¹³C and ²⁷Al NMR and Potentiometric Study on the Interaction between Aluminium Ions and Quinolic Acid in Acidic Aqueous Solutions

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The interaction between aluminium ion (Al) and quinolic acid (L) in acidic aqueous solution was investigated by potentiometry and ¹³C and ²⁷Al NMR spectroscopy. In the ²⁷Al NMR spectra, two peaks were observed at 8 and 15.6 ppm, which were assigned to AlL and AlL₂ complexes, respectively. The ¹³C NMR spectra provide clear evidence that the L acts as a bidentate ligand and that the L coordinates with a nitrogen atom and an oxygen atom of the adjacent carboxylic group to form a chelate complex with a five-membered ring. From a potentiometric study, the formation constants (log β₁ and log β₂) for the AlL and AlL₂ complexes were estimated to be 4.52±0.02 and 7.99±0.05, respectively.

Keywords Aluminium ion, phytotoxicity, quinolic acid, functional group, natural organic compound, NMR

Although [Al(H₂O)₆]³⁺ forms complexes with various organic ligands in the hydrosphere of forests, its toxicity against plants is considerably stronger than that of the complexed forms.¹ Therefore, to understand the mechanism of aluminium phytotoxicity, investigating the interaction between aluminium ions and organic ligands containing carboxyl groups and aminocarboxyl groups is a necessary preliminary step, because the representative functional groups of natural organic compounds present in the hydrosphere are carboxyl, aminocarboxyl and phenolic groups.¹ Previously, the authors reported on the interaction between aluminium ion and tiron, salicylic acid, phthalic acid² and iminodiacetic acid³ in acidic aqueous solution. The carboxylic acids of pyridine are also reasonably considered to be candidates for the functional groups of natural organic compounds.

Among the dicarboxylic acids of pyridine, dipicolic acid (pyridine-2,6-dicarboxylic acid) seems to have the strong chelating properties required for the formation of metal complexes, because it acts as a tridentate ligand.⁴ On the other hand, we have been unable to find any reports concerning research on quinolic acid (pyridine-2,3-dicarboxylic acid) as a ligand.⁵ Although it is considered to act as a bidentate ligand, because of its molecular structure, it would be very interesting to ascertain whether it coordinates to a metal ion with the oxygen atoms of two carboxylic groups or with a nitrogen atom and an oxygen atom of the adjacent carboxylic group.

In this study, we investigated the interaction between aluminium ions and quinolic acid in acidic aqueous solutions by ¹³C and ²⁷Al NMR spectroscopy and potentiometry. In this report we present the stoichiometry of aluminium-quinolic acid complexes, their molecular structures and their formation constants.

Experimental

Preparation of sample solutions

All of the reagents used were of analytical reagent grade. An Al(NO₃)₃ stock solution was prepared by dissolving Al(NO₃)₃·9H₂O in diluted nitric acid (0.1 mol dm⁻³) and was standardized by EDTA titration. Quinolic acid was commercially obtained (Wako Pure Chemical Industry Ltd.) and dissolved in pure water. Sample solutions were prepared by mixing the Al(NO₃)₃ solution and the quinolic acid solution in the required molar ratio. The pH of the solutions was adjusted by adding a sodium hydroxide solution. For measurements of the ¹³C and ²⁷Al NMR spectra, the aluminium concentrations were 0.05 and 0.01 mol dm⁻³, respectively.

¹³C and ²⁷Al NMR spectra

The ²⁷Al NMR spectra were recorded on a JEOL GX 400 spectrometer operating at 104.2 MHz (pulse width: 20 μs, flip angle: 90°, acquisition time: 0.328 s, repetition time: 0.4 s, 512 transients). All chemical shifts are relative to the external [Al(H₂O)₆]³⁺.

The ¹³C NMR spectra were recorded on a JEOL GSX

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Fig. 1 ^{27}Al NMR spectra for sample solutions of pH 3 with various R . R : (a) 0.5, (b) 1.0, (c) 2.0, (d) 3.0, (e) 4.0, (f) 5.0. Numerals in this figure indicate the chemical shift values from $\text{Al}(\text{H}_2\text{O})_6^{3+}$.

