

Chemical species distribution and transformation in polyaluminum chemical solutions

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Abstract—The hydrolysis polymerization precipitation process of Al(III) was studied with pH titration method, and the prepared polyaluminum solutions were characterized by various experimental methods: acid depolymerization, timed complex-colorimetric procedure, ultrafiltration, X-ray diffraction and infrared absorption spectrum. The results showed that the chemical species transformation and distribution of Al(III) in the hydrolysis-polymerization process depended on $B=(OH/Al)$ ratio, pH and other factors. By their structures, the chemical species can be divided into three categories of monomeric (Al_a), polymeric (Al_b), sol or gel precipitates (Al_c) and the polymeric species may be further divided into three groups such as linear low polymer (Al_{b1}), linear high polymer (Al_{b2}) and high polymer with cyclic structure (Al_{b3}). The nominal molecular weight of polymeric species obtained by ultrafiltration was about 1000-50000 and most of them fell into a range around 10000. A scheme for the chemical speciation model of Al(III) solution was suggested.

Keywords: polymeric aluminum; hydrolysis-polymerization; polymeric species.

INTRODUCTION

In recent years, polyaluminum chloride (PAC) as a type of inorganic polymeric flocculants has been developed increasingly in China and abroad (Tang, 1977). Polyaluminum in fact is the intermediate products in hydrolysis-precipitation process of aluminum (III) salts, and it consists of a mixture of compounds whose chemical species varies very much with the mode of preparations. The general chemical formula of PAC may be written as $[Al_2(OH)_n Cl_{6-n}]$ or $[Al_m(OH)_n Cl_{3m-n}]$, whose chemical species should belong to polynuclear hydroxyl complexes from the viewpoint of coordinate chemistry and can be named as water soluble inorganic polymers, viewed with high molecular chemistry. In water and waste water treatment, it has been demonstrated that the active species responsible for coagulation and flocculation are the highly charged polymeric hydroxyl species (Hahn, 1968; Stumm, 1968).

Possessing the merits of high efficiency and extensive uses, the application of PAC flocculence is daily increasing in water and waste water treatment technology. However, early researches in China and abroad laid particular stress on the application in practice, not much

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basic research had been carried out (Tang, 1977). It will be limited in further development of PAC products because the fundamental aspects, such as the chemical species distribution and the exact nature of the active coagulation species in PAC solutions as well as its coagulation mechanisms are not very clear so far.

The aqueous chemistry of aluminum (III) and its species distribution are very complicated and diverse because of the numerous hydrolytic intermediates form prior to precipitation of aluminum hydroxide, $\text{Al}(\text{OH})_3$ (Luan, 1987). Thus in the preparation of PAC, it would be a key problem to study and control the chemical species transformation and distribution in the hydrolysis-polymerization process of $\text{Al}(\text{III})$, or to select and identify the optimal conditions for polymeric species formation with more efficiency as coagulant.

In this article, the authors will present the results of experimental studies on the chemical species distribution of $\text{Al}(\text{III})$ in polyaluminum solutions and the structure characters of polymeric species obtained by using various analytical methods, and discuss the chemical species transformation in the hydrolysis-polymerization of $\text{Al}(\text{III})$. A scheme for chemical species transformation model of $\text{Al}(\text{III})$ solution is suggested.

EXPERIMENTS AND RESULTS

1. Preparation and parameters of polyaluminum solutions

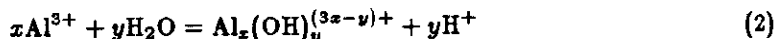
All reagents used in this research were analytical grade and dissolved in double distilled water. The stock solution of AlCl_3 was prepared as 0.5–3.0 mol/L, and the prepared solutions usually $1\text{--}5 \times 10^{-4}$ mol/L, were diluted from the stock solutions. Polyaluminum solutions were prepared by slow titration of NaOH solution to obtain the desired OH/Al ratio. The preparation process was operated in a bottle of 200 ml with a magnetic stirrer and a DZ-2 model automatic potentiometer was used to record the change of pH during the titration. The stirring intensity in titrating process was high enough to ensure the titrated base dispersed rapidly without forming of local precipitation. The final concentrations of aluminum in the prepared polyaluminum solutions were 1 mol/L and $5 \times 10^{-1}\text{--}10^{-4}$ mol/L, and the resulting solutions were transformed into polyethylene bottles and stored at 4°C after aging. The aging time was 2, 24 and 240 hours respectively.

The character of each polyaluminum solution prepared above may be described by three parameters B , M and T , where B is basicity, i.e. the OH/Al ratio of the solution, M is the molar concentration of total aluminum and T is the aging time in hour. The most important parameter of them is the basicity B because it can be directly used to express the extent of the polymerization as well as the quantity of the bound hydroxyl species in structure units of polyaluminum. According to solution chemical equilibrium concepts, a new parameter B^* is suggested to express the basicity ratio in polyiron studies recently (Tang, 1987):

$$B^* = B_0 + B - A \quad (1)$$

where B_0 is the original bound base ratio in solution before base adding, or $B_0 = 10^{-\text{pH}}/[\text{Al}]_T$; B is the concentration ratio of aluminum to base added, $B = [\text{OH}^-]_a/[\text{Al}]_T$; A is the acid added ratio, or $A = [\text{H}^+]_a/[\text{Al}]_T$; $[\text{Al}]_T$ is the total concentration of Al (III) in solution.

