HOMOGENEOUS FORCED HYDROLYSIS OF ALUMINIUM THROUGH THE THERMAL DECOMPOSITION OF UREA

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Abstract

Homogeneous hydrolysis of aluminium by decomposition of urea in solution was achieved because the urea coordinates to the Al^{3+} in solution forming $[Al(H_2O)_5(urea)]^{3+}$ and to a lesser extend $[Al(H_2O)_4(urea)_2]^{3+}$. Upon hydrolysis more hydrolysed monomeric species $[Al(H_2O)_5(OH)]^{2+}$, $[Al(H_2O)_4(OH)_2]^+$, $[Al(H_2O)_4(urea)(OH)]^{2+}$, and $[Al(H_2O)_3(urea)(OH)_2]^+$ were formed, followed by trimeric species and the Al_{13} Keggin complex $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$. The ^{27}Al NMR spectra indicated the formation of other complexes in addition to the Al_{13} at the end of the hydrolysis reaction.

**Keywords**: Al_{13}, Keggin structure, hydrolysis, nuclear magnetic resonance spectroscopy, urea

Introduction

The numerous studies that have been performed over the past 150 years on the hydrolysis and polymerisation of aluminium in aqueous solutions have been reviewed in detail by Akitt [1]. Understanding of the nature of the aluminium species formed during forced hydrolysis, such as, the tridecameric Al_{13} polymer $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, is of particular concern to many research groups in the field of catalysis, mineralogy and soil chemistry, and ceramics. Especially the application of Al_{13} complexes as pillaring agents in clay minerals is highly important (e.g., [2-4]). By intercalating the large Al_{13} complexes between the clay platelets, the specific surface area, the porous structure and the acidity of the clay material will be enhanced considerably. Al_{13} is a highly symmetric complex exhibiting a Keggin structure, consisting of a tetrahedrally coordinated central AlO_4 unit, surrounded by twelve octahedrally coordinated Al^{3+} ions (Fig. 1). Despite the large amount of publications concerning the hydrolysis of aluminium, still much confusion and controversy exist about the formation, the breakdown and the nature of hydroxy aluminium species.

The hydrolysis of aluminium, which is usually investigated by ^{27}Al NMR, is executed by addition of basic solutions or Na_2CO_3 to (acidified) aluminium salt solutions [5-18], by dissolving aluminium metal in a salt solution [5, 19-21], or by the hydrolysis of aluminium alcoholates [22, 23]. The hydroxide-to-aluminium molar ratio, n, has to be kept below 2.5 in order to form polyoxocations of aluminium instead of precipitating $Al(OH)_3$.

Up till now, almost all investigations reported in the literature on the forced hydrolysis of aluminium were performed with Al^{3+}-containing solutions to which hydroxyl ions were added by injection or dropwise addition of a base. These methods have the disadvantage that they establish large pH inhomogenities in the Al^{3+}-containing solutions, which brings about that the study of the hydrolysis of aluminium becomes inaccurate. Furthermore, scaling-up this hydrolysis procedure is impossible, because faster addition of OH^- will result in the inevitable precipitation of Al-hydroxides instead of in the formation of the Al_{13} complex. Another drawback of the above mentioned methods is that the formation of aluminium polymers during the addition of the base cannot be assessed

This paper describes a study of forced aluminium hydrolysis in solutions by decomposition of urea. By increasing the temperature of the solution above about 70°C, urea will slowly decompose in aqueous solutions. This will result in a homogeneous generation of hydroxyls in the solution according to the following overall reaction

$$CO(NH_2)_2 + 3H_2O \rightarrow 2OH^- + 2NH_4^+ + CO_2$$
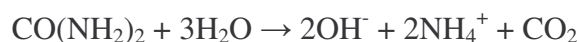
the mechanism of which was investigated by Shaw and Bordeaux [24]. Vermeulen et al. [25] and Wood et al. [26] used this method for the preparation of alumina gels. The advantage of this method is that the hydrolysis of aluminium can be followed directly with ^{27}Al NMR during the release of hydroxyl ions. More important, the procedure can be scaled-up without difficulties. This work is aimed at the characterisation of the species involved during hydrolysis of aluminium by the decomposition of urea at 90°C. Furthermore, the optimum conditions for the formation of the Al_{13} complex, which will be present in these solutions as observed by Wood et al. [26], are re-

established by varying the aluminium concentration and the OH/Al ratio (n) in solution.

Experimental

The hydrolysis of aluminium was performed according to the procedure reported by Vermeulen et al. [25]. A 1L solution was prepared by dissolving reagent grade $Al(NO_3)_3.9H_2O$ or $AlCl_3.6H_2O$ in deionised water. This solution was placed in a 3L double-walled Pyrex vessel according to the description of Van Dillen et al. [27], heated to 90°C and vigorously stirred. In some cases the pH have been previously adjusted at 1.0 to prevent self-hydrolysis of the Al^{3+} ions by addition of concentrated HNO_3. Another 1L solution was prepared by dissolving reagent grade urea in deionised water at 50°C. This solution was added to the aluminium containing solution in the vessel after which the temperature was adjusted to 90°C. The initial aluminium and urea concentrations in the combined solution were varied between 0.1 and 0.5M, and 0.3 and 2.0M, respectively. The OH^-/Al^{3+} molar ratios (= n) calculated with complete hydrolysis of the urea ranged from 6 to 8. The solutions in the vessel were stirred continuously. During the reaction, a number of 10 ml samples were pipetted from the reaction vessel, sealed in a flask, and cooled with ice-water to prevent further hydrolysis of the dissolved urea. All samples were measured with ^{27}Al NMR within one week after preparation.

