Speciation of hydroxyl-Al polymers formed through simultaneous hydrolysis of aluminum salts and urea

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Abstract

Urea hydrolysis has always been used to prepare alumina gels and little attention has been paid to the reactive polymeric Al species that is formed before alumina sol–gels occur. Based on the hydrolysis process of aluminum in urea solution at 90 °C, speciation and transformation of the reactive hydroxyl-Al polymers obtained by urea hydrolysis was investigated with Ferron assay, solution-state and solid-state ²⁷Al NMR spectroscopy. Unlike the traditional viewpoint, Keggin-Al₁₃ can form in solution without localized high alkalinity. The reaction of oligomers with Al(OH)₄[−] resulted from the dissolving of colloidal Al hydroxides is accountable for the formation of Keggin-Al₁₃. Al_{p1}, the defected structure of Al₁₃, was considered as the transient species in the transformation from Al₁₃ to crystalline Al hydroxides. Besides Al₁₃, some other reactive polymers with hexameric ring structure also exist. The two categories of Al species have different transformation models (i.e., forced hydrolysis and spontaneous hydrolysis). The forced hydrolysis model should be the main transformation pattern for Al species under the condition of strong base addition into Al solution. Sulphate ions inhibit the formation of high polymeric Al species and affect the crystal structure of the final Al precipitate.

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1. Introduction

Over the past decades, many studies have been devoted to the hydrolysis and polymerization of Al(III) [1,2]. As metastable species, some polymeric Al species in the Al hydrolysis products have unique electrical charge and structure, which play important roles in water and wastewater treatment [3–5]. Thus, many research interests have been focused largely on the preparation and speciation determination of these reactive species. Most hydroxyl-Al polymers are prepared by injection or micro-titration of strong base (e.g., NaOH, Na₂CO₃) into Al solutions [6–8]. There is little documentation about the preparation of the reactive hydroxyl-Al polymers through urea (CO(NH₂)₂) hydrolysis.

The advantage of using urea rather than strong base is that the hydrolysis process of urea is much slower, which makes the Al hydrolysis proceed gently. Furthermore, since the hydrolysis of

urea is strongly temperature dependent, the hydrolysis of urea can be easily controlled by cooling [9,10]. Therefore, the immediate formation of Al precipitate with strong base addition could be avoided with urea as alkaline agent. Although the hydrolysis of urea at elevated temperature has always been used to prepare alumina gels [11,12], little is known about the processes of formation and transformation of reactive polymeric Al species before alumina sol–gels occur.

As for the reactive polymeric Al species, the tridecameric Al₁₃ polymer [AlO₄Al₁₂(OH)₂₄(H₂O)₁₂]⁷⁺ with Keggin structure has frequently been assumed to be one of the dominant components. Many researchers suggest that the formation of Al₁₃ is due to the local concentration effect caused by base addition into Al solution [13–15]. However, the hydroxide ions released from urea hydrolysis are uniformly distributed throughout the whole solution and no localized high alkalinity will be present at any point. Thus the traditional theory is unable to explain fully the Al₁₃ formation mechanism in the solution with homogeneous distribution of hydroxide ions. Vogels et al. have reported a different mechanism on the formation of Keggin-Al₁₃: a monomer binds two Al₆ polymers to form a special Al

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intermediate complex, and then the complex undergoes structural rearrangement, including the transformation of the central monomer from six-fold to four-fold coordination, to form the Keggin- Al_{13} [16]. This deduction is still absent of direct identification.

There are currently two hydrolysis and structure transformation models (i.e., hexameric ring model and Keggin- Al_{13} model) reported in literatures about the formation of Al hydroxide precipitate in solution [3,14]. The hexameric ring model was set on the basis of “core and link” theory and deduced mainly from the experimental results. Its demonstration is the normal direct evolution of Al species to the similar structure of solid gibbsite. Though the six-member ring structure in solution has not been identified directly by instruments, this model was still approved by many researchers [14]. Since the Keggin- Al_{13} structure has been confirmed with ^{27}Al NMR spectroscopy, the Keggin- Al_{13} model is increasingly accepted and becoming the leading attitude [8,15]. However, Al species in this model are distributed discontinuously with different formation mechanism other than the six-member ring continuous model. The two models have coexisted over several decades, but neither of them can give a complete description of the Al hydrolysis process. As for the Al–urea mixture, urea hydrolysis results in a special solution environment in which hydroxide and Al ions are homogeneously distributed throughout the whole mixture. It is necessary to discuss the pathways and conditions for the formation of hydrolytic Al species and subsequent transformation to gibbsite structure under the special circumstances.