The parameter of the basicity B^* may be explained by following hydrolytic reactions of Al. The hydrolytic reaction results in reduction of pH in Al(III) solution and can be generalized as:



the hydrolytic reaction in Al(III) salt solution in fact has happened before the base adding, thus the concentration of bound $[\text{OH}^-]$ would be equal to the concentration of $[\text{H}^+]$ released by the hydrolytic reaction of Al(III) and given by following:

$$[\text{OH}^-] = \sum y[\text{Al}_x(\text{OH})_y^{(3x-y)+}] = [\text{H}^+] - [\text{OH}^-] = [\text{OH}^-]_o \quad (3)$$

where free $[\text{OH}^-]_o$ in concentrated Al(III) solution is negligible. When the base or acid is added, a change will occur in original bound OH^- and release free H^+ in solution, according to the charge or proton balance in solution:

$$\sum y[\text{Al}_x(\text{OH})_y^{(3x-y)+}] = [\text{H}^+] - [\text{OH}^-] + [\text{OH}^-]_a - [\text{H}^+]_a \quad (4)$$

$$[\text{OH}^-]_b = [\text{OH}^-]_o + [\text{OH}^-]_a - [\text{H}^+]_a \quad (5)$$

if all the terms in Equation (5) are divided by $[\text{Al}]_T$, B^* as defined in equation (1) is obtained:

$$B^* = [\text{OH}^-]_b/[\text{Al}]_T = B_0 + B - A \quad (6)$$

The parameter B^* may be used along with B . It is useful for characterization of the pH evolution. In accordance with its definition, any Al(III) solution without base or acid added can be characterized by B^* to express its hydrolytic extent and B^* varies with the concentrations of Al(III).

2. The character of hydrolysis-polymerization and precipitation for Al(III)

(1) pH evolution of Al(III) solutions during the hydrolysis-polymerization

When base was added slowly to the Al(III) salt solution, at first the pH increased rapidly, and slowly then. The typical curves for temporal pH change with increasing B^* value are given in Fig. 1. It may be seen that each curve has one plateau separated by two inflection points accordingly. The first inflection point approximately occurs in $B^* = 0.5$, and the second inflection point occurs with relation to the titrated concentration of Al(III) solutions and in range of $B^* = 2.5-2.6$ for solution with $C \geq 5 \times 10^{-2}$ mol/L, and $B^* = 2.7-2.8$ for the solution with $C \leq 5 \times 10^{-3}$ mol/L. Before the second inflection point, the pH value changes smoothly only and slightly with the increase of B^* value.

The results in Fig. 1 show that the titrated OH^- is bound strongly with aluminum ions to form various hydroxyl complex ions and held in the hydrolyzed products. The gentle

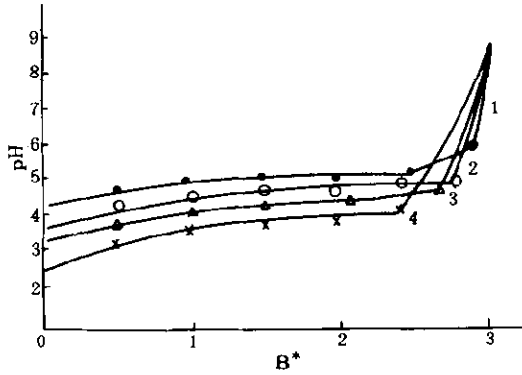


Fig. 1 Titration curves of Al(III) solutions with base addition

variation of pH curves represents the different chemical transformation processes of Al(III) during hydrolysis-polymerization (Brosset, 1968) and may be divided kinetically into three phases by the inflection points at $B^* = 0.5$ and $B^* = 2.5-2.6$: (a) Initial stage of hydrolysis is at $B^* < 0.5$. In this stage, polymerization may not begin, and the hydrolytic reaction is seen to start with the formation of monomeric and dimeric species, such as $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$ as well as $\text{Al}_2(\text{OH})_2^{4+}$. (b) Polymerization stage is in the range of $0.5 < B^* < 2.5$ for the solution with $C \geq 5 \times 10^{-2}$ mol/L. In this stage, the composition of the solutions can no longer be explained only in terms of monomeric and dimeric species. The hydrolysis-polymerization proceeds rapidly between monomers as well as dimers, and almost all of the OH^- titrated are bound in the formation of polymers and polymerization degree increases gradually with increasing B^* value. The strong binding of hydroxyl ions in the polymerization stage may be evidenced by the gentle reacting curves of pH between the first and second inflections points. (c) The formation stage of sol or gel precipitates is in $B^* > 2.5$ for solution with $C > 5 \times 10^{-2}$ mol/L. In this stage, polymers on the uptake of OH^- tend to saturate gradually, the pH of the solution starts to rise quickly and local visible precipitates can be formed when base titration is made continuously. The amount of the forming precipitates increase with the B^* value. When $B^* = 3.0$, all of the polymers would be transformed into precipitable $\text{Al}(\text{OH})_3$ (am) and the pH of the solutions would rise rapidly above 8.5.