^{27}Al NMR spectra were obtained on a Bruker AM500 spectrometer operated at 130.3 MHz (11.7 Tesla) using a 10 mm Bruker D-probe. For all measurements a 10 mm tube was used in which a 5 mm tube was placed. This internal tube was held in a coaxial position by a Teflon plug and filled with D_2O, which acted as field frequency lock. The samples were placed between the inner and outer tube. All spectra were measured at 20°C. To prevent further hydrolysis during the measurement, no higher temperatures were used. Typically, 100 to 1600 free-induction decays (FIDs) were recorded. The pulse width was 32 μs with a 1.0 s relaxation delay. The spectral width was 20 kHz. The ^{27}Al chemical shifts (δ) are reported in ppm values relatively to an external standard of an aqueous 0.1M $AlCl_3$ solution, $[Al(H_2O)_6^{3+}]$. All chemical shifts reported here represent the peak maxima. Some additional ^{27}Al NMR spectra were obtained using a Bruker WP 200 spectrometer operating at 52 MHz. The samples were measured after locking with D_2O without an internal tube containing D_2O.

The pH of the solutions during reaction was measured with a Schott-Geräde pH-Meter CG804 using electrodes from Ingold. The final turbid solutions were centrifuged and the resulting precipitates were washed three times and dried overnight at 130°C. The X-Ray powder Diffraction (XRD) patterns of the precipitate were recorded on an Enraf Nonius FR590 diffractometer.

Results And Discussion

pH and XRD measurements

The pH of the solutions was recorded to observe the hydrolysis of aluminium. Acidified solutions of pH 2 containing only urea at 90°C exhibit an almost immediate sharp pH jump from 2 to 6.5. This is followed by a gradual increase to a constant

value at 7.4 (Fig. 2), in accordance with the results of Vermeulen et al. [25]. The rate of change of pH of one acidified (curve a) and three non-acidified (curve b,c,d) Al^{3+} and urea containing solutions kept at 90°C are represented in Fig. 2. It is clear that the solutions with Al^{3+} do not show the immediate pH rise observed with solutions containing only urea, suggesting a consumption of the OH^- ions released during the hydrolysis of urea by the Al^{3+} ions in the solution.

Curve a (acidified) is divided in four regions, denoted as I to IV. Region I exhibits an initially strong rise of the pH from 1 to approximately 2.5. Region II corresponds to a relatively horizontal plateau. A second steep pH increase from approximately 3 to 4.5 is exhibited in region III, after which a period of a further slower pH rise is displayed (region IV). The non-acidified solutions exhibit similar profiles as curve a with the exception that region I is nearly absent. This implies that in region I the free acid present in solution is neutralised by the OH^- ions liberated by the decomposition of urea, while the hydrolysis of Al^{3+} (consumption of OH^-) mainly proceeds in region II. Furthermore, the regions II of curves b-d are at slightly higher pH levels (approx. pH 0.5) than that of curve a. The reaction of the previously acidified solution takes about 7 hours more to be completed than the non-acidified solutions (curve c,d) with n = 6.0. Increasing n from 6.0 (curve c) to 6.6 (curve b) results in a further drop of the reaction time by 2 hours. Consequently the most rapid procedure to perform the hydrolysis of Al^{3+} is by using a non-acidified solution with a high value of n. The use of $AlCl_3$ instead of $Al(NO_3)_3$ (curve d vs. c) as well as the Al^{3+} concentration has no considerable influence on the shape of the pH profile nor on the rate of the OH^- consumption.

The solutions within region I to III are always clear and colourless. At the beginning of region IV the solution is still clear, but after a short period of time a colloidal suspension starts to form at approximately pH 5.5. Further reaction results in the formation of a white gel. After drying, this gel exhibit an almost amorphous XRD pattern with very broad signals corresponding to bayerite [α-$Al(OH)_3$], which also has been observed in other studies [9-12, 28].

^{27}Al NMR measurements

To identify the aluminium species formed upon hydrolysis ^{27}Al NMR has been used extensively. Solutions containing only Al^{3+} from dissolved (0.50M) $AlCl_3 \cdot 6H_2O$ or $Al(NO_3)_3 \cdot 9H_2O$ without the presence of urea exhibit only one resonance peak with δ at about 0 ppm representing the octahedrally coordinated aluminium monomer $[Al(H_2O)_6]^{3+}$. The introduction of (1.50M) urea into the above mentioned solution containing 0.50M $Al(NO_3)_3$ at 20°C results in the ^{27}Al NMR spectrum represented in Fig. 3. Under these conditions no urea decomposition and, therefore, no forced hydrolysis of Al^{3+} will occur.

Besides the $[Al(H_2O)_6]^{3+}$ resonance at -0.10 ppm, two other resonances are present at high fields with δ at -2.67 and -4.47 ppm. These chemical shifts are in agreement with the results of Caminiti et al. [29], and correspond to a coordination of the Al^{3+} to the oxygen of the dissolved urea. The resonances at -2.67 and -4.47 ppm can be attributed to $[Al(H_20)_6]^{3+}$, in which one and two water ligands, respectively, have been replaced by urea ligands, viz., $[Al(H_2O)_5(urea)]^{3+}$ and $[Al(H_2O)_4(urea)_2]^{3+}$. The shift to higher

fields when replacing water ligands for urea is due to the higher basicity of urea as compared to that of H_2O.

