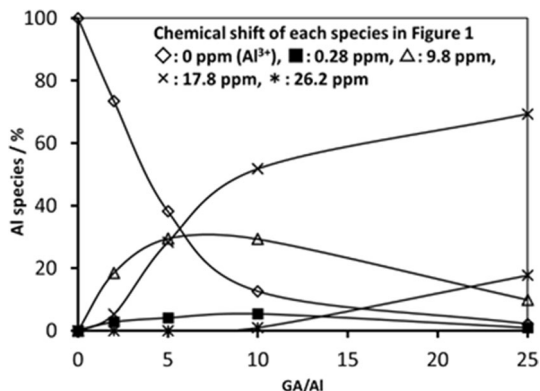


Fig. 2 Peak separation of the ^{27}Al NMR spectrum of a mixed solution of Al^{3+} and GA (GA/Al=25) at pH 3

et al. reported the interaction between Al^{3+} and acrylic acid (AA) at pH 3 and suggested the formation of a 1:1 monodentate Al-AA complex because of the slight downfield shifts (1 ppm) [29]. In this study, the peak at 0.28 ppm was assigned to the 1:1 monodentate complex. From the pK_a value, the binding site of GA in the monodentate complex may be a carboxyl group. The difference in the chemical shift of the three other peaks was similar, and the peak intensity increased with increasing GA/Al ratio, thus suggesting the formation of successive complexes.

Fig. 3 Distribution curves of Al species as functions of GA/Al molar ratios at pH 3



Both functional groups of GA (the carboxyl group and hydroxyl group) can bind to Al^{3+} by a ligand exchange reaction. At a GA/Al molar ratio of 2, the dominant Al-GA complex was observed at 9.8 ppm in the ^{27}Al NMR spectrum, while other complexes were not abundant (Fig. 3). To determine the coordination site of GA in the Al-GA complex, ^{13}C NMR spectra were recorded for a GA solution and the mixed solution of GA/Al of 2 (Fig. 4). The peaks at 179.7 and 62.5 ppm were attributed to carbon atoms in the carboxyl group and hydroxymethyl group in free GA (Fig. 4a, black down point triangle). In contrast, in the mixed solution, the peaks corresponding to free GA were not observed, and new peaks at 180.6 and 64.1 ppm were observed (Fig. 4b, white down point triangle) which can

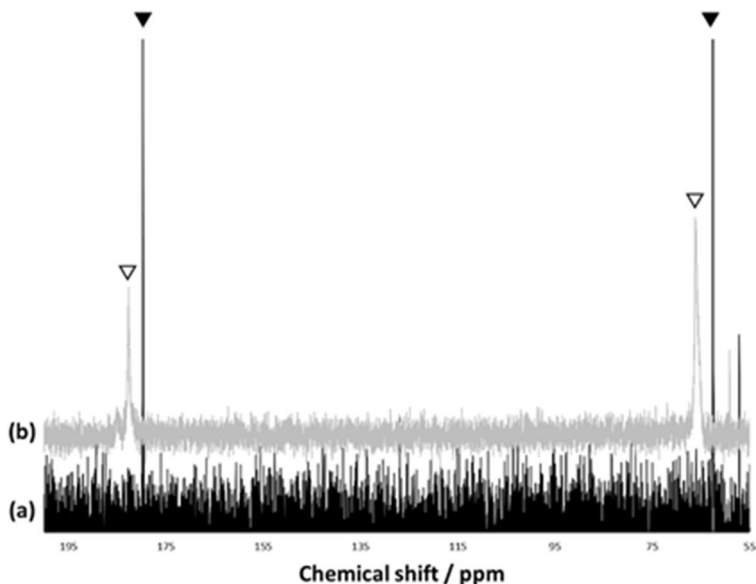


Fig. 4. ^{13}C NMR spectra of a mixed solution of Al^{3+} and GA at pH 3. **a** GA solution, **b** GA/Al=2