The pH and B^* value for the local precipitates formation and the yield of polymers are found to be dependent on the concentrations of Al(III) and base titrated and the titration rate of base. The pH and B^* for the local precipitation would be advanced when the concentrations of Al(III) and base are increased or the titration rate of base is too fast. For example, when $C = 1.0$ mol/L, the local visible precipitates formation starts at $B^* > 2.0$.

Fig.2 is the pH change of the polyaluminum solution with $C = 5 \times 10^{-2}$ mol/L after aging

24 hours. The pH of the polyaluminum solution decreases about 0.1–0.4 units after aging 24 hours as shown in Fig.2. The phenomenon shows that at a given B^* value, the hydrolysis-polymerization does not really reach an equilibrium state during the slow titration of base and would proceed continuously with the aging time to reach the equilibrium state. The polyaluminum solution at $B^* < 2.5$ can be in a quasi-equilibrium state after aging 24 hours.

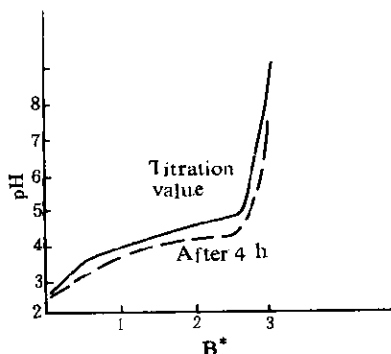


Fig. 2 pH change of polyaluminum solution after aging 24 hours

(2) The depolymerization of acidified polyaluminum solutions

To understand the reactivity of freshly prepared polyaluminum solutions, a procedure of adding acid was used to observe the acidified depolymerization. 10ml of polyaluminum solutions was drawn in a 50 ml bottle and equivalent acid (equal with the molar concentration of the titrated OH^-) was added with magnetic stirring. The pH change during the acidified depolymerization was recorded as a function of time, given in Fig. 3. It is seen that the pH of all the polyaluminum solutions decrease immediately to about 1.7–1.8 when acid is added, and then start to rise slowly. The time required for depolymerization in acid increased with increasing B^* value. Only at $B^* \leq 0.5$ the reaction with acid can be finished immediately.

In the region of $1.0 < B^* < 2.5$, the reaction with acid proceeds very slowly and the acid resisting of the polyaluminum solution enhances with increasing B^* value. In the region of $B^* > 2.7$, it is difficult to reset the pH to its original value.

The kinetic analysis on acid depolymerization shows that the breakdown of polymers is a slow process. At a given B^* value, the rate of reaction with acid in the range of $0.5 < B^* < 2.5$ will be in a first order (Hem, 1967):

$$\frac{-d(\text{OH}_b)_t}{dt} = K(\text{OH}_b)_t \quad (7)$$

where K is the first order reacting rate constant, which integrates to give:

$$\lg(\text{OH}_b)_t = \lg(\text{OH}_b)_0 - \frac{Kt}{2.303} \quad (8)$$

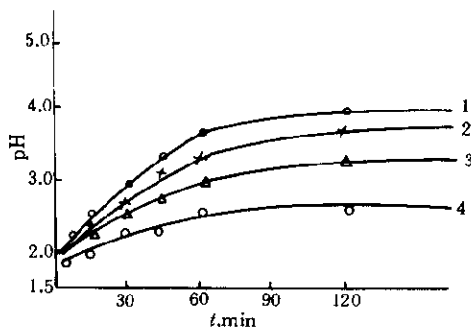


Fig. 3 pH Change of polymeric aluminum solution during acid depolymerization

where $(\text{OH}_b)_t$ and $(\text{OH}_b)_o$ are the concentration of bound $(\text{OH}_b)_t$ at t reacting time and the initial concentration of bound $(\text{OH}_b)_o$ at zero reaction time respectively. A linear relation between $(\text{OH}_b)_t$ and time t may be set by making a plot of the logarithm of hydroxyl concentration not yet depolymerized against the reaction time. The result is graphically represented in Fig.4. The intercept of the straight line would be equal to the logarithm of the concentration of (OH) at initial present.

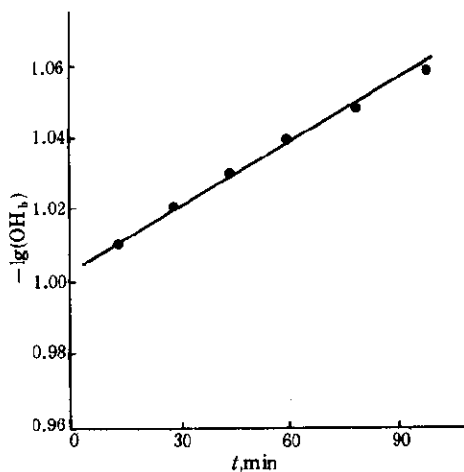


Fig. 4 The curves for the rate of reaction with acid

The studies on the kinetics of the reaction between protons and monomeric Al species show that the reaction of protons with $\text{Al}(\text{OH})^{2+}$ would be essentially controlled by diffusion and hence will proceed fast under suitable hydrodynamic conditions (Holmes, 1968). Thus it may infer that the reaction with acid would relate to the location of the OH groups in polymers.

