^{13}C and ^{27}Al NMR Study on the Interaction between Aluminium Ion and Iminodiacetic Acid in Acidic Aqueous Solutions

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Only a few potentiometric investigations have been published on the interaction between aluminium ions and iminodiacetic acid in aqueous solution. These have shown the formation of 1:1 and 1:2 Al-iminodiacetate complexes.^{1,2} In our preliminary study using ^{27}Al NMR, however, we found that another new complex was present in addition to the 1:1 and 1:2 complexes. The purpose of this study is to elucidate the stoichiometry of this third complex in aqueous solution by ^{13}C and ^{27}Al NMR.

Experimental

Preparation of sample solutions

All the reagents used were of analytical reagent grade. The $\text{Al}(\text{NO}_3)_3$ solution was prepared by dissolving crystalline $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in diluted nitric acid (0.1 mol dm^{-3}) and was standardized by EDTA titration. Iminodiacetic acid (IDA) was commercially obtained from Dojin, and was dissolved in pure water. Sample solutions were prepared by mixing the $\text{Al}(\text{NO}_3)_3$ solution and the IDA solution in the required molar ratio. The solution pH was adjusted by adding sodium hydroxide solution.

^{13}C NMR and ^{27}Al NMR spectra

The ^{27}Al NMR spectra were recorded on a JEOL GX 400 spectrometer operating at 104.2 MHz (pulse width, 20 μs ; acquisition time, 0.328 s, repetition time, 0.4 s; 512 transients). All the chemical shifts were relative to external $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. NMR measurements were carried out at room temperature after allowing the sample solution to stand for more than 24 h.

The ^{13}C NMR spectra were recorded on a JEOL GSX 400 spectrometer operating at 100.5 MHz (pulse width, 4.7–9.4 μs ; acquisition time, 3.93 s; repetition time, 8.69 s; 5000–10000 transients). The chemical shifts were relative to external TMS.

Results and Discussion

^{13}C and ^{27}Al NMR spectra

Figure 1 shows ^{27}Al NMR spectra for sample solutions with (IDA)/Al molar ratio (IDA: iminodiacetic

Fig. 1 ^{27}Al NMR spectra at various pH. pH: (a) 3.02, (b) 3.26, (c) 3.43, (d) 3.60, (e) 3.82, (f) 4.04, (g) 4.26, (h) 4.48, (i) 4.66, (j) 4.82, (k) 5.03. IDA/Al molar ratio: 5. Aluminium concentration: $10^{-2} \text{ mol dm}^{-3}$.

acid) of 5 and with various pH values. The total aluminium concentration was 10^{-2} mol dm $^{-3}$. The peak at 0 ppm was due to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, whereas peaks at 19, 22 and 38 ppm were due to aluminium-IDA complexes.

Except for a peak due to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, only a peak at 19 ppm was observed at pH 3, whereas another small peak appeared at 38 ppm at pH 3.2. In the pH range of 3.2–3.8, both peak intensities increased with pH at the expense of the peak intensity of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, suggesting that some aluminium-IDA complexes formed. Around pH 4, a peak appeared at 22 ppm as a shoulder of the peak at 19 ppm, and the peak intensity increased rapidly with increasing pH. On the other hand the peak intensity of 19 ppm (I_{19}) showed a maximum around pH 4, and the I_{22} exceeded I_{19} above pH 4.8.

Figure 2 shows ^{13}C NMR spectra for the IDA solution (a, pH 3) and two sample solutions with an IDA/Al molar ratio of 5 (b, pH 3, c, pH 5). Figure 2(a) indicates a ^{13}C NMR spectrum of free IDA at pH 3. The peaks at 51.8 and 174.1 ppm can be assigned to carbon atoms of methylene and carboxyl groups, respectively. The sample solutions in Figs. 2(b) and 2(c) correspond to (a) and (k) in Fig. 1. At pH 3, judging from the ^{27}Al NMR spectra in Fig. 1, only one kind of aluminium-IDA complex was present in the solution. In Fig. 2(b),

Fig. 2 ^{13}C NMR spectra for IDA and sample solutions. (a) IDA solution (5×10^{-2} mol dm $^{-3}$, pH 3). (b) IDA/Al molar ratio: 5; aluminium concentration: 10^{-2} mol dm $^{-3}$; pH: 3. (c) IDA/Al molar ratio: 5; aluminium concentration: 10^{-2} mol dm $^{-3}$; pH: 5.

a set of peaks due to an Al-IDA complex was observed at 56.1 (methylene) and 179.2 (carboxyl) ppm in addition to that due to the free IDA. From all the ^{27}Al NMR spectra, we concluded that at least three kinds of aluminium-IDA complexes were present in the solution. Figure 2(c) shows three sets of signals at (56.1, 179.2), (56.2, 179.3) and (57.5, 180.0) ppm.

Stoichiometry of aluminium-IDA complexes

All the ^{27}Al NMR peaks due to Al-IDA complexes appeared downfield to the reference $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ions. The chemical shifts of aluminium are governed by a diamagnetic term, *i.e.* an electron-accepting property of each carboxyl group and nitrogen atom is a major factor in determining the chemical shift. Since potentiometric study on the interaction between $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ and IDA has shown the formation of 1:1 and 1:2 complexes^{1,2}, peaks at 19 and 38 ppm in the ^{27}Al NMR spectra can be assigned to the 1:1 complex, $[\text{Al}(\text{IDA})]^+$, and 1:2 complex, $[\text{Al}(\text{IDA})_2]^-$, respectively, judging from a relationship between peak intensity and pH.