In the following sections the hydrolysis of Al^{3+} will be described. In order to compare the hydrolysis behaviour of different series of experiments it has been decided to deal with the hydrolysis in terms of the position in one of the regions indicated in Fig. 2 rather than by the pH. ^{27}Al NMR (200MHz spectrometer) measurements in region I show two resonances of octahedrally coordinated Al^{3+}: a large peak at 0.12 ppm and small peak at -2.43 ppm corresponding to $[Al(H_2O)_6]^{3+}$ and $[Al(H_2O)_5(urea)]^{3+}$, respectively. The absence of $[Al(H_2O)_4(urea)_2]^{3+}$ is possibly due to the low magnetic field, but the increase in pH indicates that certainly some urea decomposition has already occurred. The absence of new (poly)-aluminium species suggests that the hydrolysis of Al^{3+} has not yet started in this region. These findings support the conclusion from the pH measurements that the OH$^-$ ions released during the urea decomposition merely neutralise the free acid in solution.

Due to the absence of Al^{3+}-hydrolysis in region I and in order to combine an increase of the reaction rate with high resolution NMR data, the remaining experiments have been executed without previous acidification and the spectra have been measured with a 500MHz NMR spectrometer. The following two sections will give detailed descriptions of the hydrolysis of an AlCl$_3$-solution (0.50M Al^{3+}; n = 6.0; curve c) and of 0.25M and 0.10M Al(NO$_3$)$_3$-solutions (n = 6.0) at 90°C.

Solutions containing 0.50M Al^{3+} (n = 6.0)

^{27}Al NMR spectra of different stages of the hydrolysis are represented in Fig. 4. In the beginning of region II after two hours four resonances are present. Three of them are conform the earlier mentioned sharp resonances at -4.30, -2.65, and -0.09 ppm corresponding to $[Al(H_2O)_4(urea)]^{3+}$, $[Al(H_2O)_5(urea)]^{3+}$, and $[Al(H_2O)_6]^{3+}$, respectively, and a new broad peak with a δ of 3.93 ppm (Fig. 4a). Earlier studies [6-8, 19] interpreted this signal as the dimeric Al species $[Al_2(OH)_2(H_2O)_8]^{4+}$, but later studies based on ^{1}H and ^{27}Al NMR experiments demonstrated that the major Al species with δ around 4 ppm is the Al^{3+}-trimer $[Al_3O_2(OH)_4(H_2O)_8]^+$ [20].

The $[Al(H_2O)_4(urea)_2]^{3+}$ and the $[Al(H_2O)_5(urea)]^{3+}$ complexes remain detectable until near the end of region II and the beginning of region III, respectively. In region II the $[Al(H_2O)_6]^{3+}$ resonance remains the most dominating peak, but the intensity of this resonance sharply declines at the start of region III. Midway region III, $[Al(H_2O)_6]^{3+}$ has disappeared. During the hydrolysis reaction the chemical shift of the $[Al(H_2O)_6]^{3+}$ complex is shifted to low field from -0.09 to 0.02 ppm and the linewidth increases from 18 to 118 Hz. The theoretical linewidth of the $[Al(H_2O)_6]^{3+}$ complex is 2 Hz [30]. The observed strong increase of the linewidth can be attributed to the increasing replacement of one or two H_2O ligands by OH$^-$ upon forced hydrolysis forming $[Al(H_2O)_5(OH)]^{2+}$ and $[Al(H_2O)_4(OH)_2]^+$. The partially hydrolysed monomers cannot be observed directly with ^{27}Al NMR, due to their fast proton exchange. The theoretical linewidths are 620 Hz and 890 Hz for $[Al(H_2O)_5(OH)]^{2+}$ and $[Al(H_2O)_4(OH)_2]^+$, respectively [31]. The increase of the observed linewidth of the monomer signal is, therefore, indirect evidence for the above mentioned replacement [32].

Like $[Al(H_2O)_6]^{3+}$, also the $[Al(H_2O)_5(urea)]^{3+}$ complex shows a shift of the chemical shift δ to low field and a linewidth broadening upon hydrolysis from -2.65 to -2.46 ppm and from 35 to 485 Hz, respectively. It is likely that during the hydrolysis reaction also one or two H_2O ligands of the urea complexes are replaced by OH^- and thus complexes, such as, $[Al(H_2O)_4(urea)(OH)]^{2+}$ and $[Al(H_2O)_3(urea)(OH)_2]^+$ result.

While the linewidths of the $[Al(H_2O)_6]^{3+}$, $[Al(H_2O)_5(urea)]^{3+}$, and $[Al(H_2O)_4(urea)_2]^{3+}$ species point to the release of protons from the coordinated water molecules leading to substitution of OH^- groups, the shift of the resonances to lower fields can be attributed to an increase in ionic strength of the solution [1]. The intensity of the trimer resonance at about 4 ppm remains constant up to 2/3 of region II, but drops subsequently near the beginning of region III, where no resonance corresponding to the Al trimer is detected anymore. The trimer signals are broad, 300-570 Hz, and also shift to lower field from 4.07 to 4.51 ppm, probably due to the increased ionic strength.

As soon as the trimers start to diminish, three new resonances show up. The most distinct signal is a sharp peak at about 62.8 ppm (Fig. 4b), corresponding to the central fourfold coordinated Al^{3+} of the Al_{13} complex $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ (e.g. [5]). From the beginning of region III up to the beginning of region IV, this Al_{13} signal is the main resonance exhibited with a constant δ and linewidth of about 62.7-62.8 ppm and 18-32 Hz, respectively. Fig. 4c is exhibiting only the three new resonances. The sharpness of this signal is due to the very symmetrical environment resulting in a very weak electric field gradient (strong shielding) of this central fourfold coordinated Al cation. The δ being unaffected upon hydrolysis of the Al_{13} complex is probably caused by the shielding of the central Al^{3+} ion of the Al_{13} complex by the 12 sixfold coordinated Al^{3+} cations [1]. At the end of region IV, near its disappearance, the Al_{13} peak starts to broaden to 59 Hz, which suggests a change in the chemical environment of the central fourfold coordinated Al.

