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Aluminum-27 NMR Study of Aluminum(III) Interactions with Hydroxy Carboxylic Acids

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Aluminum-27 NMR has been of increasing use in determining the structures of Al(III) complexes in solution [1], although most studies to date have been of non-aqueous solutions. The linewidths of ^{27}Al NMR resonances are strongly dependent on the symmetry of the complex because of the nuclear quadrupole moment of aluminum [1, 2], and on exchange processes. Thus most early ^{27}Al NMR studies reported only signals from species of high symmetry, and these signals were often from several species in fast exchange.

Aluminum-27 NMR studies of Al(III) in aqueous solution have concentrated on the nature of the species present in high pH systems [3, 4], on aggregation phenomena [5], and on studies of hydration spheres in the presence of simple unidentate inorganic ligands such as F^-, SO_4^{2-}, and PO_4^{3-} [1], and very few studies with organic ligands have been reported. Toy *et al.* [6] studied the chelates of several hydroxy carboxylic acids by ^{27}Al NMR and concluded that the only detectable signals were from the $Al(H_2O)_6^{3+}$ and aluminate, $Al(OH)_4^-$, species at low and high pH respectively and that the species present at intermediate pH were all polymeric. Jaber *et al.* [7] studied the Al(III) oxalic acid chelates in aqueous solution and identified three species. Karlik *et al.* [2] studied the interaction of Al(III) with carboxylic acids in aqueous solution, including citric acid for which they found several signals with chemical shifts between 0 and 20 ppm. To our knowledge no other ^{27}Al NMR studies have been reported of the interaction of hydroxy carboxylic acids with aluminum.

Stability constants for several Al(III) hydroxy carboxylic acid complexes have been reported. Manning and Ranamoorthy [8] studied the Al(III) tartrate system and reported unexpectedly high stability constants. Rajan *et al.* [9] studied Al(III) citrate and found a stable 1:1 complex below pH 7 that polymerizes at higher pH. Motekaitos and Martell [10] showed that many monomeric species are present in aqueous solutions of hydroxy carboxylic acids and that the hydroxyl protons are readily displaced in the Al(III) complexes leading to coordination of the hydroxyl oxygen to the aluminum.

The aluminum chelates of the hydroxy carboxylic acids are of special interest because several of the ligands occur in environmental water systems and may be important in the transport of aluminum. Recent reports of aluminum buildup in some regions of the cerebral cortex of patients with Alzheimer's disease [11] have raised the possibility that studies of aluminum–chelate interactions may be of medical importance [9].

Experimental

Reagent grade D-tartaric acid, citric acid, malonic acid, oxalic acid, DL-malic acid, DL-mandelic acid, and potassium aluminum sulfate were obtained from Aldrich Chemical Company and used without further purification. Aluminum was added as concentrated aqueous solutions of $KAl(SO_4)_2$. The pH was adjusted with NaOH or $HClO_4$ and was measured using a Corning Model 130 pH meter. Deuterium oxide was used in place of water to provide an NMR lock signal.

NMR spectra were obtained at 25 °C using a Bruker 250-WM FT spectrometer operating at 65.18 MHz. Typically 500 scans were accumulated per spectrum. Chemical shifts are referenced to the $Al(H_2O)_6^{3+}$ signal from an acidic solution of aluminum perchlorate in D_2O used as an external standard. An extremely broad underlying signal from aluminum in the spectrometer probe caused baseline curvature but did not affect observation of the aluminum-containing species in solution.

Results and Discussion

Aluminum-27 NMR spectra were recorded for aluminum:ligand ratios of 1:1, 1:3 and 1:30 between pH 1 and 13 with ligand concentrations of 0.2 M. No appreciable differences except in relative intensities of the peaks were noted for solutions of different aluminum:ligand ratios and thus only results for 1:3 ratios are reported here. At $pH < 1$ the $Al(H_2O)_6^{3+}$ signal was observed in all solutions at 0 ppm, and the $Al(OH)_4^-$ signal was observed in all solutions above pH 11 at 80.1 ppm. No peaks were detected near 62 ppm due to the $[Al_{13}(OH)_{24}O_4]^{7+}$ that is found in aqueous solutions of Al(III) [12]. The aluminum-27 resonance peaks were all broad, as expected for systems of lower than octahedral symmetry. Linewidths were typically at least 200 Hz. Lines of width greater than about 2000 Hz are probably undetectable under current acquisition conditions.

Oxalic Acid

At pH 0.5 two peaks were observed, at 11.9 and 6.8 ppm, as well as the resonance due to $Al(H_2O)_6^{3+}$.

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At pH 1 these were replaced by a peak at 12.5 ppm. Above pH 1 this was gradually replaced by a single peak at 16.3 ppm, which persisted to pH 9. All of these peaks had relatively narrow linewidths of about 200 Hz. Above pH 7, when precipitate was present, there was also a broader shoulder at 13.3 ppm. Our results indicate that all species are in slow exchange on the NMR timescale. The results are in substantial agreement with those of Jaber *et al.* [7]. The major peak observed between pH 1 and 9 at 16.3 ppm is due to $[ML_3]^{3-}$. Above pH 7 this decomposes to aluminum hydroxide which dissolves to form aluminate above pH 10, in agreement with potentiometric data [13, 14] that show aluminum oxalate has a relatively low stability constant. The peaks at 6.8 and 12.5 ppm have been ascribed to $[AlL]^+$ and $[AlL_2]^-$ respectively [7]. We observe two additional resonances, at 11.9 ppm at low pH, and at 13.3 ppm at pH > 7 but are unable to assign structures to them at this stage.

