

KINETICS OF BOEHMITE PRECIPITATION FROM SUPERSATURATED SODIUM ALUMINATE SOLUTIONS WITH ETHANOL-WATER SOLVENT

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Abstract

Boehmite was prepared from supersaturated sodium aluminates solutions with ethanol-water solvent. The results of thermo-gravimetric analyzer and XRD showed that the product was mixture of boehmite and gibbsite, and the mass ratio of gibbsite and boehmite varied greatly with different process conditions. This work presents the effects of mass ratio of ethanol and temperature on the precipitation rate and phase compositions of alumina hydrate. The ratio of AlOOH in the product increased significantly with the increase of mass ratio of ethanol because the precipitation of gibbsite was restrained. When the solvent was pure ethanol, the ratio of AlOOH in the product reaches the peak of 90%. Ethanol reduces the free caustic concentration and increases initial supersaturation coefficient significantly. The boehmite activation energy of precipitation in ethanol solvent was 13.7 kJ/mol, indicated that ethanol reduces effectively energy barrier of boehmite from sodium aluminate solutions and it was controlled by diffusion process.

Introduction

In the industrial of aluminum, gibbsite is precipitated from sodium aluminate solution, and then get alumina by calcination. Therefore energy consumption is a main problem of production cost. However, thermodynamically if precipitation products are boehmite, energy consumption in the calcination process is decreased by 60%. Joanne Loh et al. suggested that calcination of boehmite substituting for gibbsite could save 12 % energy consuming of the process in alumina production [1]. Therefore, precipitation boehmite substituting for gibbsite from sodium aluminate solution is a reliable energy saving measure for alumina technology.

Both boehmite and gibbsite can be precipitated from sodium aluminate solution [2], and it is a co-precipitation process. The type of products can be transformed or regulated by the control reaction conditions in solution. Misra et al. [3] and Filippou et al. [4] prepared boehmite from sodium aluminate solution at 115~145 °C by adding boehmite seed. Li [5] prepared boehmite seed by hydrothermal method and obtained mixture of boehmite and gibbsite from sodium aluminate solution with concentration of 110 g/L (expressed as Al₂O₃) at 95 °C for 40 h, and the precipitation ratio was about 40% and 70% of product was boehmite. However, there are some disadvantages, such as low precipitation ratio, high precipitation temperature and high seed ratio (SR). Therefore, a bottleneck to increase the precipitation ratio of boehmite from sodium aluminate solution for improving Bayer process by transforming the type of product comes into being. Pnias et al. [6] studied solubility of boehmite and interfacial action between seed and solution, and the results indicated that free alkali in the solution played a key role in inhibition of precipitation boehmite. Organic additive can promote

crystal growth, prolong agglomeration time and increase the size of products[7]; meanwhile, it can affect the growth rate of some specific crystal faces, and thus change the size and structure properties of crystal [8, 9]. Wang et al. [10] intensified the preparation of gibbsite from sodium aluminate solution by adding methanol. The precipitation ratio was more than 80% for 4 h, indicating that methanol as medium can decrease concentration of free alkali and increase supersaturation. As a result, the precipitation ratio was accelerated. But due to harmful to the health, methanol was restricted in operation process. In addition, once methanol and sodium aluminate solution were mixed, gibbsite generated quickly, which was detrimental to the formation of boehmite. Ethanol and some organic solvent can form compound with gibbsite, and thus inhibited the growth of gibbsite crystal; also, when a large amount of ethanol was added in sodium aluminate solution, dilution crystallization occurred resulting in an increase of reaction rate. Lu Baolin et al. [11] found that macromolecule surfactant can promote effectively the adsorption of solute molecule, decrease surface tension of crystal seed and surface energy of crystal precipitation. In summary, organic additives can significantly affect precipitation process and improve size and morphology of product. However, the influence of additive on boehmite precipitation from sodium aluminate solution, especially the precipitation kinetics, was rarely investigated.

