

## Influence of thermal history on conversion of aluminate species in sodium aluminate solution



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**Abstract:** It is necessary to clarify the influence of thermal history on the conversion of aluminate species in sodium aluminate solution in order to optimize Bayer alumina production. The interconversion of various solution species in the systems was investigated by measuring the infrared spectra of sodium aluminate solution with different compositions after separate heat treatment, dilution and concentration. The results show that increasing temperature or prolonging holding time favors the transformation of  $\text{Al}_2\text{O}(\text{OH})_6^{2-}$  to Al—OH vibration (condensed  $\text{AlO}_4$  tetrahedral aluminate ion) at about  $880\text{ cm}^{-1}$  and  $\text{Al}(\text{OH})_4^-$ .  $\text{Al}_2\text{O}(\text{OH})_6^{2-}$  and Al—OH tetrahedral dimer ions convert rapidly to  $\text{Al}(\text{OH})_4^-$  during the dilution process; however, the back transformation of  $\text{Al}(\text{OH})_4^-$  to the Al—OH tetrahedral dimer ions can occur in diluted sodium aluminate solution. As for the concentration process, the transformation of  $\text{Al}(\text{OH})_4^-$  to  $\text{Al}_2\text{O}(\text{OH})_6^{2-}$  and Al—OH tetrahedral dimer ions can take place, while it is relatively difficult to transform to  $\text{Al}_2\text{O}(\text{OH})_6^{2-}$ .

**Key words:** aluminate ions; structural changes; infrared spectrum; thermal history

### 1 Introduction

Sodium aluminate solution is an important carrier of alumina in alumina production process. The Bayer process mainly consists of bauxite digestion, dilution and sedimentation of digested slurry, gibbsite precipitation from purified sodium aluminate solution, concentration of the spent liquor by evaporation. The thermal history of sodium aluminate solution is quite different due to the sodium aluminate solutions with different compositions undergoing different temperatures and residence time. Generally, thermal history has an important effect on the nucleation and metastable zone width of solutions which mainly depend on the ion structure and physical purity [1]. The research shows that the ion structure of sodium aluminate solution affects its physicochemical properties and thus influences the related processes of alumina production [2]. Therefore, it is of great importance to study the influence of thermal history on the conversion of aluminate species in sodium aluminate solutions.

Up to now, many researches on the influence of solution compositions on the ion structure of sodium aluminate solution have been published. The existence of

dominant monomeric tetrahydroxy aluminate ions ( $\text{Al}(\text{OH})_4^-$ ) and Al(III)-containing dimers (e.g.  $\text{Al}_2\text{O}(\text{OH})_6^{2-}$  and  $\text{Al}_2(\text{OH})_8^{2-}$ ) as minor species in synthetic Bayer liquors has been well established [3–7]. Furthermore, the distribution of aluminate species is affected by solution compositions. Aluminate ions in sodium aluminate solution with low concentration and caustic ratio (molar ratio of  $\text{Na}_2\text{O}$  to  $\text{Al}_2\text{O}_3$ , expressed as  $\alpha_k$ ) are dominantly in the form of monomers ( $\text{Al}(\text{OH})_4^-$ ), and the amount of  $\text{Al}(\text{OH})_4^-$  reduces while the amount of  $\text{Al}_2\text{O}(\text{OH})_6^{2-}$  increases correspondingly with increasing solution concentration and caustic molar ratio. A small quantity of  $\text{Al}(\text{OH})_6^{3-}$  appears only in the solution with high concentration and caustic ratio [8]. The influence of impurities on the ion structure was also reported in Ref. [9]. Although the influence of solution compositions on the ion structure has been well understood, the effects of thermal history on the ion structure remain ambiguous with no definite description. ZHANG et al [10] measured the ion structure of sodium aluminate solution obtained by bauxite digestion at 255 and 130 °C, respectively, and the results showed that the dominant aluminate anion is  $\text{Al}(\text{OH})_4^-$  for the digestion temperature of 255 °C while polymerized aluminate ions and  $\text{Al}(\text{OH})_4^-$  coexist for

the digestion temperature of 130 °C. CHEN et al [11] examined the change of aluminate species of the sodium aluminate solution prepared by dissolving aluminum in sodium hydroxide aqueous solution and then placing at room temperature for various time. The aluminate ion structure change of the sodium aluminate solution treated by magnetic field and then placed for different time was also observed in Ref. [12]. The facts mentioned on indicate that the ion structures of aluminate solutions are affected by the thermal history of solutions. Unfortunately, to our best knowledge, no systematic and deep investigations about the variation of various Al(III)-containing species during the thermal treatment process were not yet fully understood till now. Under this consideration, a detailed study was done on aluminate species conversion behavior of aluminate solutions with different compositions treated at different temperatures for various time, with the attempt to clarify the influence of thermal history on aluminate species transformation and ultimately to provide theoretical guidance for Bayer alumina production.