At $B^* < 0.5$, the rapid reaction with acid should be the singly bound OH ions (not bridged) in monomeric species, because the formation of monomeric species, no bridged hydroxyl, are mainly present in this range. But the slow acidified kinetics process at $B^* > 1.0$ could be interpreted as a slow attack of bridged hydroxyl ($\text{Al} \langle \text{OH} \rangle \text{Al}$) in the polymers by H^+ protons in acid. If the OH does not exist as a bridge, it will immediately be neutralized. The results show that the OH bridge bound is very stable and not easily be broken down (Stol, 1976).

3. The distribution of species and nominal molecular weight (NMW)

(1) Determination of species distribution by a timed colorimetric method

A timed complex-colorimetric analysis procedure with ferron-phenanthroline reagents is used to analyze the species distribution of polyaluminum solutions (Bersillon, 1978). Al(III) reacts with ferron to form Al-ferron complex at pH 5, the characteristic absorption wavelength for the Al-ferron complex is at 370 nm. The timed colorimetric procedure is based on the observation that different types of hydrolyzed hydroxyl aluminum complex ions react with the colorimetric reagent with different rates. Different dissociation rates may arise from differences in the strength of the bonds between aluminum atom and hydroxyl groups or from differences in the size and structure of the species. Therefore, it will be possible to differentiate the chemical species distribution of Al(III) for the polyaluminum solutions according to the rate of the dissociation-complex reaction.

Absorbances of different species of Al(III) for the polyaluminum solutions are directly determined by a 721 model spectrophotometer. The concentration distribution of the various species in the polyaluminum solutions are estimated from the absorbance as a function of time, and the result is given in Fig. 5.

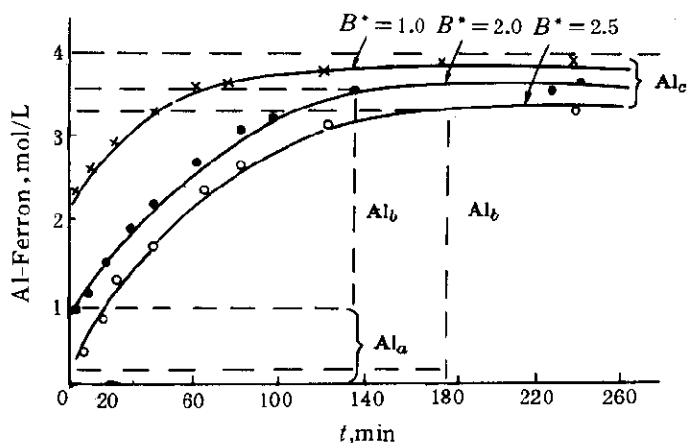


Fig. 5 Curves for reaction of polyaluminum with ferron

The dissociation-complex reaction of polyaluminum species with ferron, as shown in Fig.5, will be a slow reaction process. The rate of reaction decreases gradually with increasing B^* value until the reaction reaches an equilibrium state. The reaction of polyaluminum with ferron may be regarded as a competition for aluminum ions by hydroxyl groups in polyaluminum and the active functional groups in ferron. Thus the progress of reaction can reflect the species distribution and structural transformation in the polyaluminum solutions. With the increase of B^* value, the structural units and size of polymers grow continuously, and the dissociation-complex of ferron on aluminum ions in the polymers will become much more difficult to proceed.

According to the rate of the reaction, we may divide the reaction process into four stages related with four groups of species (Luan, 1988): monomeric species (Al_a) is represented by the concentration of instantaneous reaction with ferron at zero time; low polymers (Al_{b1}) is represented by the concentration of faster reaction with ferron at 60 minutes; high polymers (Al_{b2} and Al_{b3}) is represented by the concentration of slow reaction with ferron at 60–180 minutes and $Al_b = Al_{b1} + Al_{b2} + Al_{b3}$, species of sol or gel (Al_c) are represented by the concentration of all unreacted with ferron after 180 minutes.

The change of concentration for three groups of species in the polyaluminum solution with $C = 5 \times 10^{-2}$ mol/L as a function of B^* value and aging time are calculated and shown graphically in Fig. 6.