The aim of this study is to prepare hydroxyl-Al polymers by urea hydrolysis and to investigate the speciation of the Al hydrolysis products with ^{27}Al NMR spectroscopy and Ferron assay. Emphasis will be laid on the formation and transformation model of hydrolytic Al species, especially the formation mechanism of Al_{13} polycation, in urea solution. In order to understand the effect of anionic ions on the Al hydrolysis, two Al salts, AlCl_3 , $\text{Al}_2(\text{SO}_4)_3$ were used to prepare hydroxyl-Al polymers.

2. Materials and methods

2.1. Sample preparation

In this study, deionized water was used to prepare all the solutions and all the reagents were analytical grade chemicals. A 1-L solution containing 0.1 mol Al/L AlCl_3 (or $\text{Al}_2(\text{SO}_4)_3$) and 0.4 mol/L urea were prepared and transferred into a double-layered glass reactor. The temperature in the reactor was maintained at 90 °C by circulating water from a water bath into the water jacket of the reactor. Under rapid stirring, 15-mL samples were taken from the reactor during the Al hydrolysis process and cooled in refrigerator to prevent further hydrolysis of urea. The hydrolysis of urea without Al was also conducted and monitored under the same condition.

The samples after cooling were aged for 24 h at room temperature and their final pH values were measured with MP220 pH meter (Mettler Toledo, Switzerland) before they were preserved at 4 °C for analysis.

2.2. Solution-state ^{27}Al NMR spectroscopy

500 MHz ^{27}Al NMR (Brookhaven Co., U.S.A.) was used in this study. The instrumental settings and experimental conditions were: NS = 128, P1 = 20 μs , PL1 = –3 dB. Solvent: D_2O , and $T = 298\text{ K}$. The inner standard was 0.05 mol/L $\text{Al}(\text{OD})_4^-$ solution and its chemical shift is 80 ppm. The signals near 0, 3–4 and 62.5 ppm represent mononuclear Al (Al_m), trimeric Al (Al_3) and the tetrahedral $\text{Al}(\text{O})_4$ core (and 1/13 content) of Al_{13} ($[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$), respectively. The concentration of each species was determined by the ratio of the integrated intensity of its corresponding peak to that of $\text{Al}(\text{OD})_4^-$ at 80 ppm. The Al_{13} content was calculated by multiplying the $\text{Al}(\text{O})_4$ concentration by 13. The amount of the undetectable species (Al_{un}) was obtained by subtracting the sum of the detected Al species from the total Al (Al_t) concentration [14].

2.3. Ferron assay

The detailed procedures for the preparation of Ferron colorimetric solution can be found in Wang et al. [5]. For the speciation of each sample, 5.5 mL Ferron colorimetric solution was firstly transferred into a graduated glass tube and diluted to 25 mL. Then, 20 μL test Al solution was added to the tube and the reaction time was recorded simultaneously. After homogeneous mixing, the reacting sample was quickly added to a 1-cm quartz cell. The timed absorbance measurements, using a UV–VIS 8500 spectrophotometer (Tianmei Co., China), were carried out at 366 nm after 30 s and recorded for further 7200 s. The speciation of Al was operationally divided: the absorbance from 0 to 30 s was ascribed to Al_a (mononuclear Al), and that from 30 to 7200 s to Al_b (reactive hydroxyl-Al polymers), then Al_c (colloidal or precipitated Al species) was obtained by total Al (Al_t) minus Al_a and Al_b .