## 2 Experimental

### 2.1 Preparation of sodium aluminate solution

According to the preset composition of the solution, the pre-weighed aluminum hydroxide and sodium hydroxide (analytical reagents, Kermel Chemical Reagent Corporation of Tianjin, China) were added into deionized water, stirred and boiled for certain time till the aluminum hydroxide was dissolved completely. The as-prepared aluminate solution was then filtered to remove the fine solids and the filtrate was kept in a sealed polyethylene bottle for the experimental use.

### 2.2 Spectroscopy analyses of sodium aluminate solutions

The IR spectra of thin films of aluminate solutions between KBr plates were collected on a FT-IR 6700 spectrometer with 4  $\text{cm}^{-1}$  resolution (manufactured by Nicolet Co., USA). The reliability and the repeatability of the potassium bromide (KBr) pellet technique for measuring the aluminate solution were established [2].

Infrared measurements at different temperature were performed using an attachment (HC-32 Heated/Cooled Transmission Cell) when solution temperature was below 100 °C. When solution temperature was in the range of 100–140 °C and 160–260 °C, the solutions were respectively kept in self-made DY-8 low-pressure group autoclave (with the maximum temperature less than 140 °C and the temperature accuracy of  $\pm 1$  °C) and XYF-d44 $\times$ 6 self-made high-pressure group autoclave (with the maximum temperature of 350 °C and the

temperature accuracy of  $\pm 1$  °C) at preset temperatures for a certain time, and then their infrared spectra were collected immediately by the coating method after the solution being cooled abruptly. The infrared spectrum of the solution after keeping at a constant temperature of 90 °C in low-pressure group autoclave by the coating method is almost the same with that obtained by the online heated/cooled transmission cell at the same temperature, indicating that the infrared spectra of sodium aluminate solutions obtained by the above method are credible.

## 3 Results and discussion

### 3.1 Influence of temperature on conversion of aluminate species in sodium aluminate solution

In alumina production process, different unit operations correspond to different temperatures which fluctuate greatly. Thus it is necessary to study the influence of temperature on the conversion of aluminate species in sodium aluminate solution. In view of this, sodium aluminate solutions with different concentrations and caustic ratio were held at different temperatures for 24 h, then the IR spectra were measured.

The infrared spectra of the sodium aluminate solutions with low caustic molar ratio and medium concentrations after being kept at different temperatures are shown in Fig. 1. As shown in Fig. 1, there are characteristic absorption peaks at 550, 635, 720 and 880  $\text{cm}^{-1}$  in the IR spectra of sodium aluminate solutions when the solutions are held at 25–250 °C with low caustic ratio and caustic soda concentration (as  $\rho(\text{Na}_2\text{O})$ ) less than 170 g/L. It is generally known that 550  $\text{cm}^{-1}$  corresponds to the Al—O—Al vibration bands ( $\text{Al}_2\text{O}(\text{OH})_6^{2-}$ ), 635  $\text{cm}^{-1}$  and 720  $\text{cm}^{-1}$  correspond to Al—OH symmetry and anti-symmetry stretching bands, respectively (both corresponding to  $\text{Al}(\text{OH})_4^-$ ). However, it is still uncertain about the vibration mode of the 880  $\text{cm}^{-1}$  band. At present, the dominant view about this is that 880  $\text{cm}^{-1}$  corresponds to the Al—OH vibration (condensed  $\text{AlO}_4$  tetrahedral aluminate ion). As shown previously [2,3,13–17], 635, 720 and 880  $\text{cm}^{-1}$  bands are all assigned to Al—OH tetrahedral structure.

Moreover, the absorption peak intensity at 720  $\text{cm}^{-1}$  is much greater than that at other bands, suggesting that  $\text{Al}(\text{OH})_4^-$  is the main aluminate ion in the sodium aluminate solution. Additionally, a broad weak absorption peak is observed at 550  $\text{cm}^{-1}$  corresponding to Al—O—Al vibration bands of  $\text{Al}_2\text{O}(\text{OH})_6^{2-}$  [3,8], indicating that there is a small quantity of  $\text{Al}_2\text{O}(\text{OH})_6^{2-}$  in the solution. By comparing each curve in Fig. 1, it can also show that the conversion of aluminate species in sodium aluminate solution is little affected by the

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