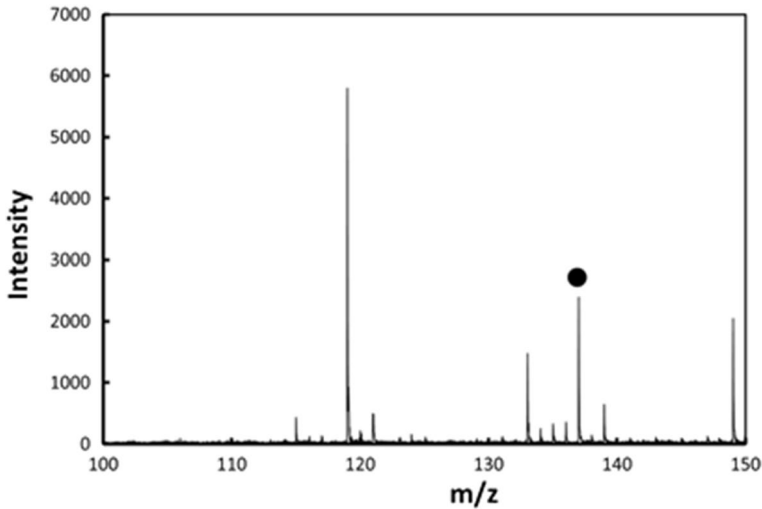
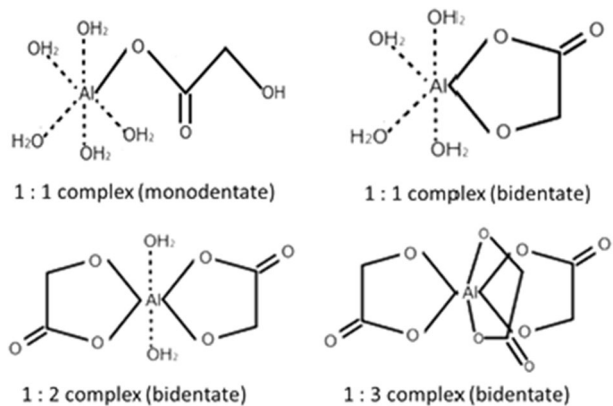


Fig. 5 ESI-MS spectrum of a mixed solution of Al^{3+} and GA (GA/Al=2) at pH 3

be assigned to the carboxyl and hydroxymethyl groups in the Al-GA complex. From the ^{13}C NMR spectra, the binding sites of GA with Al^{3+} were both carboxylic and hydroxymethyl groups. In addition, the ESI-MS spectrum of the same sample is shown in Fig. 5. The peak at $m/z=137.03$ (black circle) is attributed to $[\text{Al}(\text{OCH}_2\text{COO})(\text{H}_2\text{O})_2]^+$. From the results of ^{13}C NMR and ESI-MS measurements, the peak at 9.8 ppm in ^{27}Al NMR spectra of the mixed solution with GA/Al molar ratio of 2 could be identified as a 1:1 AIGA⁺ bidentate complex. It was also shown that Al^{3+} formed a bidentate complex with a carboxyl and a hydroxymethyl groups. Since the additivity law of chemical shift was established for the three other peaks of Al-GA complexes (9.8, 17.8, and 26.2 ppm), it was considered that 1:1–1:3 chelate complexes were successively formed. These results indicate that GA can form monodentate and bidentate complexes with Al^{3+} . The structural formulae of the suggested Al-GA complexes are shown in Fig. 6.

Fig. 6 Proposed structures of Al-GA complexes



3.2 Conditional Formation Constants of Al-GA Complexes

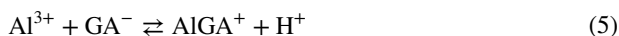
The results revealed that GA formed multiple complexes with Al^{3+} at pH 3. Successively, the conditional formation constant ($\log_{10}K$) of each complex and the overall formation constant (β) of the bidentate complex were determined from the ^{27}Al NMR results. Considering the pK_a value of GA (3.83) (1), the reactions with Al^{3+} were considered as (3), (5), (7), and (9). From the pK_a value, it was found that approximately 13% of carboxylic groups dissociated at pH 3. The hydration of Al^{3+} was omitted for simplicity. Using the result of peak separation from the ^{27}Al NMR spectra and the total Al^{3+} and GA concentrations, which were determined in the preparation of the solutions, the concentration of each complex was determined. Here, K_a , K_{1m} , K_{1b} , K_{2b} , and K_{3b} indicate the dissociation constant of GA, and the formation constants of 1:1 monodentate, 1:1 bidentate, 1:2 bidentate, and 1:3 bidentate Al-GA complexes, respectively.



