

Comparison of the Hydrolyses of Gallium(III) and Aluminium(III) Solutions by Nuclear Magnetic Resonance Spectroscopy

Susan M. Bradley, Ronald A. Kydd,* and Raghav Yamdagni

Department of Chemistry, University of Calgary, Calgary, Alberta T2N 1N4, Canada

A quantitative ^{71}Ga n.m.r. study of the base hydrolysis of gallium(III) salt solutions has been undertaken. The resulting spectra were very similar to the ^{27}Al n.m.r. spectra obtained for aluminium solutions hydrolysed under analogous conditions. No evidence was observed of any species different from those seen for aluminium, despite the fact that the eventual outcomes of the hydrolyses are different, *i.e.* precipitation of an oxyhydroxide of diaspore structure in the case of gallium, and the eventual formation of a gibbsite hydroxide phase in the case of aluminium. For aluminium, the formation of the $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ tridecamer is well known, and the formation of an analogous species for gallium has also been proposed. Although the ^{71}Ga n.m.r. studies undertaken herein appear to show that much less of the gallium polyoxycation is formed than is the case for aluminium, clay mineral pillaring studies have suggested that this apparent difference is not real. Through consideration of both the extremely broad nature of the tetrahedral gallium peak and the high quadrupole moment of the ^{71}Ga nucleus, it is proposed that the gallium tridecamer is much more distorted than the aluminium species, and that the integrated area of the n.m.r. peak assigned to this species does not accurately represent the amount actually present in solution.

The $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ polyoxycation species which forms upon the hydrolysis of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ solutions¹⁻⁵ has been the subject of much interest for its ability to intercalate clay minerals, producing catalytically active pillared clays.⁶⁻¹⁰ A recent study¹¹ has revealed evidence which suggests strongly that a polycationic species of analogous structure forms upon the hydrolysis of $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ solutions. A ^{71}Ga n.m.r. peak observed at 172 p.p.m. {relative to $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ } is in the position expected for a tetrahedrally co-ordinated gallium nucleus analogous to the central tetrahedral aluminium in the Al_{13} modified-Keggin structure. In addition, pillaring studies revealed that the species intercalated into clay minerals from the gallium solutions has the 'height' appropriate to a $[\text{GaO}_4\text{Ga}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ polyoxycation.¹¹

Although gallium and aluminium do form oxide, hydroxide, and oxyhydroxide species of analogous structures, the conditions under which they are formed are somewhat different. For example, the solid phase which is formed through the base hydrolysis of gallium(III) is the oxyhydroxide of diaspore structure. For aluminium, however, the initial hydroxide precipitate is amorphous but eventually transforms into the gibbsite polymorph. This clearly indicates that some differences must exist between the species formed upon the hydrolysis of aluminium and gallium(III) salt solutions. In order to investigate further the proposal that $[\text{GaO}_4\text{Ga}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ species is indeed formed upon hydrolysis, and also to investigate the possible formation of any other species unique to gallium, quantitative ^{71}Ga and ^{27}Al n.m.r. studies have been undertaken of the base hydrolyses of $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ solutions.

Experimental

Aqueous solutions of Al^{3+} and Ga^{3+} were prepared from $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Aldrich, 99%) and GaCl_3 (Aldrich, 99.99%), and characterized as previously described.¹¹ The ^{71}Ga n.m.r. spectra (122.03 MHz) were obtained on a Bruker AM-400 spectrometer as previously described.¹¹ Quantitative spectra