400 spectrometer operating at 100.5 MHz (pulse width: 4.7 μs , acquisition time: 3.93 s, repetition time: 8.69 s, 5000 – 10000 transients). Each sample solution was placed in a glass tube 5 mm in diameter. A D_2O solution of sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) enclosed in a glass tube 2.5 mm in diameter was used as an external standard. The chemical shifts were relative to TMS by using the DSS as a secondary reference.

The NMR measurements were carried out at ambient temperature after allowing the sample solutions to stand for more than 24 h.

Potentiometry

The potentiometric titration was made according to a 1996 report.⁶ This experiment was carried out in 0.5 mol dm^{-3} KNO_3 as the supporting electrolyte, using a Towa Model HM-60V pH meter equipped with a combination electrode. The aluminium concentration employed was 10^{-3} and 5×10^{-4} mol dm^{-3} (Al:quinolic acid=1:1 and 1:4) and the solution temperature was maintained at $25 \pm 0.1^\circ\text{C}$. A CO_2 free solution of KOH was prepared by the procedure described in the ref. 4. The calculations of formation constants for complexes of aluminium with quinolic acid were carried out on a PSEQUAD program.⁷

Fig. 2 ^{27}Al NMR spectra for sample solutions of pH 4.5 with R . R : (a) 0.5, (b) 1.0, (c) 2.0, (d) 3.0, (e) 5.0. Numerals in this figure indicate the chemical shift values from $\text{Al}(\text{H}_2\text{O})_6^{3+}$.

Results and Discussion

^{27}Al NMR spectra

Figure 1 gives the ^{27}Al NMR spectra for sample solutions of pH 3 with various ligand/Al molar ratios (R , ligand: quinolinic acid). The aluminium concentration was 10^{-2} mol dm^{-3} . A sharp peak at 0 ppm is due to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, whereas the broad peaks at 8 and 15.6 ppm are due to aluminium-quinolinic acid complexes. Aluminium ion in the complexes is considered to be 6-coordinated. Their peak intensities increased with increasing R at the expense of the peak due to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$.

Figure 2 gives the ^{27}Al NMR spectra for sample solutions of pH 4.5 with various R values. With an R value of 0.5, only a peak at 8 ppm was observed in addition to the peak due to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. With an R value of 1, the peak at 8 ppm grew considerably, and a small peak was also observed at 15.6 ppm. Above an R value of 2, the peak at 15.6 ppm became the main peak, incorporating the 8 ppm peak. Judging from the relationship between peak intensity and R or pH, the two peaks at 8 and 15.6 ppm can be assigned to 1:1 and 1:2 complexes of aluminium (Al) with quinolinic acid (L): AIL and AIL_2 .

^{13}C NMR spectra

Figure 3 gives the ^{13}C NMR spectra for a sample

Fig. 3 ^{13}C NMR spectrum for the sample solution of pH 3 with $R=1$.

Fig. 4 ^{13}C NMR chemical shifts for carbon atoms due to the formation of aluminium complexes with quinolic acid. (a) AIL complex (pH=3, $R=1$), (b) AIL_2 complex (pH=4.5, $R=5$). $\rightarrow$: downfield shift, $\cdots\rightarrow$: upfield shift.

solution of pH 3 with an R value of 1: the peaks at 125–150 ppm are due to the carbons of the benzene ring, while those at 168.8 and 173.4 ppm to the carboxylic groups. The peak assignment for the free quinolic acid is indicated by small letters. The peaks due to the 1:1 complex are indicated by the symbol $\blacktriangledown$. The chemical shifts due to the formation of the AIL and AIL_2 complexes are shown in Fig. 4: $\cdots\rightarrow$ indicates the upfield shift and $\rightarrow$ the downfield shift. To identify the coordination sites of aluminium ion, the chemical shift differences of carboxylic carbons, f and g, or carbons, a and e, from free quinolic acid are important information. The carboxylic carbon, g, and the carbons of the

Fig. 5 Titration curves at 25°C. Titrant: 0.1 mol dm^{-3} KOH solution. (a) $R=0$, quinolic acid, (b) $R=1$, (c) $R=4$.