$$K_a = [\text{H}^+][\text{GA}^-]/[\text{GA}] = 1.50 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3} \quad (2)$$

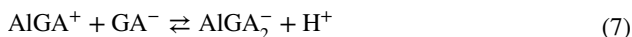


$$K_{1m} = [\text{AIGA}^{2+}]/[\text{Al}^{3+}][\text{GA}^-] \quad (4)$$

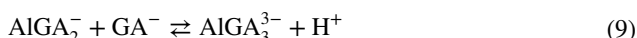


In the formation of the bidentate complex, H^+ was released from an OH group.

$$K_{1b} = [\text{AIGA}^+][\text{H}^+]/[\text{Al}^{3+}][\text{GA}^-] \quad (6)$$



$$K_{2b} = [\text{AIGA}_2^-][\text{H}^+]/[\text{AIGA}^+][\text{GA}^-] \quad (8)$$



$$K_{3b} = [\text{AIGA}_3^{3-}][\text{H}^+]/[\text{AIGA}_2^-][\text{GA}^-] \quad (10)$$

From the mass balance equation of Al^{3+} and GA, the total Al and GA concentrations were calculated as follows. $[\text{H}^+]$ was constant at $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ (pH 3).

$$[\text{Al}]_{\text{total}} = [\text{Al}^{3+}] + [\text{AIGA}^{2+}] + [\text{AIGA}^+] + [\text{AIGA}_2^-] + [\text{AIGA}_3^{3-}] \quad (11)$$

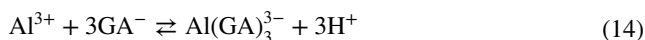
If $[\text{Al}]_{\text{total}}$ is known, $[\text{Al}^{3+}]$, $[\text{AIGA}^{2+}]$, $[\text{AIGA}^+]$, $[\text{AIGA}_2^-]$ and $[\text{AIGA}_3^{3-}]$ can be calculated from the peak separation of the ^{27}Al NMR spectra.

$$[\text{GA}]_{\text{total}} = [\text{GA}] + [\text{GA}^-] + [\text{AIGA}^{2+}] + [\text{AIGA}^+] + 2[\text{AIGA}_2^-] + 3[\text{AIGA}_3^{3-}] \quad (12)$$

$$[\text{GA}^-] = ([\text{GA}]_{\text{total}} - [\text{AlGA}^{2+}] - [\text{AlGA}^+] - 2[\text{AlGA}_2^-] - 3[\text{AlGA}_3^{3-}]) / (1 + [\text{H}^+]/K_a) \quad (13)$$

As $[\text{GA}]_{\text{total}}$, $[\text{AlGA}^{2+}]$, $[\text{AlGA}^+]$, $[\text{AlGA}_2^-]$, $[\text{AlGA}_3^{3-}]$, $[\text{H}^+]$ and K_a are known, $[\text{GA}^-]$ can be easily calculated. Consequently, the formation constant of Eqs. 4, 6, 8 and 10 can be calculated.

The $\log_{10} K$ values of the complexes at pH 3 were present in Table 1. In addition, from these results, the overall formation constant of three bidentate complexes at a GA/Al molar ratio of 25 was calculated. The overall reaction and the overall formation constant ($\log_{10} \beta$) of the bidentate complexes are represented as (14) and (15). The $\log_{10} \beta$ was calculated to be -1.65 .



$$\beta = [\text{Al}(\text{GA})_3^{3-}][\text{H}^+]^3 / [\text{Al}^{3+}][\text{GA}^-]^3 \quad (15)$$