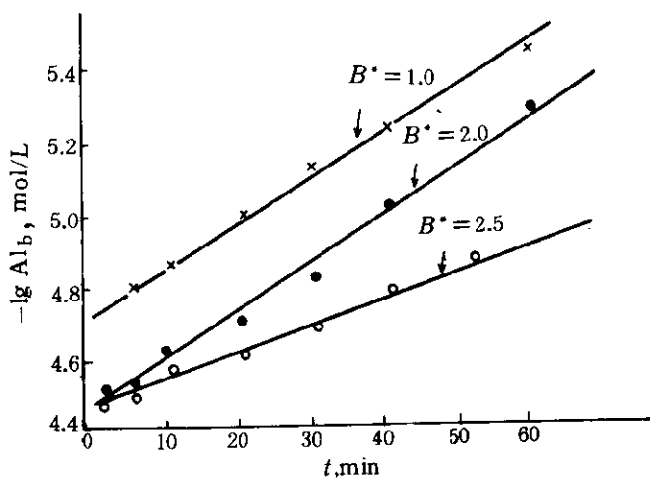


Fig. 6 Transformation and distribution of three groups of Al(III) species in polyaluminum solution as a function of B^* and aging time

It is seen in Fig. 6 that in addition to Al species, instantaneous reacting monomeric (Al_a) and inert reacting species (Al_c) are always present in the solution. Their respective proportions vary with the preparation conditions of the solution. Under a given condition, Al_a species at

$B^* < 1$ occupies about 50–70% in predominance. In the region $1 < B^* < 2.5$, Al_b species is about 50–85% predominant and the percentage increases with the B^* value. When $B^* > 2.5$, Al_c species increases rapidly with the B^* value (to 35%). The concentration of polyaluminum solutions will also affect the species distribution. For example, when $C > 10^{-1}$ mol/L and $B^* > 2.2$ – 2.3 , the content of Al_b may reach 70–85%. At lower B^* , as shown in Fig.6, the content of Al_a decreases but Al_b increases with the aging time, and at higher B^* , the content of Al_a remains constant but Al_b decreases slowly and Al_c increases with the aging time. The results have shown that the three groups of species in the polyaluminum solutions transform each other and tend slowly to the high polymers.

The content of Al_b not yet dissociated-complexed can be obtained by subtracting the contents of complexed $Al_a + Al_b$ and Al_c from total concentration $Al(III)$ at a given time. By plotting the logarithm of not yet dissociated-complexed Al_b versus the reaction time, a straight line is obtained. Its intercept on ordinate is equal to $-\log(Al_b)_0$ at zero reaction time, and is graphically represented in Fig. 7. The result shows that the reaction of the dissociation-complex also follows the first order law:

$$\lg(Al_b)_t = \lg(Al_b)_0 - \frac{kt}{2.303} \quad (9)$$

where $(Al_b)_0$ is the content of the initial Al_b in the solution. The rate constant k of Al-feron complex obtained from Fig.7 was found to be $1.2 \pm 0.5 \times 10^{-2}$ /min when $B^* < 2.0$, and 7.2×10^{-3} /min when $B^* = 2.5$. This is in agreement with those demonstrated in literatures (Parthasarathy, 1985; Smith, 1971).

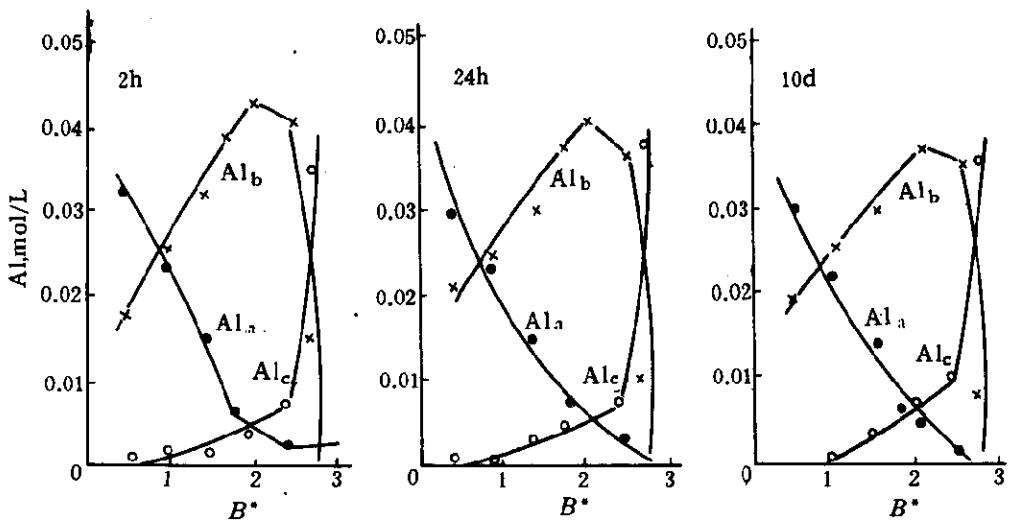


Fig. 7 Concentrations of Al species as functions of B^* at 24 hours and 10 days

(2) The nominal molecular weight (NMW) measured by ultrafiltration

In order to identify the state of molecular weight distribution in the polyaluminum solutions, various types of filter and ultrafilter membrane are used to separate polyaluminum solutions into fractions. The total aluminum species in each fraction is determined by the timed complex colourimetric method. The results are summarized in Table 1 and 2, respectively.