Table 1 Experimental details of the pH measurements at 25°C

Initial concentration/ mmol dm^{-3}		pH range		Data points
Metal	Ligand	Measured	Computed	
—	1.014	3.1–6.0	—	—
0.9805	1.014	2.5–6.0	2.5–3.5	23
0.4950	2.027	2.7–6.0	2.7–4.01	54

benzene ring, e, b and a, shifted upfield, whereas the carboxylic carbon, f, and carbons of the benzene ring, d and c, shifted downfield. If an aluminium ion coordinated with two carboxylic groups to form a chelate complex, the carboxylic carbon, f, should shift upfield, and since the chelate complex would have a seven-membered ring, it would be relatively unstable. On the other hand, the two carbons, e and a, which are adjacent to the nitrogen atom, shifted upfield, indicating that the aluminium ion actually coordinates with the nitrogen atom.^{8,9} Therefore, it is quite clear that quinolic acid coordinates to an aluminium ion with a nitrogen atom and an oxygen atom of the adjacent carboxylic group to form a chelate complex with a five-membered ring.

Potentiometric study

Figure 5 gives the titration curves. The experimental details are given in Table 1. Based on the ^{27}Al NMR results, only the AIL and AIL_2 complexes were considered in the analysis of the titration curve. Since the hydrolysis of aluminium ion becomes appreciable above pH 3.5 (aluminium concentration <10 mmol dm^{-3}), data below pH 3.5 was used for the analysis in the case of $R=1$. When $R=4$, data below pH 4 was used. The hydrolysis reaction is probably negligible below pH 4, especially when the amount of quinolic acid considerably exceeds that of aluminium ion. The $\text{pK}_{\text{a}1}$ and $\text{pK}_{\text{a}2}$ values used for quinolic acid were 4.62 and 6.89, in accordance with a previously published report.¹⁰

In Table 2, the equilibrium reactions and the corre-

Table 2 Formation constants ($\log \beta_1$ and $\log \beta_2$ of aluminium complexes with quinolic acid in a $0.5 \text{ mol dm}^{-3} \text{ KNO}_3$ solution at 25°C)

Reaction	$\log \beta$
$\text{Al} + \text{L} \rightleftharpoons \text{AIL}$	4.52 ± 0.02
$\text{Al} + 2\text{L} \rightleftharpoons \text{AIL}_2$	7.99 ± 0.05

L: quinolic acid.

sponding formation constants are summarized. In spite of the bidentate ligand, the formation constants for the aluminium complexes of quinolic acid are almost equal to those of dipicolic acid, which acts as a tridentate ligand ($\log \beta_1=4.87$ and $\log \beta_2=8.32$).¹ This is considered to be caused by the chelate effect: the aluminium complexes of quinolic acid have five-membered rings.

Figure 6 gives the distribution diagrams in the cases of $R=1$ and 4. Above pH 3, the complex formation of aluminium ions and quinolic acid proceeds. At pH 3 the AIL complex is predominant, but the proportion of the AIL₂ complex increases with increasing pH.

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References

1. T. E. Lewis, "Environmental Chemistry and Toxicology of Aluminium", Lewis Publishers, 1990.
2. T. Yokoyama, H. Abe, T. Kurisaki and H. Wakita, *Anal. Sci.*, **13**, 425 (1997).
3. T. Yokoyama, H. Abe, T. Kurisaki and H. Wakita, *Anal. Sci.*, **15**, 1 (1999).
4. A. Napoli, *Talanta*, **15**, 189 (1968).
5. R. M. Smith and A. E. Martell, "Critical Stability Constants", Vol. 16, 1989.
6. T. Kurisaki, T. Yamaguchi, M. Fujiwara, R. Kiraly and H. Wakita, *J. Chem. Soc., Dalton Trans.*, 1996, 3727.
7. PSEQUAD, L. Zekany and I. Nagypal, in "Computational Methods for the Determination of Stability Constants", ed. D. Leggett, Plenum, New York, 1985.
8. T. Kojima, T. Usui, T. Tanase, M. Yashiro, S. Yoshikawa, R. Kuroda and M. Hidai, *Inorg. Chem.*, **29**, 446 (1990).
9. T. Kojima, T. Usui, A. Shimada, T. Tanase, R. Yoshioka, R. Kuroda, S. Yano, M. Hidai, M. Kato, K. Kobayashi, T. Sakurai and Y. Yoshikawa, *Inorg. Chem.*, **30**, 4536 (1991).
10. C. Petitfaux and R. Fournaise, *Bull. Soc. Chim. France*, **3**, 914 (1972).

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Fig. 6 Distribution diagrams for aluminium complexes with quinolic acid. M: $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, L: quinolic acid, ML: AIL complex, ML₂: AIL₂ complex. (a) $R=1$. (b) $R=4$.