^{27}Al AND ^{31}P NMR STUDY ON THE INTERACTION BETWEEN AL-EDTA COMPLEX AND H_2PO_4^- IONS IN AQUEOUS SOLUTION

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Abstract - An interaction between Al-EDTA and H_2PO_4^- was investigated at pH 4.5 using ^{27}Al and ^{31}P NMR spectroscopy, and the formation of a mixed ligand complex, Al-EDTA- H_2PO_4^- was detected. The chemical shift values of the mixed ligand complex from the external standard ($\text{Al}(\text{H}_2\text{O})_6^{3+}$ in ^{27}Al NMR and 85% H_3PO_4 in ^{31}P NMR) were 28 and -4.4 ppm. The formation constant of the mixed ligand complex was estimated to be 35.

Key words Al-EDTA, Mixed ligand complex, ^{27}Al NMR, ^{31}P NMR

EDTA (Ethylenediaminetetraacetic acid) is a hexadentate ligand. However, for some metal-EDTA complex in aqueous solution, there is evidence that only five of the six EDTA sites are bound to metal ions [1,2]. Hence, introduction of a second ligand to the complex can be envisioned. Although the structure of the Al-EDTA complex in aqueous solution is still uncertain, the formation of some mixed ligand complexes, Al-EDTA-X (X=F and S), was confirmed from potentiometric investigations [3,4]

A system composed of Al-EDTA and phosphate ions can be regarded as a model to investigate the behaviour of aluminium in environmental water and in human pathological conditions such as Alzheimer's disease. The purpose of this report is to describe the results of an ^{27}Al and ^{31}P NMR study on the formation of a mixed ligand complex due to an interaction between an Al-EDTA complex and a H_2PO_4^- ions

EXPERIMENTAL

Preparation of sample solutions. Al-EDTA solution. A known amount of aluminium nitrate solution ($0.1 \text{ mol dm}^{-3} \text{ HNO}_3$) was added to an EDTA·2Na solution. The solution was adjusted to pH 3 with a sodium hydroxide solution, heated to the boiling point, and adjusted to pH 4.5 after cooling.

Sample solutions. Various amounts of NaH_2PO_4 solution (pH 4.5) were added to constant amounts of the Al-EDTA solution.

NMR measurement. The ^{27}Al and ^{31}P NMR spectra were recorded on a JEOL spectrometer JNM-GX 400 operating at 104.2 and 161.9 MHz at 20 °C, using a 10 mm i.d. spinning sample tube. Under experimental conditions used, it was experimentally confirmed that quantitative data can be obtained.

RESULTS AND DISCUSSION

The concentration of Al-EDTA in the sample solutions was $0.012 \text{ mol dm}^{-3}$, and the P/Al ratio was in the range 0.5–10. As all the sample solutions were prepared to pH 4.5, H_2PO_4^- ions were the predominant phosphorous oxoanions.

Figure 1 shows the ^{27}Al NMR spectra of the Al-EDTA complex and the sample solutions. With increasing P/Al ratio, the intensity of the right peak increased, while that of the left peak decreased in reciprocal fashion, suggesting that a mixed ligand complex was formed. The left peak (38 ppm from $\text{Al}(\text{H}_2\text{O})_6^{3+}$) is due to the Al-EDTA complex, and the right peak (28 ppm) to the mixed ligand complex. Figure 2 shows the ^{31}P NMR spectrum of a sample with a P/Al ratio of 4. The left peak (3 ppm from 85% H_3PO_4) is due to H_2PO_4^- , and the right peak (-4.4 ppm) to the mixed ligand complex. In all the sample solutions, only two peaks were observed in ^{27}Al and ^{31}P NMR and the chemical shift values of all the peaks were constant within the limit of experimental error, regardless of the P/Al ratios. These facts indicate that only one mixed ligand complex, 1:1 Al-EDTA- H_2PO_4^- , was formed.

In a preliminary experiment of an ^{27}Al NMR study of Al-NTA (Nitrilotriacetic acid) it was suggested that the effect of O and N atoms on the chemical shift was fairly equal. Judging from the chemical shift value of Al-EDTA in Fig. 1, aluminium ion in the Al-EDTA is probably penta-coordinated [5], although the exact structure is uncertain. But the aluminium ion in the mixed ligand complex can be considered to be hexa-coordinated. Accordingly, the interaction between Al-EDTA (Y) and H_2PO_4^- (L) may be expressed as

By deconvoluting the ^{27}Al NMR spectra, the formation constant of the mixed ligand complex, YL, was estimated to be 35.

Fig. 1. ^{27}Al NMR spectra

Fig. 2. ^{31}P NMR spectrum

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