



# Homogeneous nucleation of $\text{Al}(\text{OH})_3$ crystals from supersaturated sodium aluminate solution investigated by in situ conductivity



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## ABSTRACT

The homogeneous nucleation process of  $\text{Al}(\text{OH})_3$  crystals from supersaturated sodium aluminate solution was investigated by a homemade online conductance testing system. Combined with the turbidity and equivalent circuit of conductometry, the conductance curve was divided into five regions, where the charge and discharge region, adsorption region and ionic polymerization region were identified as induction period in the decomposition process of sodium aluminate solution. According to the homogenous nucleation theory, the nucleation kinetics during the decomposition process was studied with the intermediate concentration solution at 333 K. The results showed that the solid–liquid interfacial energy was  $26.1 \text{ mJ} \cdot \text{m}^{-2}$ , critical nucleation radius was 2.6–3.8 nm and the apparent reaction order was 2.9. Meanwhile, UV–vis spectra of sodium aluminate solution in homogeneous process were investigated with decomposition time, where three peaks were observed at 220, 260, and 370 nm, respectively. Combined with the conductance curve, the ionic structure change and nucleation mechanism have been discussed.

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## 1. Introduction

The Bayer process for the production of alumina ( $\text{Al}_2\text{O}_3$ ) from bauxite involves a low decomposition ratio and slow crystal growth from supersaturated sodium aluminate solution. For now, the decomposition mechanism and structure of sodium aluminate solution are still not completely understood, which makes it difficult to find effective way to improve the quality of product and decomposition efficiency.

The precipitation of  $\text{Al}(\text{OH})_3$  from sodium aluminate solution inevitably undergoes a transformation from tetrahedron ( $\text{Al}(\text{OH})_4$ ) to octahedral ( $\text{Al}(\text{OH})_6$ ), related to the crystallization with chemical reaction, which is different from general crystallization process. With the development of testing methods, the investigation on the decomposition mechanism of sodium aluminate solution is going deep into micro-level. Gerson and Loh considered that aluminium hydroxide seeds dissolved partially during the decomposition of sodium aluminate solution to generate certain effective composition for nucleation, and the nucleation of  $\text{Al}(\text{OH})_3$  crystals occurred in the bulk phase of solution instead of the seed surface (Gerson et al., 1996; Loh et al., 2000). Addai-Mensah presented that the crystal growth of gibbsite evolved from bayerite to gibbsite during the precipitation of  $\text{Al}(\text{OH})_3$ , where the cations of  $\text{Na}^+$  and  $\text{K}^+$  were participated in the crystallization, forming  $(\text{K}^+)\text{Na}^+\text{Al}(\text{OH})_4^-$  ion pairs (<1 nm) first, then relax polymer net

(<10 nm). The network polymers were densified to form high-density polymer (10–50 nm) to produce crystal nucleus of aluminium hydroxide (Addai-Mensah et al., 1998; Addai-Mensah and Ralston, 1999; Counter et al., 1999). The cations that participated in the crystallization were verified by the different morphologies of  $\text{Al}(\text{OH})_3$  crystals, which precipitated from sodium aluminate and potassium aluminate solutions (Prestidge and Ametov, 2000; Sweegers et al., 2001), respectively. Soar believed that the precipitation of  $\text{Al}(\text{OH})_3$  might go through competing growth pathways: growth by addition of small species in high supersaturated sodium aluminate solution and growth by agglomeration in the low supersaturated sodium aluminate solution (Soar et al., 2000). Li H found that particle enlargement to an average diameter less than 300 nm was mainly via a nuclei/single particle growth mechanism in intermediate concentration solution. At larger sizes, particle aggregation was the predominant mechanism. Bayerite crystallization predominated from dilute sodium aluminate solutions. Solutions with an intermediate NaOH concentration gave rise to a dimorphic phase mixture. For the concentrated solutions, particle size enlargement occurred substantially through aggregation even at particle sizes <300 nm. Gibbsite was the major component crystallized from concentrated solutions (Li et al., 2005).

With the further investigation on the decomposition mechanism of sodium aluminate solution, the coincident viewpoint is that, the structure of sodium aluminate solution is transformed at the initial stage during the precipitation of  $\text{Al}(\text{OH})_3$ ; there are two kinds of crystals, bayerite and gibbsite, crystallized from sodium aluminate solutions,

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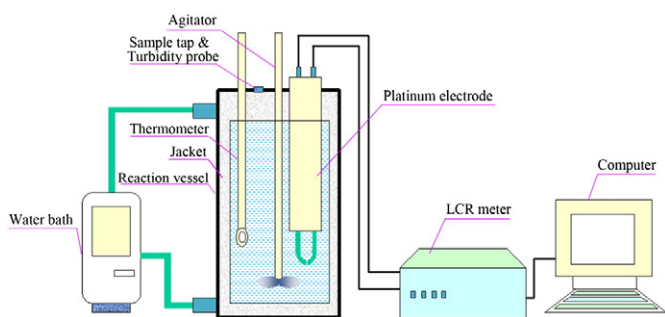


Fig. 1. Homemade online conductance testing system for sodium aluminate solution.

and the two crystals can convert mutually; the cations participate in the crystallization; and the structures of crystals are dependent on the temperature, concentration and solution preparation.