2.4. Solid-state ^{27}Al NMR spectroscopy

The samples were filtered using Millipore filter membrane of 0.45 μm and the Al_t concentration in filtrate was measured with ICP-OES (Perkin-Elmer Co., U.S.A.). The colloidal or precipitated Al retained by filter was freeze-dried and analyzed with solid-state NMR spectroscopy. ^{27}Al MAS NMR spectra were recorded on a Varian INOVA300 spectrometer at 78.2 MHz with a 6 mm chemagnetics double resonance solid-state probe. The main experimental parameters included a pulse width of 0.3 μs , recycle delay of 1 s, line broadening of 60 Hz, and spinning speed of 7 kHz. The reference chemical shift (0 ppm) was adjusted with 1 mol/L AlCl_3 solution [17].

3. Results and discussion

3.1. Hydrolysis of $\text{Al}_2(\text{SO}_4)_3$ and AlCl_3 in urea solution

Urea is highly soluble in water and its controlled hydrolysis in aqueous solutions can be summarized as follows:

Fig. 1. The pH changes of urea and the Al-urea solutions with time at 90 °C.

The rate of urea hydrolysis is dependent upon temperature and duration of heating. At room temperature the hydrolysis is extremely slow, but at 70–100 °C, it is rapid enough to yield a practicable reaction rate [9]. The solution pH increase during hydrolysis of 0.3 mol/L urea at 90 °C is shown in Fig. 1. The basic properties of urea itself are negligible, but a hot urea solution undergoes hydrolysis to form hydroxide ions. It can be seen that the pH value of the hot urea solution increases quickly from 6.65 to 8.01 in the initial stage of urea hydrolysis, followed by a gradual increase to a constant value at 9.03. The maximum pH depends on the concentration of ammonium in solution, and there exists equilibrium between the ammonia formed by hydrolysis and that lost by volatilization [18]. In the absence of ammonium, the maximum pH value of the urea solution is about 9.03. The pH changes of the 0.4 mol/L urea solutions containing 0.1 mol/L AlCl₃ and 0.05 mol/L Al₂(SO₄)₃ with time at 90 °C are also presented in Fig. 1. It is clear that the pH curves of the solutions with Al³⁺ significantly differ from the curve observed with the solution containing only urea. The complexation reaction of various Al species with hydroxide ions liberated from urea hydrolysis contributed to the difference. Furthermore, the increase of the ionic strength in solutions with aluminum salts also decreased the hydrolysis rate of urea. An immediate pH increase can also be observed on each curve in the first 2 h, which suggests that the OH[−] ions released during the hydrolysis of urea in the initial stage were neutralized by the free H⁺ present in solution. However, no significant increase of pH value can be observed in the subsequent period of time. The reason is that the released OH[−] ions were consumed by the hydrolysis and polymerization of aluminum. When a second steep rise of pH happened, most Al species existed in solution began to transform into colloidal or precipitated Al.

The urea solutions containing AlCl₃ (simplified as AC-urea solution) or Al₂(SO₄)₃ (simplified as AS-urea solution) are transparent before reaching certain pH values. For the AC-urea solution, colloidal suspension occurred at pH of about 5.16, while for AS-urea solution, the corresponding pH is about 3.72. This pH difference were found to be associated with the type

Fig. 2. Distributions of total Al concentration in Al₂(SO₄)₃-urea solution and AlCl₃-urea solution during the hydrolysis process of urea and Al at 90 °C.

of counter anions and not influenced by the concentration of other constituents [12]. In the case of AlCl₃-urea reaction, due to the poor coordinating ability of chloride with Al, the reaction of hydroxide ions with aluminum to form larger, charged polymeric species via hydroxyl- or oxy-bonds was not significantly interfered. While for the Al₂(SO₄)₃-urea reaction, due to the higher coordinating ability of sulphate with Al, the formation of large soluble polymeric Al species was strongly inhibited and precipitate was observed within 10 h of hydrolysis reaction. In fact, the precipitation occurred from the beginning of the Al₂(SO₄)₃-urea reaction. This can be testified by the measurement of total dissolved Al concentration during the hydrolysis reaction (Fig. 2).

Clearly, the total dissolved Al concentration in AS-urea solution decreased continuously during the whole reaction time, which indicates that some Al species had transformed into colloidal or precipitated Al from the beginning of the Al hydrolysis. However, no significant change of the total dissolved Al concentration in AC-urea solution was detected during the former stage of the reaction. Only after a long period of time (ca. 17 h), with the increase of pH and the size of polymeric Al species, the precipitation of Al species was initiated and the total dissolved Al concentration decreased rapidly.