Citric Acid

Many resonances were observed as the pH was varied. Below pH 2 the $Al(H_2O)_6{}^{3+}$ resonance at 0.0 ppm ($\Delta\nu \simeq 8$ Hz) was accompanied by a broader ($\Delta\nu \simeq 500$ Hz) peak at 6.9 ppm. At pH 2, very little $Al(H_2O)_6{}^{3+}$ remained, but three peaks were observed at 14.0 ($\Delta\nu \simeq 500$ Hz), 21.1 ($\Delta\nu \simeq 300$ Hz), and 28.1 ppm ($\Delta\nu \simeq 250$ Hz), with a shoulder at 9.3 ppm which is strongest at pH 2. These three peaks are strongest at pH 3 but remain visible until pH 11. Additional weak peaks are observed at 6.5 ppm at pH 3 to 6. The aluminate peak grows after pH 10.

These results differ from those of Karlik *et al.* [2] who observed only the aluminate and the $Al(H_2O)_6{}^{3+}$ signals, and one other broader line whose position and width varied with pH. They interpreted their results in terms of fast exchange between several species. Our results indicate slow exchange between several species. We are unable to explain the difference although we note that their results were obtained in 10 mM solution, about 20 times more dilute than our solutions.

Because we observe several peaks we can correlate the NMR data with potentiometric titration data [9, 10]. The major species present between pH 5 and 8 has been reported to be $[AlH_{-1}L]^-$ with a tridentate citrate [10]. Accordingly we attribute the peak at 14.0 ppm to this species. The peak at 9.3 ppm is probably due to $[AlHL]^+$ coordinated through a single carboxylate resulting in a smaller quadrupole effect, leaving the peak at 21.1 ppm due to [AlL]. The peak at 28.1 ppm is always small and is apparently due to a species not shown by the potentiometric data.

D-Tartaric Acid

At pH < 0.5 a single resonance is observed at 11 ppm ($\Delta\nu \simeq 600$ Hz). As the pH was raised this broadened and shifted downfield to 23 ppm at pH 2. Between pH 2 and 8 no signals were observed although the $Al(H_2O)_6{}^{3+}$ peak persisted to pH 4. A strong signal was observed at 33.4 ppm ($\Delta\nu \simeq 450$ Hz) at pH > 8. The aluminate peak was observed above pH 10.5. Potentiometric data for the tartrate system indicate seven aluminum-containing species with significant concentrations [10]. Our results for pH < 2 suggest fast exchange between several species. Between pH 2 and 8 we observe no ^{27}Al NMR signals which suggests structures of low symmetry. Only at pH > 8 is there a single relatively narrow resonance with maximum intensity at about pH 11. We attribute this to a fairly symmetrical species, probably $[AlH_{-6}L_3]^{9-}$, in which the ligand is fully deprotonated and the aluminum is in a symmetrical octahedral environment [850018].

Malonic Acid

At pH below 1, the $Al(H_2O)_6{}^{3+}$ resonance and a broader peak at 1.0 ppm ($\Delta\nu \simeq 250$ Hz) are observed. Between pH 1 and 9 there is a peak at 2.2 ppm ($\Delta\nu \simeq 150$ Hz), although at pH near 1 the position of this is pH-dependent indicating two species in fast exchange. Between pH 7 and 12 extensive precipitation occurred, presumably of aluminum hydroxide since the stability constant of aluminum malonate is rather low [15]. At pH > 1 the symmetrical complex $[AlL_3]^{3-}$ predominates while at pH < 1 there appear to be several species in fast exchange.

DL-Malic Acid

Below pH 2 there is a peak at 7.6 ppm ($\Delta\nu \simeq 350$ Hz) in addition to the $Al(H_2O)_6{}^{3+}$ resonance while between pH 2 and 8, there are three peaks, at −0.7 ($\Delta\nu \simeq 200$ Hz), 12.0 ($\Delta\nu \simeq 400$ Hz), and 18.9 ppm ($\Delta\nu \simeq 400$ Hz). Above pH 12, only the aluminate peak remains. The three peaks found between pH 2 and 8 can be attributed to the [AlL], $[AlH_{-1}L]^-$, and $[AlH_{-2}L]^{2-}$ species identified by potentiometric titration [16] although peak intensities need to be correlated with pH before specific assignments can be made.

DL-Mandelic Acid

Between pH 0 and 1 a signal was observed at 7.5 ppm ($\Delta\nu \simeq 400$ Hz) while between pH 2 and 8, only a broader signal ($\Delta\nu \simeq 700$ Hz) at 26.6 ppm was present. The broad signal present above pH 2 is probably due to $[AlL_3]^{3-}$ [17].

In contrast to the results of Toy *et al.* [6], many ^{27}Al NMR resonances from aqueous solutions containing Al(III) and carboxylate ligands have been detected. The NMR spectra show the marked pH dependence anticipated on the basis of potentiometric titration studies, and at higher concentrations than used by Karlik *et al.* [2] most of the species are in slow exchange except those present in very acidic solutions. The observation of distinct signals from several species suggests that the ^{27}Al NMR chemical shifts may be able to be correlated with potentiometric titration data, especially if accurate linewidths and intensities are measured. Such studies are fundamental to the understanding of the relationship between the aluminum chemical shift and the aluminum ligand environment. Even on the basis of the limited data reported here, it appears that chemical shifts progressively increase with pH, suggesting that additivity rules may be applicable. Accordingly, an extensive quantitative ^{27}Al, ^{13}C, and ^{1}H NMR study of solutions of aluminum(III) and various carboxylic acid ligands is in progress.

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