Table 1 Results of the ultrafiltration of polyaluminum solutions

$[Al]_T$ (mol/L)	B^*	The fractions separated by membranes $[Al]_f/[Al]_T$, (%) [*]							
		0.45 μ	0.2 μ	XM100 (100000)	XM50 (50000)	PM10 (10000)	YM5 (5000)	UM2 (1000)	UM05 (500)
0.005	1.0	98	100	92	82	80	65	51	9
	2.0	97	98	78	70	68	21	8.2	3
0.05	0.5	100	100	98	96	94	88	72	20
	1.0	100	97	94	84	82	76	55	12
	1.5	98	96	94	80	85	65	42	14
	2.0	96	92	87	77	80	39	22	4
	2.5	95	96	76	66	68	20	8.4	<1
	2.7	9.4							
0.33	2.0	98	97	78	80	73	61	5.4	2.5
1.00	2.0	97	98	82	61	68	54	10.5	5

* $[Al]_f$ and $[Al]_T$ are the concentrations of Al in polyaluminum solutions unfiltered and total, respectively. Number in brackets represents the nominal molecular weights determined by ultrafilter membranes.

Table 2 The distribution and NMW of species in the polyaluminum solutions

$[Al]_T$, mol/L	B^*	Al_a	Al_b	Al_c	Distribution ranges of NMW of Al_b
0.05	0.5	72	28	0	<1000
	1.0	55	45	0	1000-5000
	1.5	42	54	4	1000-5000
	2.0	22	73	6	5000-10000
	2.5	4.6	82	13.4	10000-50000

It is noted that the percentage of filterable aluminum species in each fraction is related to the total concentration of the polyaluminum solutions, B^* value, rate of base added and aging time. It generally decreases with the increase of B^* . The analytical results of ultrafiltration fractions and the timed colorimetric method show that the concentration of ultrafilterable aluminum in the fraction with NMW below 1000 is equal to the content of Al_a measured by the timed complex colorimetric method. The intercepted part by XM 100 ultrafilter membrane, whose NMW are above 100000, is equal to the content of Al_c , thus the distribution range

of NMW for Al_b is estimated roughly between 1000–50000, and the fractions below 10000 are predominant. In the polyaluminum solution of 5×10^{-2} mol/L, as shown in Table 2, the monomers and the low polymers with the NMW about 1000 are predominant when $B^* < 1.0$. In the range of $B^* = 1.0$ –2.0, the NMW obviously increases and its range is about 1000–10000. In the range of $B^* = 2.0$ –2.5, the distribution range of NMW is in 10000–50000. In addition, it is found that the polyaluminum solution of the fraction below 50000 is comparatively stable and can not form visible precipitates after longterm aging. However, the fraction of Al_c intercepted by XM100 seems to have different quality with visible precipitates formed for $B^* > 2.7$. It may be a colloidal sol with higher polymerization degree. The polymeric sol will transform into a gel precipitates after long aging time.

(9) The identification of species structure

The polyaluminum solutions with various B^* value were dried in a water bath at 80–90°C and under infrared lamplight below 60°C. Then the solid samples were examined by using a Y-2 model X-ray diffraction spectrometer and a FTS-20 model Fourier infrared absorption spectrometer, respectively. The results were given in Fig. 8 and Fig. 9, respectively.

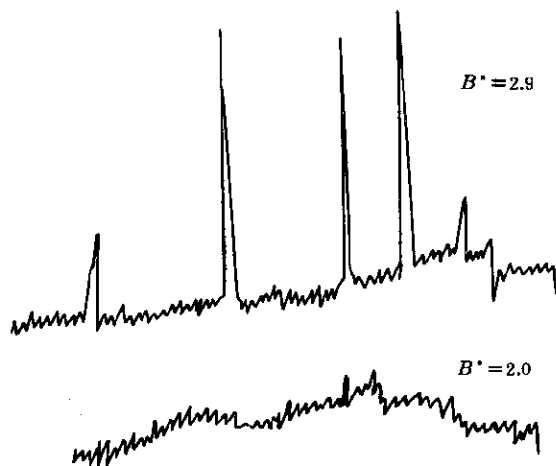


Fig. 8 X-ray diffraction patterns of solidified polyaluminum samples

In Fig. 8, the X-ray diffraction spectrum with sharp peaks upper represents the hotted solidification sample with $B^* = 2.9$ and that with relative level peaks lower represents the dried sample at low temperature and $B^* = 2.0$. The pattern shows that two samples of polyaluminum have different species structures, the sample hotted solidification appeared with obvious diffraction peak will possess the gibbsite crystalline structure and is insoluble in water, but the sample dried under infrared lamplight does not appear a characteristic diffraction peak, possess amorphous structure to X-ray diffraction, and is soluble in water (Hso, 1964).