3.2. Speciation of hydrolysis products of aluminum

3.2.1. Mononuclear aluminum species

At room temperature, with the addition of urea into Al solution, one or two water ligands in [Al(H₂O)₆]³⁺ will be quickly replaced by urea molecules, and such products can be identified on the ²⁷Al NMR spectra of AC-urea (Fig. 3a) and AS-urea (Fig. 3b) solutions. According to previous studies, the resonance at about 0 ppm is attributed to [Al(H₂O)₆]³⁺, and those at about −2.95 and −5.86 ppm are attributed to [Al(H₂O)₅(urea)]³⁺ and [Al(H₂O)₄(urea)₂]³⁺, respectively [19]. Both Al-urea complexes were detected in the AS-urea solution, but only the former was observed in the AC-urea solution. For the spectrum of AS-urea solution (Fig. 3b), the existence of sulphate also con-

Fig. 3. Solution-state ^{27}Al NMR spectra of AlCl_3 -urea solution (a) and $\text{Al}_2(\text{SO}_4)_3$ -urea solution (b) before the hydrolysis of urea and Al. The figures in circles have been enlarged 10 times.

tributes to another resonance peak at about -3.61 ppm. With the hydrolysis of aluminum going on, the contents of the two complexes became less but remained detectable in solutions for a long period of time (data not shown). Because the contents of the two complexes were relatively low, the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ complex is the dominant constituent of mononuclear Al species (Al_m) in the samples.

Once the temperature was increased to 90°C , the significant hydrolysis of urea resulted in different Al hydrolysis products. Fig. 4 shows the solution-state ^{27}Al NMR spectra of the hydroly-

ysis products of AC-urea and AS-urea solutions at different reaction times. Each peak on the spectroscopy corresponds to a specific species. Since the beginning of Al hydrolysis, a new resonance appeared at about 3.5 ppm in the NMR spectra of the two sets of samples. Based on the analytical results of ^1H and ^{27}Al NMR spectroscopy, Akitt et al. assigned the major species at this chemical shift as trimer ($[\text{Al}_3\text{O}_2(\text{OH})_4(\text{H}_2\text{O})]^{8+}$) [20]. As for the spectra of AC-urea solutions, another new resonance which represents the Al_{13} polycation also appeared at 62.5 ppm and the intensity increased significantly with time (Fig. 4a). The integrated area of each peak on the spectra is related to the relative abundance of that species, so it can be seen from Fig. 4 that the Al_m content in each set of samples decreased significantly with time. For the AC-urea solution, the rapid increase in Al_{13} concentration consumed a great deal of Al_m and resulted in the obvious decrease of Al_m . However, for the AS-urea solution, no Al_{13} polycation was detected (Fig. 4b). The existence of sulphate inhibited the further polymerization of aluminum monomers or oligomers to form Al_{13} polycations. The highest polymerization degree of Al species, which could be detected with NMR spectroscopy, was trimeric Al (Al_3), but its content was relatively low in most samples. Most of the decreased Al_m in AS-urea solution was transformed into the undetectable species (Al_{un}).

3.2.2. Reactive polymeric aluminum

Besides ^{27}Al NMR spectroscopy, Ferron assay is also considered as the most popular method to study hydroxyl-Al polymers in solution. This method can differentiate all the Al species into three categories (i.e., Al_a , Al_b and Al_c), but the Al speciation results are highly dependent on the interpretation of Al-Ferron reaction kinetics. As for the ^{27}Al NMR spectroscopy, it has been widely recognized as the sole instrumental method to identify Al species directly. However, only several Al species (e.g., Al_m , Al_3 and Al_{13}) in solution can be detected to date. Therefore, neither of the two methods is adequate to characterize Al speciation. Nevertheless, the two methods can be supplementary to each other and the combination of the two methods should be a better approach to study the polymeric Al species in solution. The speciation results of the Al hydrolysis products in AC-urea solution with the above two methods are compared in Fig. 5.