In this work, the boehmite seed was added to enhance competitive preference of boehmite against gibbsite in the co-precipitation process. And by means of ethanol adding, rapid precipitation of boehmite at low temperature was realized by increasing supersaturation of the solution. The effects of mass ratio of methanol and temperature on the precipitation rate and compositions of alumina hydrate were studied in detail. On this basis, the kinetics model of boehmite precipitation from supersaturated sodium aluminates solutions with ethanol-water solvent was established preliminarily.

Materials and Methods

Aluminum hydroxide, sodium hydroxide and ethanol were analytically pure. Boehmite seeds (from Aluminum Corporation of China Limited) were industrial grade boehmite with an incomplete crystallization and few impurities, as shown in Figure 1. The experiment apparatus consisted of the reactor, a electromotor, thermometer and fastening stand, as shown in Figure 2. Sodium aluminate solution was prepared by dissolving pure gibbsite in hot caustic solution and then vacuum filtered. Mass ratio of ethanol W is the ratio of total mass of ethanol to mass of ethanol water solution. Ethanol water solutions with W of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 were prepared.

Sodium aluminate solution with pre-adjusted Al₂O₃ and Na₂O concentrations was added into the crystallizer. When the solution was heated to the required temperature, the appropriate amount of

boehmite seeds and ethanol water solution were added. Precipitation products were taken from the reactor to a centrifuge for solid-liquid separation periodically and liquid samples were analyzed for their alumina and caustic concentrations using the titration method. The final suspension was filtered and product was washed and then dried at 105 °C for 48 h. The crystallography of the product was identified by SIEMENS D5000 X-ray Diffractometry (XRD), and the weight loss of product by thermal decomposition was analyzed using a thermogravimetric analyzer (TG) (ZRY-2P, China).

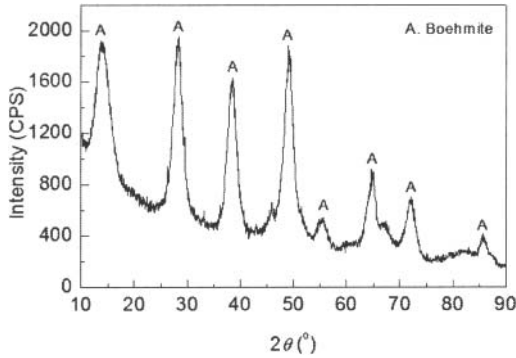


Figure 1. XRD picture of seed

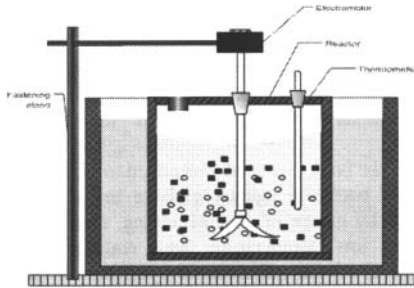


Figure 2. Schematic diagram of experiment apparatus

In the sodium aluminate solution, concentration of alumina and alkali were expressed by the mass of Al_2O_3 and Na_2O_k respectively. Seed ratio (SR) was defined as the mass of alumina added in the solution divided by the mass of alumina contained in the solution.

The molar ratio (MR) is the ratio of mole of Na_2O to Al_2O_3 :

$$MR = 1.645 C_{Na_2O} / C_{Al_2O_3} \quad (1)$$

The concentration of free caustic alkali (FC) can be expressed by:

$$FC = C_{Na_2O} - 0.6078 C_{Al_2O_3} \quad (2)$$

The precipitation ratio can be expressed as follows:

$$\eta_{Al_2O_3} = (1 - MR_0 / MR_m) \times 100\% \quad (3)$$

The coefficient of supersaturation, σ , can be expressed as follows:

$$\sigma = (C - C_{eq}) / C_{eq} \quad (4)$$

$$C_{eq} = C_{Na_2O}(6.2106 - 2486.7/T + 1.08753 C_{Na_2O} / T) \quad (5)$$

Where

C_{Na_2O} : concentration of caustic alkali, g/L

$C_{Al_2O_3}$: concentration of alumina, g/L

C_{eq} : equilibrium concentration of alumina, g/L

MR_0 and MR_m : molar ratio of solution before and after precipitation

T : absolute temperature, K

Results and Discussion

Effect of Mass Ratio of Ethanol on Precipitation Ratio

In order to reduce evaporation loss of ethanol in precipitation process, the precipitation experiment was carried out at 30 °C, and the other experimental conditions were as follows: $C(Al_2O_3)=110$ g/L, $MR=1.53$, $SR=0.4$, $t=5$ h, the volume ratio of ethanol-water solution to sodium aluminate solution (VR)= 1:1. As shown in Figure 3, the precipitation process of sodium aluminate solution can be divided into three regions. Firstly, the initial stage of precipitation was defined as rapid precipitation region, at which the precipitation rate was increased sharply with time, up to 70% within 1 h; secondly, the interim of precipitation was defined as slow precipitation region, at which the precipitation rate was increased gradually with time, up to 85% from 1 to 3 h; lastly, the final stage of reaction was defined as precipitation equilibrium region, at which the precipitation reaction got close to equilibrium and the precipitation rate was almost unchanged with time, only by 3% within 2h.

At the rapid precipitation region, with increasing of W , precipitation rate of sodium aluminate solution accelerated greatly. When $W=0$, precipitation rate was slow, and precipitation ratio was less than 10% in the first hour; when $W=1$, precipitation ratio was nearly 80% in the first hour. Generally, Precipitation ratio of traditional seeded precipitation only reached to about 50% in 60 h. However, precipitation ratio of seeded precipitation with ethanol-water solvent reached to 50% within just 30 min. These results indicated that the precipitation of sodium aluminate solution was promoted significantly by adding ethanol.

The main reason for low precipitation rate of traditional seeded precipitation is the existence of free caustic alkali in initial sodium aluminate solution and freshly formed in precipitation. Free caustic alkali not only decreased supersaturation of reaction solution, but also absorbed on the surface of seed and made the surface negatively charged. As a result, the bonding of growth unit and seed was more difficult, leading to the decrease of precipitation ratio. Initial FC in sodium aluminate solution at different mass ratios of ethanol is shown in Table I. With the mass ratio of ethanol increasing, initial FC in sodium aluminate solution decreased from 17.1 g/L at $W=0$ to 0.8 g/L at $W=1.0$. As concentration of free caustic decreased, the supersaturation of reaction solution was increased. As a result, the precipitation ratio increased [12]. With the precipitation reaction progressing, a number of free caustic alkalis freshly generated, and then precipitation ratio increased slowly in the slow precipitation region as showed in Figure 3.

Table I. Initial free caustic at different mass ratio of ethanol to water-ethanol solvent (W)

Mass ratio of ethanol, W	0.0	0.2	0.4	0.6	0.8	1.0
Free caustic (FC) (g/L)	17.1	13.8	10.6	7.3	4.1	0.8

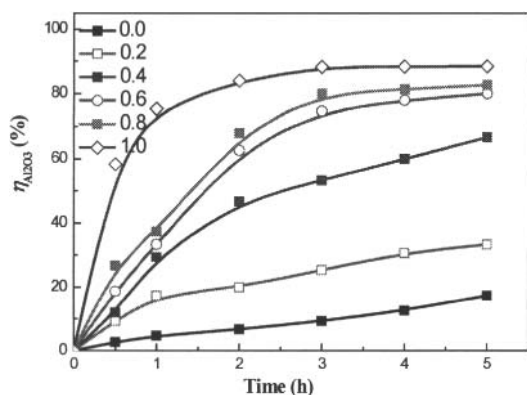


Figure 3. Effects of mass ratio of ethanol to water-ethanol solvent (W) on precipitation rate of sodium aluminate solutions