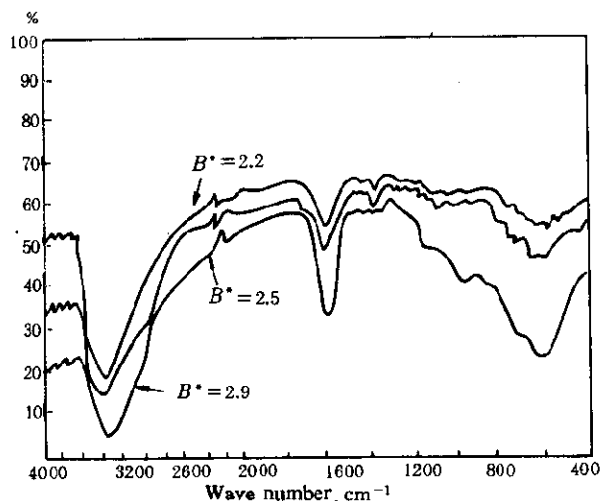


Fig. 9 Infrared spectra of solid polyaluminum samples

Fig.9 are the infrared spectra for three solid samples of polyaluminum with $B^* = 2.2$, $B^* = 2.5$ and $B^* = 2.9$, respectively. It is seen from the spectra that main absorption bands are the high-frequency band at $3420\text{--}3540\text{cm}^{-1}$, the medium-frequency band at $2480\text{--}2560\text{cm}^{-1}$ and the low-frequency band at $580\text{--}1250\text{cm}^{-1}$. For the hydroxyl absorption band, the infrared spectra of polyaluminum is very similar as compared with that of solid gibbsite, particularly in the absorption band at $3420\text{--}3540\text{cm}^{-1}$. In addition to expanding and contracting vibration of the hydroxyl between $3000\text{--}3700\text{cm}^{-1}$, there is parallel moving vibration of the edd bound hydroxyl between $400\text{--}1200\text{cm}^{-1}$ (Farmer, 1982). Therefore, at least three different kinds of OH stretching vibration can be used to characterize such a structure in Fig. 9. The high frequency band observed at $3420\text{--}3540\text{cm}^{-1}$ may be the OH directly bound to the Al ions since the complex OH stretching band of the solid gibbsite appears at $3,540\text{cm}^{-1}$. The intensity of this band reinforces increases with the increase of B^* value. The medium-frequency band observed at 1640 and $2480\text{--}2500\text{cm}^{-1}$ may attribute to the hydrogen bound of water molecular strongly to form hydronium (Peng, 1982). The low-frequency band observed at $580\text{--}1250\text{cm}^{-1}$ may be the hydroxyl located on the edges of polymers. The result shows that the polymerization degree of polyaluminum will increase continually with the increase of B^* value and tends eventually to form a crystal structure of gibbsite.

4. Characteristics of species transformation and distribution

According to our experimental results and previous researches (Luan, 1988), a scheme for the chemical species transformation and distribution of Al (III) in the hydrolysis-polymerization and precipitation processes is suggested in Fig. 10.

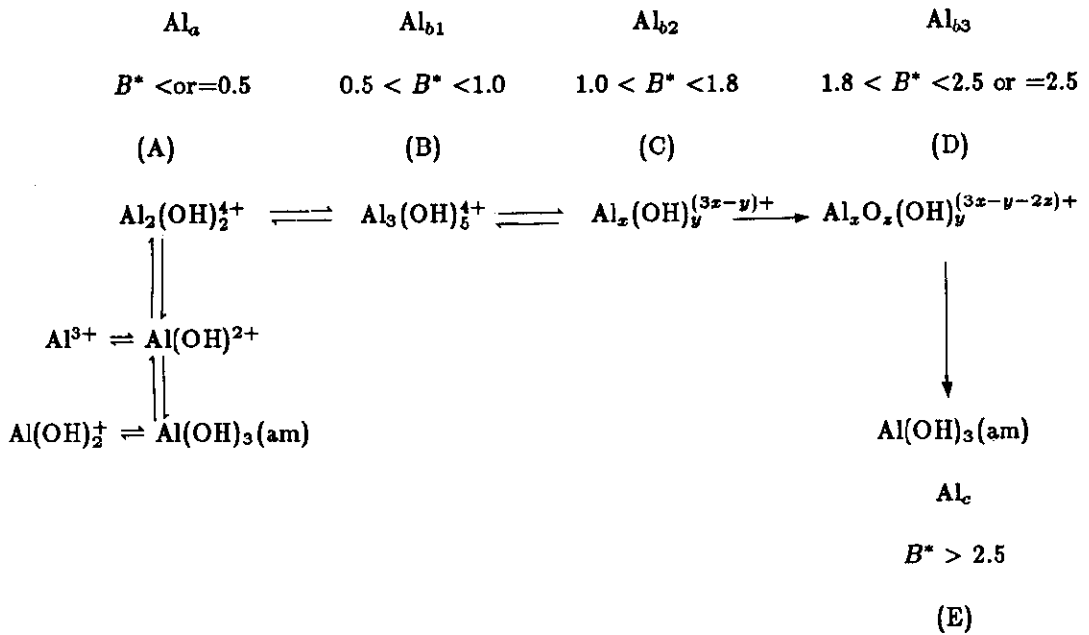


Fig. 10 A scheme for chemical speciation model of Al (III) in hydrolysis-polymerization and precipitation processes

The aluminum species are classified as the following types corresponding to the groups described previously. Type (A) is in the range of $B^* < 0.5$, corresponding to the Al_a group. In this type, the formation of species in the hydrolysis would mainly be monomeric hydroxyl complex ions, such as Al^{3+} ; $Al(OH)^{2+}$; $Al(OH)_2^+$. In addition, the formation of some dimeric hydroxyl complex ions, $Al_2(OH)_2^{4+}$, can also present as the beginning of the hydrolysis-polymerization. In the operation, it is also possible to form directly local precipitates, $Al(OH)_3$ when the concentration or rate of base added is too high or fast. However, the $Al(OH)_3$ is less likely to be stable at $B^* < 2.5$. It can be gradually dissolved again in following process of heating and stirring.