Fig. 4. Solution-state ^{27}Al NMR spectra of the AlCl_3 -urea solution (a) at various Al hydrolysis times (2 h, 8 h, 14 h, 17 h, 19 h, 23 h) and $\text{Al}_2(\text{SO}_4)_3$ -urea solution (b) with various Al hydrolysis times (2 h, 8 h, 15 h, 18 h).

Fig. 5. Speciation of the Al hydrolysis products in AlCl_3 -urea solution at various reaction times with Ferron assay and solution-state ^{27}Al NMR spectroscopy.

It can be seen from Fig. 5b that, there existed a consistency in the change of the speciation result of Ferron assay with that of NMR spectroscopy. From the beginning, the contents of the reactive polymers (Al_b) and Al_{13} increased gradually with reaction time, and then decreased rapidly. Their maximum values occurred at the time just before large amount of colloidal suspension appeared. The changes in Al_{13} content can be seen more clearly from the relative intensity distribution of peaks at 62.5 ppm in Fig. 4a. However, it is shown in Fig. 5b that the fractions of the reactive hydroxyl-Al polymers (Al_b) determined by Ferron assay in most samples are higher than those of Al_{13} determined with NMR spectroscopy. Only in certain samples with maximum contents of Al_b and Al_{13} , the two species can be considered equivalent. Therefore, besides Al_{13} polymers, some other Al species also existed as reactive hydroxyl-Al polymers (Al_b). Though these species cannot be detected by NMR spectroscopy, they can react with Ferron. These Al species might be composed of some polymers with lower polymerization degree than Al_{13} in the former stage of Al hydrolysis. However, in the latter stage, these species should have higher polymerization degree than Al_{13} [6]. Although these Al species are undetectable by ^{27}Al NMR spectroscopy, with the analysis technique of small angle X-ray scattering (SAXS), Singhal and Keefer assigned the undetected Al fraction (Al_{un}) to six-member ring Al_6 species. Al_6 ($\text{Al}_6(\text{OH})_{12}^{6+}$), in which six octahedrally coordinated Al atoms are bridged by dual OH groups, has been believed to play a crucial role in the hydrolyzation of Al and the formation of colloidal or precipitated Al for a long period of time [21]. It is usually observed that the contents of mononuclear Al species (Al_a) determined by using Ferron assay are larger than those (i.e., Al_m) determined by NMR spectroscopy (Fig. 5a). A possible explanation is that some low polymeric Al species which may react with Ferron instantly are also included in the mononu-

Fig. 6. Speciation of the hydrolysis products in $\text{Al}_2(\text{SO}_4)_3$ -urea solution at various reaction times with Ferron assay and solution-state ^{27}Al NMR spectroscopy.

clear Al fraction determined with Ferron assay, while these low polymeric species could contain some Al_6 species [14].

Thus, it can be concluded that besides mononuclear Al species and Al_{13} , some other Al_6 species also existed in the hydrolysis products of AC-urea solution, and their existence mainly accounted for the difference between the undetectable Al species (Al_{un}) in NMR spectroscopy with the Al_c fraction determined by Ferron assay in most samples (Fig. 5c).

The existence of Al_6 species can also be inferred from the speciation results of the AS-urea solution obtained with the above two methods (Fig. 6). Unlike the speciation results of AC-urea solution, no Al_{13} polycation was detected in the AS-urea solution. However, the reactive polymeric Al species (Al_b) were still detected with Ferron assay (Fig. 6). The content of this Al fraction gradually decreased with time and became undetectable at the time when all the Al species in solution aggregated into precipitated Al. Additionally, the large difference between the contents of Al_a and those of Al_m , which accounted for the main part of the difference between Al_{un} and Al_c , also existed in all samples and the difference was relatively larger before the obvious colloidal and precipitated Al appeared in solution.

3.2.3. Colloidal or precipitated Al

Colloidal or precipitated Al species (Al_c) had no detectable reaction with Ferron during the observed time. In the former stage of urea and Al hydrolysis, most Al_m aggregate into reactive polymeric Al species (Al_b) and the Al_c content were relatively small. For the AC-urea solution, no obvious colloidal suspension or precipitates were observed in this stage. The total dissolved Al (Al_t) content had no significant decrease (as shown in Fig. 2). However, the Al_c species were still detectable with Ferron assay and their contents increased gradually with time (Fig. 5c). Thus, the Al_c fractions in this stage are composed of soluble high polymeric Al species, although these species could not react with Ferron in the observed time.