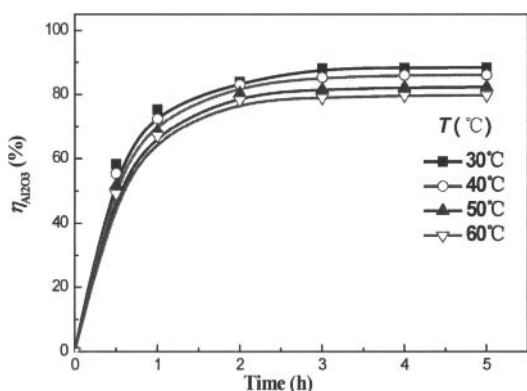


Figure 4. Effects of temperatures on precipitation rate ($\eta_{Al_2O_3}$) of sodium aluminate solutions

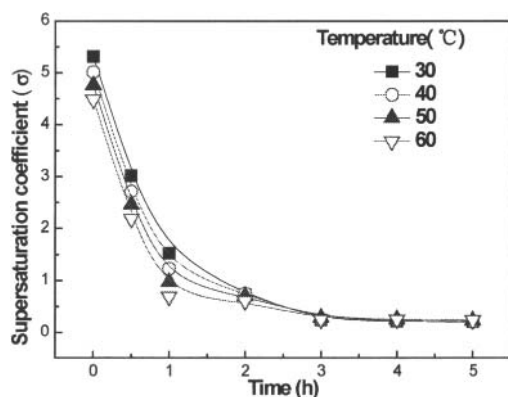


Figure 5. Effect of temperature on supersaturation coefficient (σ) of sodium aluminate solutions

Table II. Weight loss of the products at different mass ratio of ethanol to water-ethanol solvent (W)

Mass ratio of ethanol to water-ethanol solvent, (W)	0.0	0.2	0.4	0.6	0.8	1.0
Weight loss of product (%)	26.77	24.42	21.87	19.51	18.53	16.96

Effect of Temperature on Precipitation Ratio

According to the results above, precipitation ratio increased greatly when W was 1.0. Therefore, to study the effect of temperature on precipitation ratio of sodium aluminate solution, the experiments were carried out with ethanol-water solution of $W=1.0$. As shown in Figure 4, the effect of temperature on precipitation ratio was obvious, and low temperature favors precipitation of sodium aluminate solution. When the temperature rose from 30 to 60°C, precipitation ratio decreased from 88% to 79% within 5 h.

Supersaturation coefficient (σ) of sodium aluminate solutions in precipitation process at different temperature was shown in Figure 5. In the initial stage, as the temperature was decreased, the supersaturation coefficient was increased, leading to an increase of driving force of reaction and precipitation rate. As reaction proceeded, concentration of free caustic increased due to freshly formed OH^- , thus supersaturation coefficient of solution decreased. As a result, the precipitation rate reduced gradually. In final stage, the concentration of alumina reached nearly equilibrium value, and thus both supersaturation coefficient and driving force of reaction were almost closed to 0. The precipitation of sodium aluminate solution became very slowly.

Effect of Mass Ratio of Methanol on Phase Compositions of Alumina Hydrate

Theoretically, the weight loss of dehydration for gibbsite and boehmite is 34.62% and 15.00% respectively. The total weight loss of product is set as RR . And the mass ratio of $AlOOH$ and $Al(OH)_3$ in the product can be expressed as:

$$\omega(AlOOH) = (0.3462 - RR) / 0.1962 = 1.765 - 5.097RR \quad (6)$$

$$\omega(Al(OH)_3) = 5.097RR - 0.765 \quad (7)$$

Weight loss of the products at different mass ratio of ethanol to water-ethanol solvent was shown in Table II, and the effect of mass ratio of ethanol to water-ethanol solvent on composition of the products was shown in Figure 6(a). The mass ratio of boehmite in product increased with mass ratio of ethanol to water-ethanol solvent rising. When the mass ratio of ethanol to water-ethanol solvent (W) increased from 0 to 1.0, the mass ratio of boehmite in product increased from 40% to 90%.