Type (B) is in the range of $B^* = 0.5-1.0$, corresponding to Al_{b1} group. In this range, the monomers and dimers start to form polynuclear species, mainly some linear-structural low polymers, for example $Al_3(OH)_5^{4+}$ and $Al_4(OH)_6^{6+}$, and their characters are possession of low polymerization degree but high charge.

Type (C) is in the range of $B^* = 1.0-1.8$, corresponding to Al_{b2} group. In this range, the formation of species will mainly be some linear-structural high polymers, for example $Al_6(OH)_{10}^{8+}$ and $Al_8(OH)_{16}^{8+}$, whose character is possession of middlesized polymerization degree and higher charge. The polymers may be represented by $Al_x(OH)_y^{(3x-y)+}$. The followed polymerization

after continuous titration of base would result in a successive increasing of both polymerization degree and charge. At the same time, the electrostatic repulsion between polymers which will affect the progress of further polymerization and will also be strengthened gradually. However, the formed polymers will still carry out hydrolysis reaction and result in the hydroxyl increase but the charge decrease. Thus the alternative development between polymerization and hydrolysis will finally result in forming of higher size polymers with low charge.

Type (D) is in the range of $1.8 < B^* < 2.5$, corresponding to Al_b group. In this range, the polymerization degree of polymers will rapidly increase and the net positive charge per aluminum in the polymers will decrease gradually with the increase of B^* value, but all the hydroxyl polymers will remain to possess the positive charge. At the meantime, the structure of polymers starts to transform from the linear units into cyclic units and part of the oxygen bridges between Al atoms transform into oxolation bridges. The polymeric species can be written as $Al_xO_y(OH)_z^{(3x-y-2z)+}$, for instance, $Al_{13}O_4(OH)_{24}^{7+}$ or $Al_{13}O_4(OH)_{26}^{5+}$, which have been demonstrated by many researchers (Akitt, 1972; Bottero, 1982). This type of polymers is characterized by possessing high polymerization degree and medium charge.

Type (E) is in the range of $B^* > 2.5$, corresponding to Al_c group. In this range, most of the polymeric hydroxyl complex ions are bound into the formation of cyclic structures. The structures of cyclic units will further grow and the net charge per aluminum in the polymers will further decrease with the increase of B^* value. A new process which results in the polymers aggregation each other to form solid precipitate will start to occur when the charge is sufficiently reduced. Thus the colloidal gel with three dimensional space structure which can further transform into an amorphous solid precipitate, $Al(OH)_3(am)$, will be obtained by mutually sticking of the high polymers with cyclic sheet units of two dimensional space structure.

The model and the classification suggested by our experimental results, as described above, will only represent the general regularity for the hydrolysis-polymerization and precipitation processes of Al(III). The representative species of polyaluminum in each group will only be the predominant species in the co-existence of various species at a given range of B^* . To identify more accurately the species distribution and transformation in polyaluminum solution, particularly in the concentrated solutions, need to proceed the research still further and more thoroughly.

CONCLUSION

The species transformation and distribution in polyaluminum solutions, as shown by the experimental results above, will depend on B^* value, the concentrations of Al (III) and the rate of base added as well as aging temperature and time. The titration curves with base may be divided kinetically into three phases by the inflection points at $B^* < 0.5$ and $B^* < 2.5$. At $B^* < 0.5$ formation of species in polyaluminum solutions is mainly the monomeric species (Al_a), whose nominal molecular weight are below 500. At $1 < B^* < 2.5$, the formation of species is

mainly the polymeric species (Al_b), whose nominal molecular weight are about in the range of 1000-50000 and most of them are below 10000. At $2.5 < B^* < 3.0$, the formation of species are the polymeric sol or gel precipitates (Al_v) whose nominal molecular weight are above 50000-100000. The Al_b of polymeric species may be further divided into three groups, such as linear low polymers (Al_{b1}), linear high polymers (Al_{b2}) and high polymers with cyclic structures (Al_{b3}) according to the results of the rate of acidified depolymerization and dissociation-complex of ferron on the polyaluminum solutions.

The hydrolysis and polymerization in the preparation of polyaluminum solutions will proceed simultaneously and alternately, and tend to form the polymers with low charge and high polymerization degree. The species structure of polymers change with the increase of B^* value and transform from the linear to the cyclic until forming the solid $Al(OH)_3$. The reaction process and the species transformation is represented by a schedule for chemical speciation model given in Fig. 10.

Although the experimental results and the model may not reflect thoroughly and accurately the chemical species transformation and distribution in the hydrolysis-polymerization process of $Al(III)$, it may be of practical use to study on the mechanisms of coagulation for polyaluminum and provide some useful information for further development of polyaluminum products.

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