With the hydrolysis of urea, the concentration of hydroxyl ions increased, and consequently more colloidal or precipi-

Fig. 7. Solid-state ^{27}Al NMR spectra of the freeze-dried Al_c fractions taken from AlCl_3 -urea solution (a) and $\text{Al}_2(\text{SO}_4)_3$ -urea solution (b).

tated Al (Al_c) was formed. When the mononuclear Al and Al_{13} were almost completely consumed, the insoluble Al fraction in AC-urea solution was collected through filtration and freeze-dried for solid-state NMR analysis (Fig. 7a). Two resonance peaks were observed in the spectrum. There is a much stronger peak at about 0 ppm, which corresponds to the octahedrally coordinated Al [22]. Another peak appears at 64.5 ppm, which is attributed to Al_{p1} polycation, a defected Al_{13} structure in which one octahedron is lost [17]. Using X-ray powder diffraction (XRD) method, Vogels et al. had ever found that the dried solid of Al precipitate exhibited bayerite [$\alpha\text{-Al}(\text{OH})_3$] structure. Similar findings were also reported in other studies [23]. Therefore, it can be inferred that all the initial soluble Al species could be transformed into two kinds of insoluble Al structures (i.e., Al_{p1} and $\alpha\text{-Al}(\text{OH})_3$) with reaction time in the AC-urea hydrolysis system. Numerous studies have found that all the Al species in solution will finally transform into crystalline Al hydroxides (i.e., gibbsite, bayerite or nondstrandite) upon aging [14]. Thus the Al_{p1} could be considered as the intermediate species in the transformation of Al_{13} to the crystalline Al hydroxides.

As far as the AS-urea system is concerned, colloidal or precipitated Al occurred from the beginning of the Al hydrolysis because of the existence of sulphate ions in solution. The composition of the initial precipitated Al was identified to be $\text{Al}_4(\text{OH})_{10}\text{SO}_4$. Since this species is neutral, it could form

compact primary particles, which subsequently aggregate into granular precipitate upon reaction with hydroxyl ions. Higher solution pH favors nucleation of gibbsite, while lower pH favors bohemite [11]. Thus, the insoluble Al species formed in AS-urea system could have two kinds of structures, but both of them produced resonance at 0 ppm (Fig. 7b). Although no Al_{13} polycation was detected in AS-solution, a weak resonance peak at ca. 62 ppm, the characteristic resonance of tetrahedral $\text{Al}(\text{O})_4$, was observed in the solid-state NMR spectroscopy of precipitated Al (Fig. 7b). It indicates that a little amount of Al_{13} or its aggregation was formed during hydrolysis, but they could be precipitated quickly with sulphate ions in solution [19,24].

3.3. Al species transformation model

With the hydroxyl ions released from urea hydrolysis in hot solution, mononuclear Al species can quickly hydrolyze into low polymeric species (e.g., Al_3) and then evolve into higher polymers. Among these intermediate Al species, Al_{13} has always been the focus of many studies not only because of its special structure and relative high stability but also of its wide application in many fields [14]. $\text{Al}(\text{OH})_4^-$ is believed to be the required precursor of Al_{13} by many researchers, and $\text{Al}(\text{OH})_4^-$ is formed at the point of base addition due to local concentration effect [13]. Although $\text{Al}(\text{OH})_4^-$ is stable only under alkaline condition, the interaction between $\text{Al}(\text{OH})_4^-$ and octahedrally coordinated Al can be rapid enough to form Al_{13} before $\text{Al}(\text{OH})_4^-$ disappears in acidic solution.

Hydroxide ions liberated from urea hydrolysis are homogeneously distributed in the aluminum and urea mixture. Upon stirring, the *in situ* evolution of carbon dioxide and ammonia throughout the solution results in negligible fluctuation in the system homogeneity [12]. Thus, no localized high alkalinity could be formed in the reaction solution. Therefore, the traditional theory might not be appropriate to explain the formation mechanism of Al_{13} polycation in this study.