were obtained by allowing sufficient time for complete relaxation between scans. A tetrachlorogallate ($[\text{GaCl}_4]^-$) solution was prepared by dissolving $\text{GaO}(\text{OH}) \cdot \text{H}_2\text{O}$ in 4.0 mol dm^{-3} HCl, then diluting with concentrated HCl to the required concentration. The resulting solution was sufficiently acidic (approximately 10 mol dm^{-3} in HCl) to prevent any equilibrium between $[\text{GaCl}_4]^-$ and $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ from forming. This solution was used as an insert to provide a standard peak (248.0 p.p.m.) for integration. The $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ solutions were then hydrolysed to specific OH/Ga mole ratios by adding 0.2 mol dm^{-3} NaOH dropwise at as constant a rate as possible (*ca.* $1 \text{ cm}^3 \text{ min}^{-1}$), under vigorous stirring. These solutions were aged in a water-bath at 40°C until they were no longer visibly turbid, and then cooled quickly in an ice-bath. For some samples, particularly those having low OH/Ga ratios, this aging step was not required as the samples were not cloudy following hydrolysis. To each sample D_2O was added quantitatively to provide an external field-frequency lock. The final solution concentrations were approximately 0.05 mol dm^{-3} . The ^{71}Ga n.m.r. spectra were run for a series of samples having hydrolysis ratios of $0 \leq \text{OH/Ga} \leq 2.5:1$. The ^{27}Al n.m.r. spectra (52.13 MHz) of hydrolysed $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ solutions prepared in an identical manner (except that the water-bath was held at 80°C) were run using a Varian XL-200 spectrometer, as previously described.¹² Although such spectra for aluminium have already been published, several groups have reported slightly different observations in terms of the relative amounts of the various species present as a function of OH/Al ratio.^{4,5,13-16} This is believed to be due to subtle variations in sample preparation techniques (*e.g.* stirring rate, temperature of the solutions, type of base used, rate of addition of base, *etc.*). For this reason it was felt that to permit an accurate comparison to be made of the results for the two metals, the solutions would have to be prepared in an identical manner for both cases, and therefore this study was undertaken for aluminium as well as for gallium.

Pillared clay samples were prepared by the addition of the hydrolysed solutions to stirred suspensions of Na^+ -exchanged STx-1 montmorillonite (Source Clay Minerals Repository,

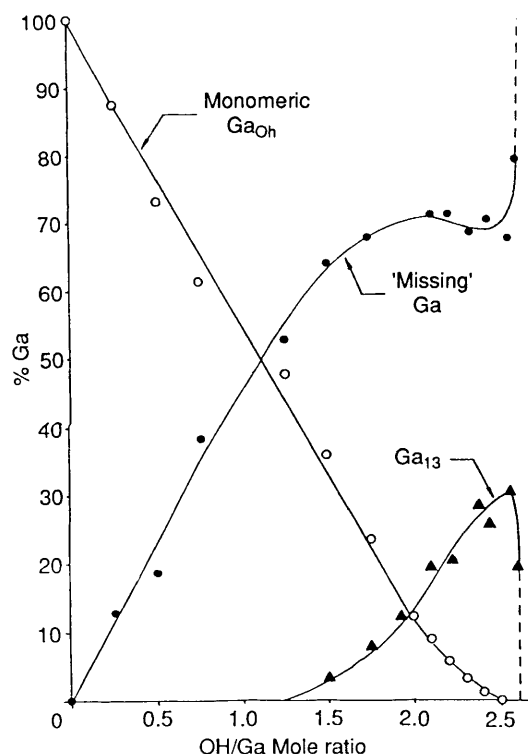


Figure 1. A plot of the gallium species present in solution as a function of the degree of hydrolysis, as revealed by ^{71}Ga n.m.r. spectra

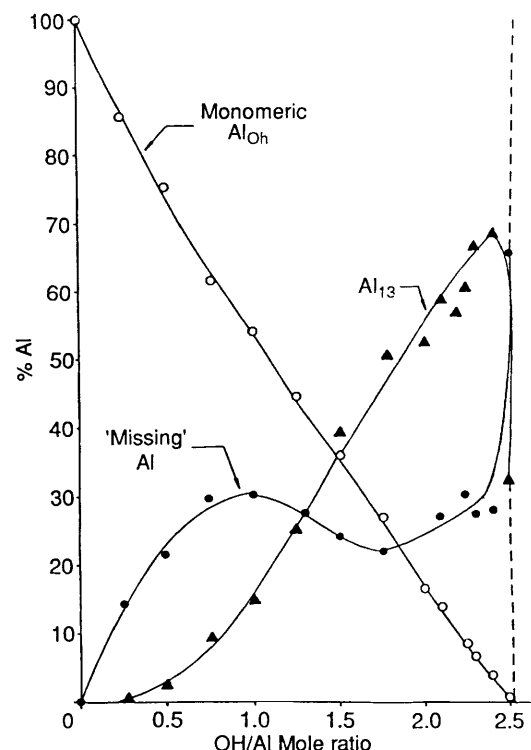
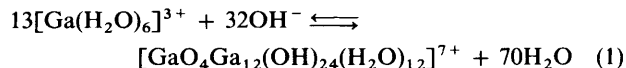