The effect of mass ratio of ethanol to water-ethanol solvent on precipitation selectivity of sodium aluminate solutions was shown in Figure 6(b), and precipitation selectivity of sodium aluminate solutions was defined as the ratio of reaction solution, which transformed to one type of product, to that transformed to total products. As the mass ratio of ethanol to water-ethanol solvent increased, the precipitation selectivity of boehmite was increased. This trend was in accord to that of the products composition. This result indicated that with the mass ratio of ethanol increasing boehmite tended to precipitate prior to gibbsite from sodium aluminate solution. Therefore, adding ethanol favored the generation of boehmite. As shown in Table I, FC reduced in sodium aluminates solutions with the increase of ethanol content.

Thus, the kinetic condition for boehmite precipitation was intensified, leading to the increase of the mass ratio of AlOOH in the product. On the other hand, Paulaime et al. [13] found that hydroxyl-containing organic compounds can form stable compounds with growth unit of gibbsite in precipitation from sodium aluminate solution, which had a negative effect on gibbsite precipitation. Therefore, the adding ethanol inhibited generation of gibbsite and improve the selectivity of boehmite precipitation.

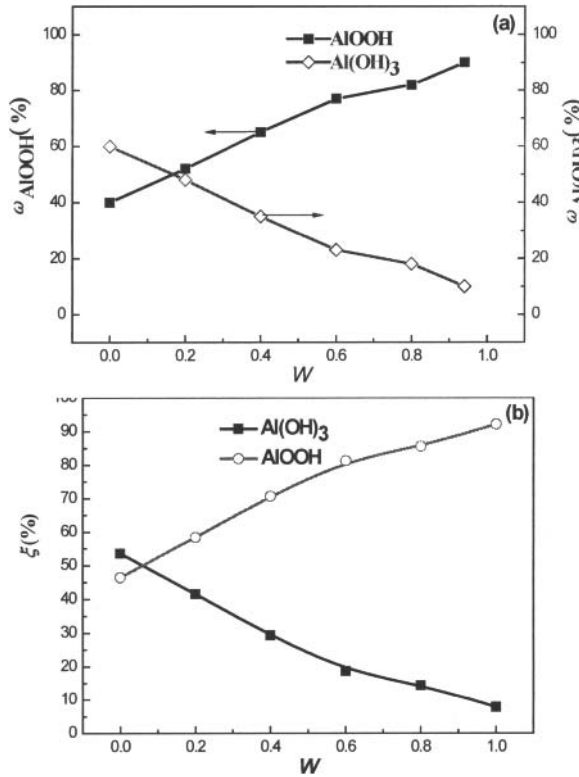


Figure 6. Effect of mass ratio of ethanol to water-ethanol solvent (W) on composition of the products (a) and precipitation selectivity of sodium aluminate solutions (b)

Effect of Temperature on the Mass Ratio of Boehmite in Product

Figure 7 showed XRD pattern of products at different temperature. The result suggested that the products are mixture of boehmite and gibbsite and the content of boehmite was major. The main peak of boehmite is (001), and $d_{001}=0.632$ nm. As d_{001} is between 0.62~0.65 nm, the mixture product consists of psuedo-boehmite and boehmite [14, 15].