As for the hot urea solution, urea could hydrolyze at a much high rate because of its high initial concentration and the high solution temperature. The existence of excess hydroxyl ions in solution unavoidably resulted in the formation of non-reactive polymeric or colloidal Al hydroxides [10]. This can be inferred from the Al_c distributions in Figs. 5c and 6. The concentrations of the Al_c fraction in the two Al-urea solutions were relative high since the beginning of Al hydrolysis and increased quickly with time until all of the soluble Al species aggregated into precipitate. With the urea hydrolysis going on, excessive hydroxide ions could react with colloidal or precipitated Al and result in the formation of $\text{Al}(\text{OH})_4^-$, which could react with Al oligomers (e.g., Al_3) to form Al_{13} [13,25]. The formation of the oligomers (e.g., Al_3) in solution was mainly ascribed to the chemical thermodynamic reaction of Al in solution. Since the urea concentration adopted in this study was relatively high, large amount of hydroxyl ions would be released with time, and consequently higher content of Al_{13} and other polymers (i.e., Al_{p1}) were able to be formed until they were degraded or finally transformed into colloidal or precipitated Al (i.e., gibbsite, bayerite or nondstrandite). Excessive $\text{Al}(\text{OH})_4^-$, which was

Fig. 8. Schematic diagram on the transformation model of Keggin- Al_{13} in urea solution.

not consumed by formation of Al_{13} favored the precipitation of Al hydroxide. A schematic description of the Al transformation process is given in Fig. 8.

Most of the Al species in Fig. 8 are detectable with ^{27}Al NMR spectroscopy. However, some other low and high reactive polymeric species, which cannot be detected with NMR spectroscopy (i.e., Al_{un}) were able to be confirmed by the combination of Ferron assay and NMR spectroscopy. For the speciation results of AS-urea solution, no Al_{13} polycation has been detected with NMR spectroscopy, but the Al_6 fraction was still observed with Ferron assay, and these species also finally transformed into precipitated Al. Thus another Al species transformation model should exist:

As mentioned above, the reactive polymers in the equation was supposed to be Al_6 species, and the basic unit of these species is $\text{Al}_6(\text{OH})_{12}(\text{H}_2\text{O})_{12}^{6+}[\text{Al}_6]$ or $\text{Al}_{10}(\text{OH})_{22}(\text{H}_2\text{O})_{16}^{8+}$ (double hexameric rings). Moreover, the precipitated Al was also reported to be composed of Al_6 species in many previous works [26]. Thus, the structure of the reactive hydroxyl-Al polymers resembled that of precipitated Al. This model, referred as the “core-link” or “hexameric ring” model in literatures can better explain the continuous transformation of Al species from mononuclear Al to the precipitated Al (i.e., $\text{Al}(\text{OH})_3$) [27]. However, this model cannot explain the formation process and the structure of Al_{13} ($\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$). Therefore, neither of these two models is adequate to describe the entire transformation process of Al species, but their combination could be able to better reflect the actual Al hydrolysis mechanisms.

As shown in Fig. 5b, Keggin- Al_{13} polycation was detected as the dominant reactive species in AC-urea mixture within a long duration. It implies that with the release of hydroxide ions, most monomers were more inclined to transform into Keggin- Al_{13} . The Keggin- Al_{13} model can be denominated as forced hydrolysis model (Fig. 8). It has been pointed out that some other reactive species with six-member ring structure were also formed by the polymerization of monomers in solution. However, the contents of these species were relatively low and most hydroxide ions released by urea hydrolysis took part in the formation of Keggin- Al_{13} . It is known that the addition of strong base is not the necessary condition for the development of these species in hexameric ring model. Thus the hexameric ring model can also be denominated as spontaneous hydrolysis model. Although the

above two hydrolysis models coexist in the hydrolysis process, the Keggin- Al_{13} model should be the main transformation pattern of Al species when relatively high OH^- concentration exists in solution.

4. Conclusions

Keggin- Al_{13} could be formed in hot Al-urea solution with homogeneous distribution of hydroxide ions. Besides the Al_{13} polymers, some other reactive polymers with six-member ring structure were also detected in the mixture. The Keggin- Al_{13} model and the hexameric ring model could coexist in the Al hydrolysis process. The existence of sulphate ions had great influence on the hydrolysis process of aluminum in urea solution.

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