Figure 2. A plot of the aluminium species present in solution as a function of the degree of hydrolysis, as revealed by ^{27}Al n.m.r. spectra

University of Missouri). The d_{001} basal spacings of oriented thin films were obtained by powder X-ray diffraction using the method previously described.¹¹

Results

The ^{71}Ga n.m.r. spectra of the hydrolysed aqueous gallium solutions exhibited a broadening and an approximately linear decrease in the intensity of the $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ peak (0 p.p.m.) as hydrolysis progressed (Figure 1). This is in accordance with the observations made by Akitt and co-workers for the hydrolysis of both aqueous aluminium³ and gallium^{16,17} solutions. This broadening has been attributed to the formation of partially hydrolysed monomeric species. A small peak at 172 p.p.m. {with respect to $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ } previously assigned¹¹ to a tetrahedrally co-ordinated gallium surrounded by 12 octahedrally co-ordinated galliums (*i.e.*, Ga_{13}), in a structure similar to that of the aluminium tridecamer first became apparent at an OH/Ga ratio of approximately 1.50:1. This peak then increased in intensity as hydrolysis progressed, up to a ratio of 2.45:1, following which it rapidly decreased in intensity. To ensure that chloride ions were not interfering, a parallel study was carried out in which gallium nitrate was used. When n.m.r. spectra of the hydrolysed solutions were obtained, no differences in peak position or width were found, compared to the solutions containing chloride, and the d_{001} spacings of pillared clay samples (see below) were also identical. For solutions having an hydrolysis ratio of above 2.50:1, aging did not result in a clearing of the solution, but in the eventual precipitation of the oxyhydroxide. This observation is reasonable for the argument of the formation of a $[\text{GaO}_4\text{Ga}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ tridecamer, as the OH/Ga ratio required for its complete formation would be (32/13:1 = 2.46:1), according to equation (1).



All of these observations are very similar to the case of aluminium solutions hydrolysed in the same manner (Figure 2). Although the Al_{13} peak (62.5 p.p.m.) first appeared at a somewhat lower hydrolysis ratio (*ca.* 0.25:1), it also reached a maximum intensity at an OH/Al ratio of approximately 2.45:1, and then sharply decreased. In addition, solutions having an OH/Al ratio of much above 2.50:1 could also not be prepared readily, as aging led to the precipitation of the hydroxide, rather than a decrease in the turbidity of the solutions.

In both cases, extremely broad peaks centred slightly downfield of the hexa-aquametal ion peaks (0 p.p.m.) became apparent at high hydrolysis ratios (*e.g.* 2.5:1). The chemical shifts of these peaks indicate that the metals are octahedrally co-ordinated, and their extreme widths signify very low symmetry environments. In the case of aluminium, high-temperature studies (*ca.* 80 °C) have been used to narrow this peak, and subsequent integration found it to represent approximately 12 times the amount of aluminium represented by the tetrahedral aluminium peak, and to have a chemical shift of 10–15 p.p.m.^{18,19} Therefore it has been logically attributed to the octahedrally co-ordinated aluminiums in the tridecamer. Unfortunately in the case of gallium, much longer times are required to run the n.m.r. spectra in order to obtain accurate integration (due to ^{71}Ga having a lower n.m.r. receptivity than ^{27}Al), and in addition the hydrolysed solutions have extremely low thermal stabilities. Therefore this technique has not been successful in determining either an accurate chemical shift for the extremely broad peak observed, or whether or not it could in fact represent 12 times the area of the tetrahedral gallium peak. The fact that hydrolysis for both Ga and Al can result in turbid solutions which can be made clear by an aging process involving