The mass ratios of boehmite in products at different temperatures were shown in Table III. The main component of products was boehmite under the experiment conditions: 30~60 °C and mass ratio of ethanol to water-ethanol solvent $W=1.0$. The mass ratio of boehmite in products decreased with temperature rising. The thermodynamics of precipitation of sodium aluminate solution shows a possibility of gibbsite or boehmite precipitation from the reaction solution at lower than 100 °C without seed [16, 17]. Although kinetics factor for gibbsite is superior to that for boehmite, induced crystallization rate of boehmite was intensified

greatly by adding ethanol and boehmite seed. Thus, boehmite is the main product. As shown in Figure 5 above, supersaturation of sodium aluminate solution reduced with temperature rising, and precipitation ratio decreased by about 10%. This was because boehmite dominating crystallization was weakened. Therefore, the mass ratio of boehmite in the products decreased, while that of gibbsite increased.

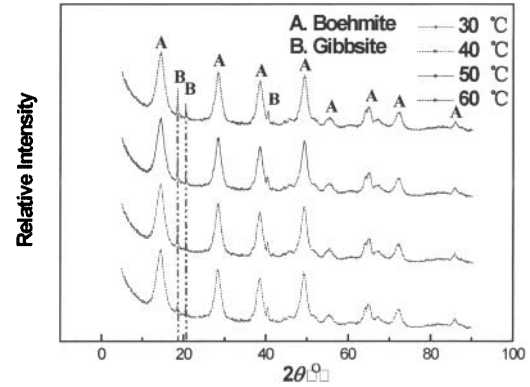


Figure 7. XRD patterns of the products obtained at different temperatures

Table III. Weight Loss and Composition of the Products Obtained at Different Temperatures

Temperature. (°C)	Weight loss of product (%)	Mass ratio of AlOOH, ω _{AlOOH} (%)	Mass ratio of Al(OH) ₃ , ω _{Al(OH)3} (%)
30	16.96	90	10
40	17.74	86	14
50	18.53	82	18
60	19.12	79	21

Kinetics of Boehmite Precipitation From Supersaturated Sodium Aluminates Solutions With Ethanol-water Solvent

The rate determining step was alumina hydrate precipitation from sodium aluminate solution [18], the supersaturation was driving force of the reaction and defined as the difference between the actual concentration of alumina in solution and equilibrium concentration at that conditions. So the rate equation of boehmite precipitation was given by the following equation:

$$\frac{dC}{dt} = -k(C - C_e)^n \quad (8)$$

For caustic influences greatly on precipitation from sodium aluminate solution, different kinetics of precipitation from sodium aluminate solution got by some investigators, which can be summed up as

$$\frac{dC}{dt} = -\frac{k(C - C_e)^n}{N_k^n} \quad (9)$$

Where:

k : reaction rate constant

C : the concentration of alumina in solution, g/L

C_e : equilibrium concentration of alumina in solution, g/L, obtained by Misra equation

N_k : concentration of caustic in solution, g/L
 n_1 : order of supersaturation in precipitation process
 n_2 : order of caustic in precipitation process

On the basis of Arrhenius equation, reaction rate constant k can be expressed as

$$k = A^* e^{-\frac{E_a}{RT}} \quad (10)$$

Where

- A^* : pre-exponential factor
- E_a : apparent activation energy, kJ/mol
- R : ideal gas constant, J/(mol*K)
- T : absolute temperature, K

Kinetics of boehmite precipitation from supersaturated sodium aluminates solutions with ethanol-water solvent was assumed as second order, so rate equation can be expressed as

$$\frac{dC}{dt} = -k(C - C_e)^2 \quad (11)$$

$$C_e = N_k \exp\left(6.2103 - \frac{2486.7}{T} + \frac{1.08753}{T} N_k\right) \quad (12)$$

Where

N_k : concentration of caustic in solution, g/L
 The integration of the above rate equation in the following solution:

$$\frac{1}{C - C_e} = kt \quad (13)$$

As sodium aluminate solution and ethanol were mixed at volume ratio of 1:1, thus the concentration in mixed solution reduced to a half, and equilibrium concentration of alumina in mixed solution was considered to reduce to a half. The plots of $1/(C - C_e)$ versus t were given in Figure 8, and $1/(C - C_e)$ was a linear function of t . So the experimental results confirmed the validity of kinetic model. The rate constants were calculated from the slopes of $1/(C - C_e)$ versus t , which was presented in Table IV.