This study revealed that stable Al-GA complexes can be formed at pH 3. Comparing the reactivity of GA with that of AA, both of which have one carboxylic group, the formation constant of Al-GA complex was larger than that of Al-AA complex [29]. This is presumed to be due to that GA has a hydroxyl group in addition to the carboxylic group. The difference of pK_a value of GA (3.83) and AA (4.35) may be due to the large electronegativity of oxygen atom in the hydroxyl group. On the other hand, when we compared the reactivity of GA with those of SA [30] and DHTPA [28] having one carboxylic and one hydroxyl and two carboxylic and two hydroxyl groups, respectively, the reactivity of GA was smaller than the two acids. The $\log_{10} K$ of the 1:1 bidentate complexes (Al-SA and Al-DHTPA) were 2.48 and 1.09. This may be due to rigidity of the GA which is a small aliphatic molecule and steric fitness to Al^{3+} of the aromatic SA and DHTPA. Due to the rigidity, the formation constant of the monodentate Al-GA complex may be large compared with those of the bidentate Al-GA complexes. In SA, DHTPA, etc., carboxyl groups and hydroxyl groups that form a chelate structure are bonded to adjacent carbons. Therefore, it is considered that the distances between each carbon atom and the functional group are suitable to form a chelate structure thermodynamically. On the other hand, considering the structure of GA, the carboxyl and hydroxyl groups are attached to the same carbon atom. It is therefore considered to be difficult to form a chelate complex due to the rigidity of the structure. We believe that this is the reason why the formation constant of the monodentate complex was larger in the complex formation between GA and Al^{3+} .

From the above results, when carboxyl and hydroxyl groups are present in the vicinity of a natural insoluble organic macromolecule which has a complicated structure, such as humic acid, they can act as a reaction site for immobilizing Al^{3+} . In addition, in terms of the interaction between Al^{3+} and simple carboxylic acid, several studies have been

Table 1 Conditional formation constants of Al-GA complexes

GA/Al molar ratio in mixed solution	2	5	10	25
$\log_{10} K_{1m}$	0.99	1.07	1.32	0.94
$\log_{10} K_{1b}$	-1.12	-1.00	-0.90	-0.96
$\log_{10} K_{2b}$	-1.07	-0.91	-1.02	-0.77
$\log_{10} K_{3b}$	-	-	-3.01	-2.21

conducted on the complexation between Al^{3+} and simple dicarboxylic acids. However, this study revealed that even a simple organic acid bearing only one carboxylic and one hydroxyl group, such as GA, can form a chelate structure and stable complexes in the environment. These results strongly suggest that fulvic acid and simple organic compounds in the soil can effectively decrease in the toxicity of Al^{3+} dissolved in an acidic environment. We also expect that this research will provide useful information for the discussion of complex formation between HS and Al^{3+} in the environment.

4 Conclusion

The complexation of Al^{3+} and GA was investigated at pH 3. GA has a one carboxyl and one hydroxyl groups in the structure and has a possibility of the formation of chelate structure with Al^{3+} . The NMR and ESI–MS results revealed that GA can form various Al-GA complexes, including a monodentate complex and three bidentate complexes (AlGA^+ , AlGA_2^- , and AlGA_3^{3-}) at pH 3. The $\log_{10} K$ values of each complex were determined from ^{27}Al NMR measurement. The $\log_{10} K$ value of each complex was calculated and the overall formation constant of three bidentate complex was also determined ($\log_{10} \beta$: -1.65). Although the bidentate chelate complex formation was important in the cases of SA and DHTPA, monodentate complex formation with a carboxylic group was essential in the case of GA. This may indicate that the coordination system consisting of a carboxyl group and a hydroxyl group on the two neighboring carbon atoms such as SA and DHTPA shows larger chelate effect for Al^{3+} , while, the coordination system consisting of a carboxylic group and a hydroxyl group on a carbon atom such as GA prefers the monodentate complex formation with the carboxylic group. Based on our results, when considering the complex formation reaction between HS and Al, it is thought that the structure in which functional groups are present on adjacent carbon atoms is more likely to be a site for complex formation with Al than the structure with multiple functional groups on one carbon atom like GA. The coordination systems consisting of a carboxylic group and a hydroxyl group can render Al^{3+} immobile even in acidic conditions and consequently decrease its toxicity in hydrosphere.

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Author Contributions All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by ME and TT. The first draft of the manuscript was written by ME and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Declarations

Conflict of interest The authors hereby declare no existing financial interests concerning these research studies.

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