The second new signal appears as a very broad (2200- 3100 Hz) resonance peaking at 11.9 ppm corresponding to Al^{3+} in sixfold coordination. The δ initially rises to 12.6 ppm at the start of region III, but declines to 4.9 ppm in region IV indicating a clear change of the nature of this species. It must be mentioned that the presence of two overlapping resonances cannot be excluded. In the literature dealing with metal-hydrolysed solutions, species with δ around 12 ppm are attributed to the sixfold coordinated Al^{3+} cations of the Al_{13} complex [19-21]. However, this species is nearly invisible with ^{27}Al NMR at room temperature (RT), which is caused by the very large quadrupolar line broadening due to the low symmetry around the aluminium ions. This suggests that the Al species in this study, all measured at RT, reflect another or a combination of other sixfold coordinated Al species.

The third new resonance arises as a very broad signal with a linewidth between 1400-2500 Hz peaking at 70- 71 ppm and is due to a fourfold coordinated Al species. Like the sixfold coordinated Al species, this resonance is also observed in metal-hydrolysed solutions [20, 21]. Monomeric Al^{3+} in fourfold coordination, $[Al(OH)_4]^-$, is only stable at high pH levels and exhibits a chemical shift δ of 80 ppm [1]. Therefore $[Al(OH)_4]^-$ can be excluded as the new species. Fu et al. [21] suggested a dimeric Al_{13} complex, $(Al_{13})_2$, for the resonance at 70 ppm, although other complexes, such as, Al_{20} and Al_{41}, have been proposed too [6, 33].

Just before the formation of the precipitate, two new peaks are apparent at 67 and -8 ppm, corresponding to fourfold and sixfold coordinated Al^{3+}, respectively, as can been seen in Fig. 4d. In only one study concerning the hydrolysis of aluminium metal a resonance at -9 ppm was observed [20], although no further explanation was presented. The peak at 67 ppm is superimposed on the fourfold coordinated Al peak (see Fig. 4d). It is interesting to note that after the formation of the Al-precipitate, the supernatant after centrifugation does not show any NMR detectable Al species, although it might still be possible that large polymeric Al species are present in the solution unobservable with ^{27}Al NMR.

The use of $Al(NO_3)_3$ instead of $AlCl_3$ does not bring about any change in the species formed upon hydrolysis as well as in the rate of reaction, which is in complete accordance with Akitt [1] and Changui et al. [34]. The Cl^- and NO_3^- anions appear not to interact with the Al^{3+} cation. Increase of n from 6.0 to 8.0 accelerates the hydrolysis of Al^{3+}. However, the Al species involved do not differ from those observed in the above mentioned reaction process and will, therefore, not be described in detail.

Solutions containing 0.25 or 0.10M Al^{3+} (n = 6.0)

Two series of experiments with 0.25 and 0.10M Al^{3+}, respectively, in non-acidified solutions have been executed to identify the influence of the Al^{3+} concentration on the hydrolysis of Al^{3+}. The overall rate of hydrolysis in the solutions containing 0.25M Al^{3+} is not significantly different from that observed with the solutions containing 0.50M Al^{3+}.

Hydrolysis in 0.10M Al^{3+} solutions takes about 30 minutes more than within the 0.50M and 0.25M Al^{3+} solutions. The hydrolysis reaction in solutions containing 0.10M and 0.25M Al^{3+} exhibit some differences as compared to 0.50M Al^{3+}. The $[Al(H_2O)_4(urea)_2]^{3+}$ resonance has not been observed. In the 0.50M Al solution the $[Al(H_2O)_4(urea)_2]^{3+}$ resonance displays a very low intensity. It is likely that by lowering the Al concentration to 0.25M or 0.10M the intensity of this resonance is too low to be observed with ^{27}Al NMR. Furthermore, the development of the above described sixfold and fourfold coordinated Al species is very vague, especially in 0.10M Al^{3+} solutions. These species seem to be present, but far less clearly than in solutions containing 0.50M Al^{3+}. Discrimination of the fourfold coordinated Al signal from the background is, therefore, very difficult. Solutions with 0.25M Al^{3+} behave intermediately between the solutions with 0.10M and 0.50M Al^{3+} with respect to the appearance of both species. The formation of these oligomeric species is apparently favoured at higher Al^{3+} concentrations, which has also been observed by Akitt et al. [20].

The $[Al(H_2O)_5(urea)]^{3+}$ resonance is observed at chemical shift values between -2.28 and -2.21 ppm (35-156 Hz) and between -2.35 and -2.19 ppm (70-112 Hz) with solutions of 0.10M and 0.25M Al^{3+}, respectively. In each concentration series only the first three measured samples contained this species. The $[Al(H_2O)_6]^{3+}$ resonance exhibit a shift of δ to low field and line broadening upon hydrolysis. In 0.10M and 0.25M solutions the δ shifts from 0.18 to 0.50 ppm and from 0.18 to 0.30 ppm with a corresponding line broadening from 25 to 85 Hz and from 22 to 60 Hz, respectively.

This suggests an increase of the ionic strength in solution and some formation of $[Al(H_2O)_5(OH)]^{2+}$ and $[Al(H_2O)_4(OH)_2]^+$.

The Al^{3+} trimer is in both solutions present with δ varying from 4.10 to 4.60 ppm with a linewidth of 165-330 Hz. The Al_{13} complex is apparent in the 0.10M and 0.25M Al-containing solutions from a sharp peak with a constant δ of 62.2-62.3 ppm and a linewidth of 11 to 20 Hz. There is no relation between the linewidth and the rate of hydrolysis. The formation and disappearance of the above mentioned Al^{3+} species are at the same locations in the pH curve as those in the solutions containing 0.50M Al^{3+}.