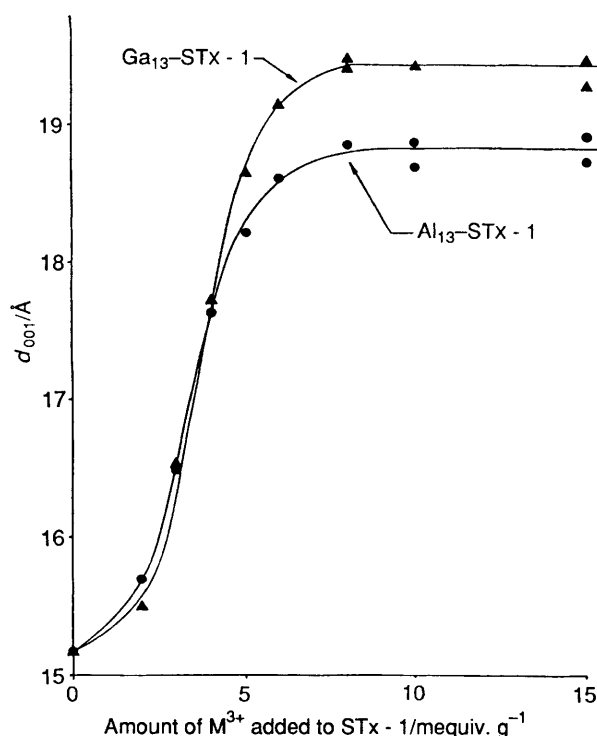


Figure 3. A plot of the d_{001} basal spacings achieved as a function of loadings of STx-1 montmorillonite with the hydrolysed aluminium and gallium(III) aqueous solutions

elevated temperatures, combined with the observation that the resulting solutions are not thermally stable, emphasizes the transitory nature of the species formed. Apparently the gallium and aluminium tridecamers are only metastable under these conditions.

The major difference which became apparent between these two systems from the n.m.r. spectra was that much less of the gallium tridecamer was interpreted to be present than was the case for the aluminium tridecamer (*i.e.*, a maximum of 30 vs. 70% of the total metal concentration, assuming that the total amount of metal involved would be equal to 13 times the amount represented by the tetrahedral peak). The primary question that arises from this, however, is whether there is indeed much less of the gallium tridecamer formed, or whether the intensity of the $\text{Ga}_{13}\text{Ga}_{12}$ peak is truly quantitative. The high quadrupole moments²⁰ of ^{71}Ga ($0.112 \times 10^{-28} \text{ m}^2$) and of ^{27}Al ($0.149 \times 10^{-28} \text{ m}^2$) mean that in both cases rapid quadrupolar relaxation generally prevents the observation of n.m.r. peaks representing species which are not highly symmetric. This $\text{Ga}_{13}\text{Ga}_{12}$ peak is extremely broad (*ca.* 1 800 Hz)¹¹ in comparison with the $\text{Al}_{13}\text{Al}_{12}$ peak (*ca.* 20 Hz).^{4,19} In theory, the nuclear properties of these two nuclei (^{71}Ga and ^{27}Al) predict that the linewidths of the gallium and aluminium peaks representing analogous species should fall in the ratio 2.34:1.¹⁶ In practice, however, the observed ratios inexplicably have always been somewhat higher than this, in some cases by as much as 10 times.¹⁶ The linewidth ratio (90:1) observed here however is sufficiently high to indicate strongly a more distorted environment in the case of the gallium tridecamer. In accordance with the high quadrupole moment of ^{71}Ga , it is possible that this n.m.r. peak does not accurately represent all of the tetrahedral gallium in the polyoxycation species.

To investigate this possibility, a different experimental approach was taken to estimate the relative amounts of the aluminium and gallium tridecamers formed upon hydrolysis.

Phyllosilicate pillaring experiments were undertaken whereby the d_{001} basal spacing achieved in pillaring was determined as a function of loading (the amount of the hydrolysed solutions added per gram of montmorillonite). Previous studies using the solutions containing the hydrous tridecamers to intercalate montmorillonite showed a maximum basal spacing of approximately 18.8 Å in the case of aluminium, and 19.4 Å for gallium.¹¹ If the reasonable assumption is made that the tridecamers are the intercalating species (as the spacings agree with calculated values) then the loadings of the different hydrolysed solutions required to reach these maximum d_{001} basal spacings can be used as an indicator of the relative amounts of the tridecamers present in each solution. The plots of this for these two instances (Figure 3) are interesting in that in both cases the maximum d_{001} basal spacing is reached at approximately the same loading (*ca.* 8 mequiv. g^{-1}); in fact the two curves are essentially superimposable. This is highly suggestive of very similar amounts of the tridecameric species being formed in both cases, which in turn suggests that the intensity of the $\text{Ga}_{13}\text{Ga}_{12}$ n.m.r. peak is not representative of the quantity of the Ga_{13} species which is actually formed in solution.