According to the homogeneous nucleation theory of supersaturated solution, induction period appears before the appearance of crystals, where the structure of sodium aluminate solution changes (Komarov et al., 1976; Mullin, 2001; Rossiter et al., 1998; Söhnel and Mullin, 1978; Söhnel and Mullin, 1988). The induction period varies from the measurements, resulting in different conclusions of homogeneous nucleation from sodium aluminate solution. Among them, a highly sensitive technique named multi-angle laser light scattering (MALLS) was used to investigate the nucleation process of  $\text{Al}(\text{OH})_3$ , where persuasive kinetic parameters were obtained (Rossiter et al., 1998). Conductivity is an important parameter of the solution, relating to the temperature, concentration of solution, and the components, structure and charges of ions. Thus the change of ions can be reflected by the conductivity. The decomposition nature of sodium aluminate solution can be described as



where the conductivity of  $\text{OH}^-$  is better than that of  $\text{Al}(\text{OH})_4^-$ . Therefore, the conductance will increase with the decomposition of sodium aluminate solution. Researchers achieved rapid analysis of solution composition by establishing the correspondence of conductance with concentration, molecular ratio and temperature of sodium aluminate solution (Li et al., 2010; Shang and Meng, 2001; Wang and Yang, 1996). The relation of structure with conductance of sodium aluminate solution was illustrated by combining the theoretical calculation with IR spectra (Li et al., 2010). However, there are few researches on the kinetic parameters of homogenous nucleation process by conductometry. In this work, a simple homemade online testing system was assembled to measure the conductance of sodium aluminate solution during the

decomposition process. Then the induction period and homogeneous nucleation kinetics can be investigated to explore the transformation of aluminate ions.

## 2. Material and methods

### 2.1. Materials

All the chemicals with analytic grade such as aluminium hydroxide and sodium hydroxide were supplied by Kermel Chemreagent Co. Limited, China. Sodium aluminate solutions were prepared by boiling and diluting the stock solutions of high concentration ( $C_{\text{Na}_2\text{O}} = 220 \text{ g}\cdot\text{L}^{-1}$ ). The stock solution was prepared with certain molecular ratio  $\alpha_k$ . Then the mass of aluminium hydroxide and sodium hydroxide can be calculated with molecular ratio  $\alpha_k$ , concentration of  $\text{Na}_2\text{O}$  and solution volume. The molecular ratio  $\alpha_k$  is expressed in Eq. (1).

$$\alpha_k = \frac{n_{\text{Na}_2\text{O}}}{n_{\text{Al}_2\text{O}_3}} = 1.645 \times \frac{C_{\text{Na}_2\text{O}}}{C_{\text{Al}_2\text{O}_3}} \quad (1)$$

where  $n_{\text{Na}_2\text{O}}$  and  $n_{\text{Al}_2\text{O}_3}$  are the moles of  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$ , respectively; and  $C_{\text{Na}_2\text{O}}$  and  $C_{\text{Al}_2\text{O}_3}$  are the concentrations of  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  in supersaturated sodium aluminate solutions, respectively, which were determined by chemical titration method.

### 2.2. Experimental procedure

Platinum electrode was made of platinum wire ( $\phi = 0.3 \text{ mm}$ ), copper wire ( $\phi = 1 \text{ mm}$ ), alkali-resisting encapsulated glass tube and jacket. In the platinum electrode, platinum wire was sealed in the glass tube, and bended to form counter electrode at the bottom. Copper wire was welded with platinum wire and connected to the external measurement circuit. Thus only platinum wire was designed to contact the solution. The online testing system of solution conductivity was assembled by water bath (Jintan Tian Jing instrument, China, HH-601), stainless steel vessel with PTFE lining, platinum electrode, LCR meter (Helpass, China, HPS2810BLCR) and computer. The configurations are shown in Fig. 1. The conductivity cell constant was calibrated by the reference solution of  $1 \text{ mol}\cdot\text{L}^{-1}$  KCl at 298 K. Then the validity of the homemade testing system was verified by the conductivities of  $1 \text{ mol}\cdot\text{L}^{-1}$  and  $0.1 \text{ mol}\cdot\text{L}^{-1}$  KCl at 308 K. The decomposition experiments of sodium aluminate solutions were carried out at constant stirrer rate, and the temperature fluctuated by 0.1 K. At 5 second intervals, resistance of sodium aluminate solution was recorded by LCR meter with a frequency of 1 kHz at 0.3 V. Each conductance curve was measured 5 times to ensure its reproducibility.

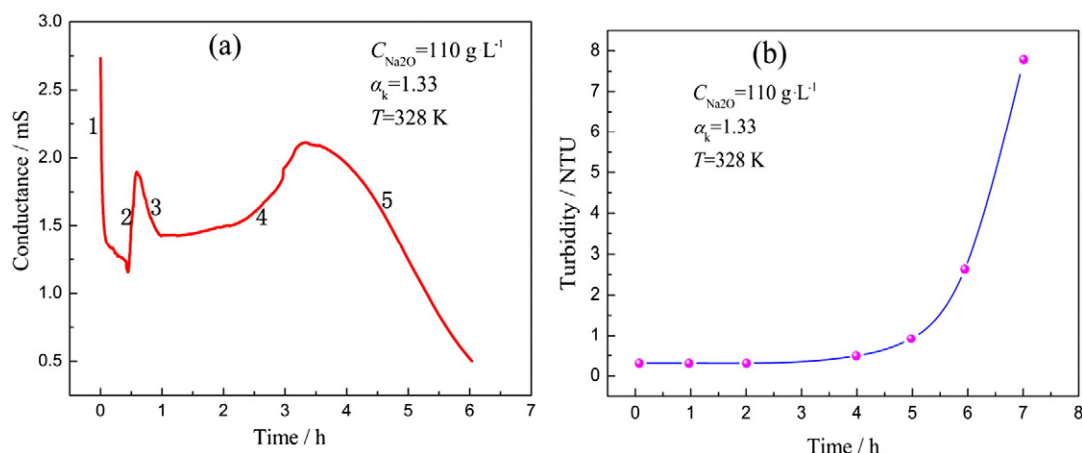


Fig. 2. Conductance (a) and turbidity (b) of supersaturated sodium aluminate solution during homogeneous nucleation process.

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