Two striking features have to be mentioned:
1) After prolonged hydrolysis (region IV) when the Al_{13} complex resonance is diminishing, some sixfold coordinated monomeric Al^{3+} starts to appear again with a δ of -0.4 to -0.9 ppm and a linewidth of 150-160 Hz in solutions of 0.1M Al^{3+}. This implies a renewed formation of a combination of $[Al(H_2O)_6]^{3+}$, $[Al(H_2O)_5(OH)]^{2+}$ and $[Al(H_2O)_4(OH)_2]^+$. The formation of monomeric Al^{3+} after prolonged ageing of hydrolysed Al solutions has also been detected by Akitt and Farthing [6], Nazar and Klein [22] and Wang and Hsu [35].
2) In an acidified solution containing 0.25M Al^{3+} (serie a) a remarkable change of the δ of Al_{13} occurred when measured with the 200 MHz spectrometer. Up to the centre of region III the Al_{13} complex exhibits a peak at 62.5-63.0 ppm. Just 15 minutes later a new sharp peak at 64.3 ppm arises next to a small peak remaining at 62.5 ppm from the 'normal' Al_{13} resonance. Another 15 minutes later only the resonance peaking at 64.3 ppm is visible. This Al complex has never been detected in all other (500 MHz) experiments (Fig. 5). Fu et al. [21] mentioned the formation of a resonance at 64.5 ppm, which they denoted as AlP_1. They suggested for AlP_1 a defect Al_{13} structure which has lost one octahedron.

Concentration of Al_{13} in solution

Up till now the formation and breakdown of the various kinds of Al complexes in solutions containing 0.10, 0.25 and 0.50M Al^{3+} have been discussed. For the possible application of the Al_{13} complex as pillaring agent in clay minerals by using this preparation method it is important to know to what extent this complex have been formed and within which stage of the hydrolysis reaction. To achieve a rapid and complete exchange of the interlayer ions with Al_{13} a high concentration of Al_{13} is desired.

As can be seen in Fig. 2 the pH curves of the different hydrolysis experiments are similar in shape, but the pH levels of the same regions with the different solutions are slightly different. As was indicated in the previous paragraphs the hydrolysis reactions in each region of the various solutions are not differing. In order to compare various solutions of different pH levels and different hydrolysis rates the pH profiles have been subdivided into 16 arbitrary units (Fig. 6) in the following manner. The pH profiles have already been subdivided into region II, III and IV. In addition to this region II is further subdivided into 10 parts, 1 up to 10. At number 10 region III starts and continues to 15, where region IV begins. From there an increase in pH of 0.2 in region IV corresponds to number 16.

Fig. 6 shows the percentage of monomeric Al^{3+} and Al_{13} as a function of the progress

of the hydrolysis reaction. The percentage of the Al^{3+} monomer relative to the total Al^{3+} content has been calculated from the integrated intensity of the signal around 0 ppm. The Al_{13} percentage has been calculated by multiplying the integrated intensity of the fourfold coordinated Al^{3+} signal around 63 ppm by 13, which accounts for the fact that the resonance only concerns one of the thirteen aluminium ions present in the complex. Due to the very broad signals of the other (oligomeric) species more reliable calculations are not possible and are, therefore, not included.

Upon hydrolysis the percentage of monomeric Al^{3+} displays a continuous decline, whereas the percentage Al_{13} increases. The percentage Al_{13} shows a maximum when all monomeric Al^{3+} has disappeared. At this point, midway region III, n will range from about 2.2 to 2.6 [7-12, 20]. The formation of Al_{13} is favoured at lower initial Al^{3+} concentrations, in accordance with Kloprogge et al. [36]. The maximum Al_{13} concentrations in solutions containing 0.50, 0.25 and 0.10M Al^{3+} are 30, 53 and 81 %, respectively, which is much higher than obtained by Kloprogge et al. [36]. Increase of n from 6.0 to 8.0 does not influence the amount of Al_{13} formed. The higher intensity of the sixfold and fourfold coordinated Al species signals in the NMR spectra of 0.50M Al^{3+} solutions as compared to that of solutions containing 0.35 and 0.10M Al^{3+} suggests that the formation of oligomeric species other than Al_{13} is favoured at higher Al^{3+} concentrations.

Hydrolysis mechanism

The initial solutions consist of the monomeric Al^{3+} species $[Al(H_2O)_6]^{3+}$, $[Al(H_2O)_5(urea)]^{3+}$, and at high Al^{3+} concentrations $[Al(H_2O)_4(urea)_2]^{3+}$ with a chemical shift δ around 0, -2.7 and -4.5 ppm, respectively. In the early stages of hydrolysis, two different reactions occur. Firstly, some of the H_2O ligands of the monomeric species are replaced by OH^- forming $[Al(H_2O)_5(OH)]^{2+}$ and $[Al(H_2O)_4(OH)_2]^+$. In a similar way reaction to complexes, such as, $[Al(H_2O)_4(urea)(OH)]^{2+}$ and $[Al(H_2O)_3(urea)(OH)_2]^+$, also proceeds. The partial substitution by hydroxyl groups is indicated by a broadening of the signal of all three resonances. Secondly, a fraction of the monomers reacts to the Al^{3+} trimer $[Al_3O_2(OH)_4(H_2O)_8]^+$ showing a peak around 4 ppm. The rate of the above mentioned hydrolysis reactions is such that the consumption of OH^- ions is almost equal to the amount of OH^- ions released into the solution by the hydrolysis of urea as indicated by the nearly horizontal plateau of the pH profiles.