Even when 12 times the amount of metal which is represented by the tetrahedral peaks is assumed to be octahedrally coordinated in the tridecameric structures, there is generally a relatively large amount of both metals remaining unaccounted for. At low hydrolysis ratios (*ca.* 1.0:1—1.5:1) aluminium is believed to form dimers and/or trimers in solution. In the case of fairly concentrated solutions (*e.g.*, 1.0 mol dm^{-3} Al) a peak is readily visible at 4.0 p.p.m., and is believed to represent these species.^{3,18,21} At lower concentrations, such as those dealt with herein (*ca.* 0.05 mol dm^{-3} Al), no such peak is observed, and instead a large amount of the aluminium in this hydrolysis range is unaccounted for, but is still likely to be present in these forms. At higher hydrolysis ratios (*e.g.* approaching 2.5:1), there is a sharp increase in the amount of aluminium which is unaccounted for, and this is generally believed to be present in the form of higher polymers such as sheets⁵ (*i.e.*, the gibbsite type of structure), or as bulky polymers formed by the coalescence of the tridecameric species.²² It is possible that some of both types of higher polymers are present. Because of the problems noted above relating to the quantitative determination of the gallium concentration from the intensity of the $\text{Ga}_{13}\text{Ga}_{12}$ peak, the amount of Ga calculated to be 'missing' (see Figure 1) may be too large. This could explain why the curve for the missing gallium reaches a plateau at a somewhat higher hydrolysis ratio than is the case for aluminium (an OH/M of *ca.* 2.0:1 vs. 1.0:1). In other respects the curves are similar in appearance, and no evidence for species other than those already suggested for aluminium could be seen. As was the case for aluminium, the gallium system also exhibited a sharp increase in the amount 'unaccounted for' at very high hydrolysis ratios (OH/M > 2.5:1), indicating the formation of larger polymers. At some point there must be a deviation in the hydrolytic behaviour of these two metals, however, as the solid phases which precipitate at a hydrolysis ratio of 3.0:1 are of different structure. Therefore the higher polymers seemingly formed in the case of gallium are likely to differ to some extent in structure from those occurring for aluminium.

Conclusion

Quantitative ^{71}Ga n.m.r. spectroscopic studies of aqueous gallium(III) solutions hydrolysed under mild conditions have revealed behaviour very similar to that observed for aluminium. In both cases, the $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ peak was found to increase in width and to decrease approximately linearly in intensity as hydrolysis progressed. This has previously, in both cases, been

attributed to the formation of partially hydrolysed monomers. A peak which had the correct chemical shift to be indicative of a tetrahedrally co-ordinated gallium nucleus (172 p.p.m.) was found to reach a maximum intensity at an hydrolysis ratio of 2.45:1 in accordance with the proposal that it represents a species analogous to the $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ polyoxocation. While n.m.r. results suggest that much less of this gallium species is formed than is the case for aluminium, clay mineral pillaring studies have indicated that very similar amounts of both species are indeed present. This discrepancy is thought to be related to a greater distortion of the gallium species which thereby causes the ^{71}Ga n.m.r. results to be non-quantitative. In addition, examination of the shapes of the curves representing the amounts of the two metals remaining 'unaccounted for' revealed similar behaviour, suggesting that similar oligomers may be formed in both cases. The amounts of both metals remaining 'unaccounted for' increased rapidly at very high hydrolysis ratios, indicating the formation of larger polymers in both cases. The fact that these two metals form different hydrolysis products, however, suggests that these higher polymers are likely to differ from one another somewhat in terms of structure. No evidence was observed by n.m.r. spectroscopy of any other species which could be designated as unique to gallium. The eventual precipitation of the gallium oxyhydroxide upon aging of the hydrolysed gallium solution was, however, found to be much more rapid than was the case for the aluminium hydroxide, even under the milder conditions used. This large difference in the kinetics of the transformations of the tridecamers may be the key factor in determining whether the final species formed is the hydroxide or oxyhydroxide.

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