For the assignment of two peaks at 19 and 22 ppm, there are three possibilities: (a) the formation of facial and meridional $[\text{Al}(\text{IDA})]^+$ isomers, (b) the formation of hydroxo complexes or (c) the formation of a 2:2 complex. In (a) and (b) cases, when the aluminium concentration varies under constant pH and IDA/Al molar ratio, the relative intensity of I_{19} and I_{22} should be constant in principle. But, in case (c), the relative

Fig. 3 ^{27}Al NMR spectra for sample solutions with different aluminium concentrations. Aluminium concentration: (a) 10^{-2} , (b) 5×10^{-3} , (c) 10^{-3} mol dm $^{-3}$. IDA/Al molar ratio: 1. pH: 4.5.

intensity should change with the aluminium concentration: the peak intensity of the 2:2 complex should increase with increasing aluminium concentration. Figure 3 shows ^{27}Al NMR spectra for sample solutions with different aluminium concentrations at pH 4.5 and IDA/Al molar ratio of 1. At $10^{-3} \text{ mol dm}^{-3}$, a peak at 19 ppm was only a signal and no peak was observed at 22 ppm. With increasing the concentration from 10^{-3} to $10^{-2} \text{ mol dm}^{-3}$, the I_{19} decreased and the I_{22} increased complementarily.

According to Johansson³, with increasing pH above 3, aluminium ion hydrolyzes and a 2:2 dimeric species, $[\text{Al}_2(\text{H}_2\text{O})_8(\mu\text{-OH})_2]^{4+}$, containing a four membered ring involving hydroxo bridges is formed. Öhman⁴ showed that in the Al-nta system (nta: nitrilotriacetate), a dimeric $[\text{Al}_2(\mu\text{-OH})_2(\text{nta})_2]^{2-}$ is preferable under high concentration, while a monomeric $[\text{Al}(\text{OH})(\text{nta})]^-$ is predominant under low concentration. Moreover some aluminium complexes with an $[\text{Al}_2(\mu\text{-OH})_2]^{4+}$ core have been structurally characterized: $[\text{Al}(\text{H}_2\text{O})_2][\text{Al}_2(\text{nta})_2(\mu\text{-OH})_2]\cdot\text{OH}\cdot 3\text{H}_2\text{O}$ ⁵, $[\text{Al}_2(\text{H}_2\text{O})_8(\mu\text{-OH})_2]\cdot(\text{SO}_4)_2\cdot 2\text{H}_2\text{O}$, $[\text{Al}(\mu\text{-OH})(\text{hbo})_2]_2$ (hbo: 2-(2'-hydroxyphenyl)-2-benzoxazolate)⁶ etc. From Fig. 3 and these facts, we can reasonably conclude that the peak at 22 ppm should be assigned to a 2:2 complex, $[\text{Al}_2(\text{IDA})_2(\mu\text{-OH})_2]$, formed by hydrolysis and condensation of two 1:1 complexes, although Iyer *et al.*² assigned the peak at 22 ppm to a monomeric hydroxo complex, $[\text{Al}(\text{IDA})(\text{OH})_2]^-$.

For monodentate complexes such as $[\text{Al}_2(\text{IDA})]^{4+}$ and $[\text{Al}(\text{IDA})]^{2+}$, if any were present, their formation should proceed with increasing pH. Their ^{27}Al NMR chemical shifts are probably around 0 ppm judging from the chemical shifts of Al-acetate complexes (unpublished

data). In the pH range 4.48 – 5.03, however, no peak was observed around 0 ppm as shown in Fig. 1. As a result we conclude that the monodentate complexes were not formed.

In conclusion, for the 1:1 complex $[\text{Al}(\text{IDA})]^+$ and its hydrolytic species, $[\text{Al}(\text{IDA})(\text{H}_2\text{O})_n(\text{OH})_{3-n}]^{(n-1)-}$, 2:2 complex $[\text{Al}_2(\text{IDA})_2(\text{OH})_2(\mu\text{-OH})_2]$ and 1:2 complex $[\text{Al}(\text{IDA})_2]^-$, the assignment of NMR signals (^{27}Al NMR and ^{13}C NMR spectra of pH 5) is as follows: (19 ppm, (56.1 ppm, 179.2 ppm)), (22 ppm, (56.2 ppm, 179.3 ppm)) and (38 ppm, (57.5 ppm, 180.0 ppm)).

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References

1. A. Liberti and A. Napoli, *J. Inorg. Nucl. Chem.*, **33**, 89 (1971).
2. R. K. Iyer, S. B. Karweer and V. K. Jain, *Magn. Reson. Chem.*, **27**, 328 (1989).
3. G. Johansson, *Acta Chem. Scand.*, **16**, 403 (1962).
4. L. O. Öhman, *Polyhedron*, **9**, 199 (1990).
5. G. C. Valle, G. G. Bombi, B. Corain, M. Favarato and M. Zatta, *J. Chem. Soc. Dalton Trans.*, **1989**, 1513.
6. H. R. Hoveyda, S. J. Rettig and C. Orvig, *Inorg. Chem.*, **32**, 4909 (1993).

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