As the hydrolysis proceeds, the elucidation of the mechanism becomes less straightforward. Soon after the formation of the trimers, three new species are produced simultaneously: Al_{13} and the sixfold and fourfold coordinated Al species as shown by ^{27}Al NMR resonances around 63, 12 and 70 ppm, respectively. It is likely that these species are formed at the cost of the Al^{3+} trimers and monomers, as indicated by the disappearance of these latter species upon further hydrolysis. The formation of Al species that cannot be observed with ^{27}Al NMR is most likely, because this problem have been reported in nearly all other studies concerning the Al hydrolysis mentioned in this paper.

The mechanism of formation of the Al_{13} complex is rather complicated. The most difficult to account for is the origin of the fourfold coordinated Al in the centre of the Al_{13} complex. Fourfold coordinated monomeric Al^{3+}, as $Al(OH)_4^-$, is only stable in

solutions at high pH levels, whereas Al_{13} is formed in acidic solutions. In the literature, it is suggested that the formation of Al_{13} is due to inhomogeneous mixing conditions in solutions at the point of injection of a base, resulting in small regions in these solutions containing $Al(OH)_4^-$. It is believed that upon stirring these anions are swept out of these regions, encountering monomeric and small oligomeric species, and thus combining to the Al_{13} complex [6, 10-12, 37]. However, the hydrolysis method applied in this study generates OH^- ions homogeneously throughout the solution without the possibility of creating liquid elements of high pH. The above mentioned mechanism is, therefore, not applicable to the results in this study.

In many studies [38-40], there are indications for $[Al_6(OH)_{12}(H_2O)_{12}]^{6+}$ species, Al_6, which consists of six octahedrally coordinated Al^{3+} ions. In Al_6, these octahedrons constitute a six-membered ring. Unfortunately, Al_6 cannot be observed directly by ^{27}Al NMR due to the quadrupolar broadening effect. It is likely that Al_6 results from reaction of monomers or small polymeric Al species. It can be supposed that a monomer is able to bind two Al_6 complexes, resulting in a structure in which the monomer is partly situated within the central cavities of both six-membered rings. Structural rearrangement of this complex, including the transformation of the central monomer from sixfold to fourfold coordination, may result in the formation of the very symmetrical Keggin structure of Al_{13}.

The fourfold coordinated Al species resonance originates, like that of Al_{13}, from fourfold coordinated Al^{3+}. To be stable in acidic solutions, this species must be shielded by a number of sixfold coordinated Al^{3+} cations. The large linewidth of the resonance indicates an environment of symmetry lower than that of Al_{13}. The sixfold coordinated Al species is usually attributed to the sixfold coordinated Al^{3+} of the Al_{13} complex and is only observed when measured at higher temperatures, viz., 70-80°C [6, 20, 21, 34]. In this study, however, this species is already apparent at RT. Moreover, in solutions of low Al^{3+} concentrations, but with a high Al_{13} content, this species (and the fourfold coordinated species) are nearly absent. This implies that this resonance does not originate from the Al_{13} structure, but is presumably related to a separate sixfold coordinated Al species, a conclusion which agrees with the findings of Nazar and Klein [22] and Fitzgerald et al. [33]. The suggestion of Fu et al. [21] for the 70 ppm resonance being related to a dimeric Al_{13} complex, $(Al_{13})_2$, seems reasonably plausible, although other species suggested to correspond to the 70 ppm resonance, which are an Al_{41} complex [33] and an Al_{20} complex [19], cannot be excluded.

Shortly before the formation of the gel, some rearrangements proceed as evidenced by changes in the NMR spectra. Firstly, with a 200 Mhz spectrometer it was observed that the δ of Al_{13} changed from 62.7 to 64.3 ppm. This seems to indicate a structural change of the complex, possibly caused by a loss of one Al^{3+} octahedron due to the polymerisation of the former Al_{13} complexes [21]. Secondly, the observed reappearance of monomeric Al^{3+} around 0 ppm after prolonged hydrolysis of formerly Al_{13}-rich solutions containing 0.1 M Al^{3+} may originate from the released Al^{3+} octahedra. Thirdly, in highly concentrated solutions a resonance at 67 ppm appears together with an octahedral peak at -8 ppm. The sixfold coordinated Al species resonance has shifted from 12 to 4.9 ppm, although it is also possible that a band at approximately 5 ppm is appearing whereas the other band is disappearing. At this stage, all Al_{13} has disappeared. A MAS-NMR experiment performed by Wood et al.

[26] of the gel shows very broad peaks at -65 and -0 ppm. It is conceivable that the combination of the 67 ppm resonance and the broad sixfold coordinated doublet at 4.9 and -9 ppm may reflect very large oligomers prior to the gel stage.

Summary

(1) The hydrolysis of aluminium by urea decomposition results in the formation of a wide variety of monomeric and polymeric Al^{3+} species according to ^{27}Al NMR measurements. The monomeric Al species include $[Al(H_2O)_6]^{3+}$, $[Al(H_2O)_5(urea)]^{3+}$, $[Al(H_2O)_4(urea)_2]^{3+}$ and the more hydrolysed monomeric species $[Al(H_2O)_5(OH)]^{2+}$, $[Al(H_2O)_4(OH)_2]^+$, $[Al(H_2O)_4(urea)(OH)]^{2+}$, and $[Al(H_2O)_3(urea)(OH)_2]^+$. The polymeric species are a trimeric complex $[Al_3O_2(OH)_4(H_2O)_8]^+$ and the Al_{13} polymer $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$. Other polymeric Al complexes are also present as indicated by broad resonances at ~ -9, (~5), ~12, ~67 and ~70 ppm together with a sharp resonance at 64.3 ppm.

(2) The formation of the Al_{13} complex mainly takes place in the near horizontal plateau of the pH curve (region II) and the beginning of region III and coincides with a disappearance of monomeric and trimeric Al^{3+}.
.
(3) The highest amount of Al_{13}, 81%, is obtained in solutions of a low Al^{3+} concentration (0.1M). Increasing the Al^{3+} concentration to 0.5M results in a maximum content of 30% Al_{13} together with other polynuclear Al^{3+} species at ~12 and ~70 ppm.

(4) The fourfold coordinated AlO_4 unit of Al_{13} does not originate from inhomogeneous conditions in solutions containing $Al(OH)_4$ as suggested in literature up to now. Formation of Al_{13} out of one Al^{3+} monomer and two Al_6 complexes is suggested in this study.

REFERENCES

[1]   J. W. Akitt, Progr. Nucl. Magn. Res. Spectrosc. 21 (1989) 1.

[2]   J. Shabtai, M. Rosell, M. Tokarz, Clays Clay Miner. 32 (1984) 99.

[3]   D. Plee, L. Gatineau, J. J. Fripiat, Clays Clay Miner. 35 (1987) 81.

[4]   J. T. Kloprogge, J. Porous Materials 5 (1998) 5.

[5]   J. W. Akitt, A. Farthing, J. Magn. Resonance 32 (1978) 345.

[6]   J. W. Akitt, A. Farthing, J. Chem. Soc., Dalton Trans. (1981) 1617.

[7]   P. M. Bertsch, W. J. Layton, R. I. Barnhisel, Soil. Sci. Soc. Amer. J. 50 (1986) 1449.

[8]   P. M. Bertsch, G. W. Thomas, R. I. Barnhisel, Soil. Sci. Soc. Amer. J. 50 (1986) 825.

[9]   J. Y. Bottero, M. Axelos, D. Tchoubar, J. M. Cases, J. J. Fripiat, J. Coll. Interface Sci 117 (1987) 47.

[10]   J. T. Kloprogge, D. Seykens, J. W. Geus, J. B. H. Jansen, J. Non-Cryst. Solids 142 (1992) 87.

[11]   J. T. Kloprogge, D. Seykens, J. W. Geus, J. B. H. Jansen, J. Non-Cryst. Solids 142 (1992) 94.

[12]   J. T. Kloprogge, D. Seykens, J. B. H. Jansen, J. W. Geus, J. Non-Cryst. Solids 142 (1992) 94.

[13]   S. Bi, C. Wang, Q. Cao, C. Zhang, Coord. Chem. Rev. 248 (2004) 441.

[14]   Y. Xu, D. Wang, H. Liu, Y. Lu, H. Tang, Coll. Surf. A: Phs. Eng. Aspects 231 (2003) 1.

[15]   Z. Jia, F. He, Z. Liu, Ind. Eng. Chem. Res. 43 (2004) 12.

[16]   C. C. Perry, K. L. Shafran, J. Inorg. Biochem. 87 (2001) 115.

[17]   F. Salvatore, M. Trifuoggi, J. Coord. Chem. 51 (2000) 271.

[18]   J. Rowsell, L. F. Nazar, J. Amer. Ceram. Soc. 122 (2000) 3777.

[19]   J. W. Akitt, A. Farthing, J. Chem. Soc., Dalton Trans. (1981) 1624.

[20]   J. W. Akitt, J. M. Elders, X. L. R. Fontaine, A. K. Kundu, J. Chem. Soc., Dalton Trans. (1989) 1889.

[21]   G. Fu, L. F. Nazar, A. D. Bain, Chem. Mater 3 (1991) 602.

[22]   L. F. Nazar, L. C. Klein, J. Am. Ceram. Soc 71 (1988) C.

[23]   R. J. M. J. Vogels, J. T. Kloprogge, P. A. Buining, D. Seykens, J. B. H. Jansen, J. W. Geus, J. Non-Cryst. Solids 191 (1995) 38.

[24]   W. H. R. Shaw, J. J. Bordeaux, J. Amer. Ceram. Soc. 77 (1955) 4729.

[25]   A. C. Vermeulen, J. W. Geus, R. J. Stol, P. L. de Bruyn, J. Coll. Interf. Sci 51 (1975) 449.

[26]   T. E. Wood, A. R. Siedle, J. R. Hill, R. P. Skarjune, C. J. Goodbrake, Mat. Res. Soc. Symp. Proc 180 (1990) 97.

[27]   A. J. van Dillen, J. W. Geus, L. A. M. Hermans, J. Van der Meijden, Proc. 6th Int. Conf. Catal. 11 (1977) 677.

[28]   C. J. Serna, J. L. White, S. L. Hem, Clays Clay Miner. 25 (1977) p 384.

[29]   R. Caminiti, G. Crisponi, V. Nurchi, A. Lai, Z, Naturforsch. 39A (1984) 1235.

[30]   J. W. Akitt, J. M. Elders, J. Chem. Soc., Faraday Trans. 81 (1985a) 1923.

[31]   J. W. Akitt, J. M. Elders, J. Chem. Soc., Faraday Trans. 81 (1985) 1923.

[32]   J. T. Kloprogge, D. Seykens, J. B. H. Jansen, J. W. Geus, J. Non-Cryst. Solids 152 (1993) 207.

[33]   J. J. Fitzgerald, L. E. Johnson, J. S. Frye, J. Magn. Resonance 84 (1989) 121.

[34]   C. Changui, W. E. E. Stone, L. Vielvoye, J.-M. Dereppe, J. Chem. Soc., Dalton Trans. (1990) 1723.

[35] W.-Z. Wang, P. H. Hsu, Clays Clay Miner. 42 (1994) 256.
[36] J. T. Kloprogge, D. Seykens, J. W. Geus, J. B. H. Jansen, J. Non-Cryst. Solids 160 (1993) 144.
[37] P. M. Bertsch, Soil Sci. Soc. Am. J 51 (1987) 825828.
[38] P. H. Hsu, T. F. Bates, Mineral. Mag. 33 (1964) 749.
[39] R. J. Stol, v. H. A. K., d. B. P. L., J. Coll. Interf. Sci 57 (1976) 115.
[40] A. Singhal, K. D. Keefer, J. Mater. Res. 9 (1994) 1973.
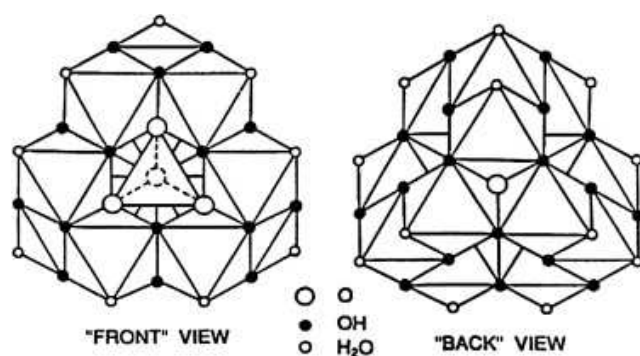
Figures

Fig. 1   Model of the Al_{13} Keggin complex.

"FRONT" VIEW   ○ O
                   ● OH   "BACK" VIEW
                   ○ H₂O

Fig. 2   pH curves during the hydrolysis of urea at 90°C: (a) acidified solution of 0.50M Al-nitrate and 1.50M urea, (b) non-acidified solution of 0.50M Al-nitrate and 1.65M urea, non-acidified solution of 0.50M Al-chloride (c) or 0.50M Al-nitrate (d) with 1.05M urea, (e) solution of 1.50M urea with initial pH of 2.
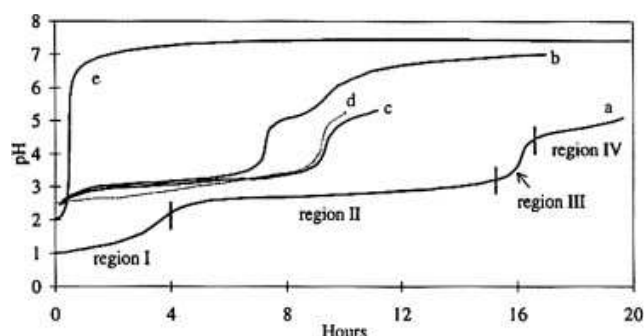

Fig. 3 ^{27}Al NMR spectrum (500MHz) of solution containing 1.50M urea and 1.50M Al-nitrate at 20°C
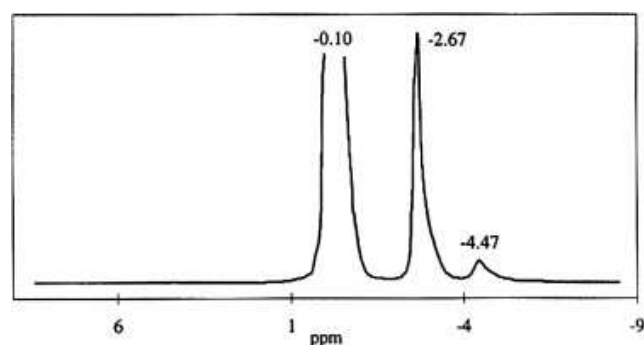
Fig. 4 ^{27}Al NMR spectra (500 MHz) of solutions containing 0.50m AlCl$_3$ and 1.50M urea kept at 90°C. (a) start region II (pH = 3.0), (b) end region II/start region III (ph = 3.5), (c) end region III (pH = 4.7) and (d) start region IV (pH = 5.3).
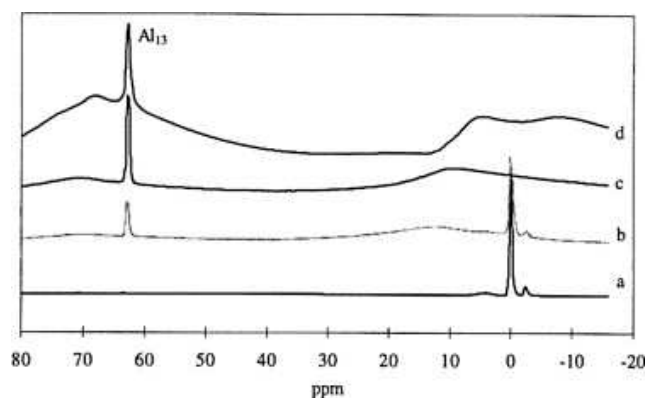

Fig. 5 ^{27}Al NMR spectrum (200 MHz) of the Al$_{13}$ complex with a peak at 63.5 ppm and a newly developed complex at 64.3 ppm.
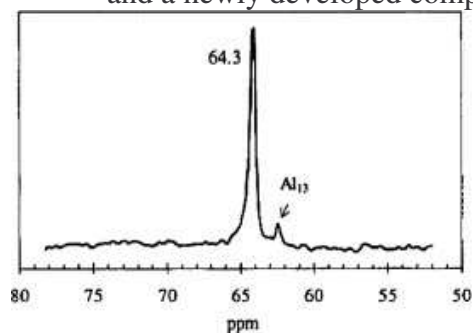

Fig. 6 The influence of the Al^{3+} concentration (0.10M fully drawn curve, 0.50M dashed curve) and the degree of hydrolysis on the amount of monomeric Al and Al$_{13}$ present in solution.