The Arrhenius plot is shown in Figure 9, and conclusion can be got that boehmite precipitation follows Arrhenius equation. As is seen from Eq.10, E_a can be obtained by the slope of the Arrhenius plot, and $E_a = 1646 * 8.314 = 13.7$ kJ/mol, which is far less than that of traditional seeded precipitation from sodium aluminate solution (56~86 kJ/mol), indicating that ethanol reduced energy barrier of the precipitation reaction and the process was controlled by diffusion process. Because ethanol added absorbed effectively free alkali in solution, thus the amount of negative groups decreased, which increased diffusion rate of aluminium-contained group to seed surface and condensation rate between them.

Table IV. Values of k at Different Temperature

T (°C)	T (K)	$\ln k$	R
30	303.15	-2.53565	0.96420
40	313.15	-2.43806	0.97023
50	323.15	-2.19078	0.98699
60	333.15	-2.07402	0.98068

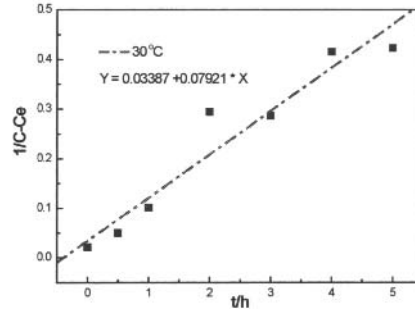
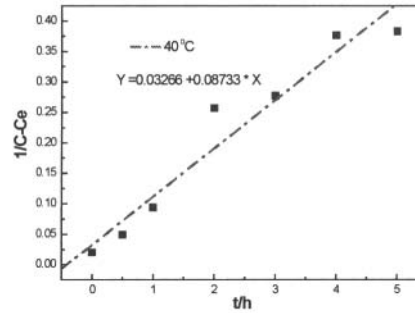
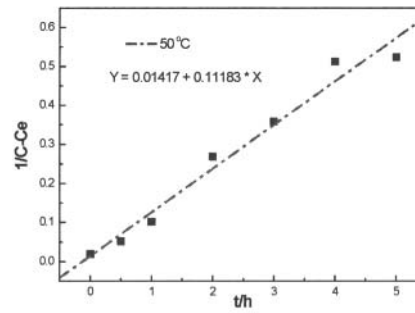
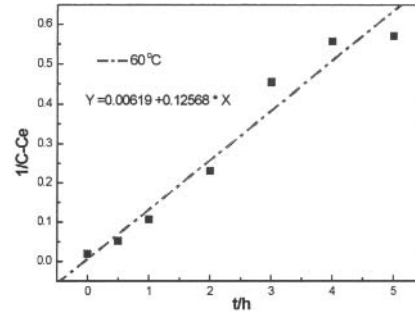


Figure 8. Plots of $1/(C - C_e)$ versus t at different temperature

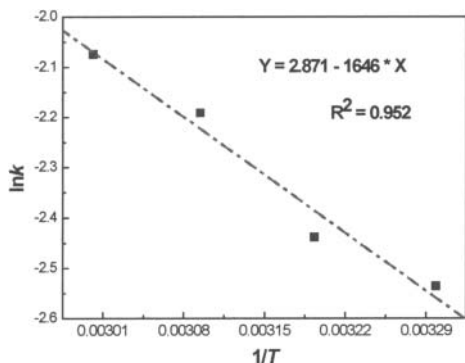


Figure 9. Arrhenius plot for boehmite precipitation from supersaturated sodium aluminates

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Conclusion

Boehmite was prepared from supersaturated sodium aluminates solutions with ethanol-water solvent and the effects of mass ratio of ethanol and temperature on the precipitation rate and phase compositions of alumina hydrate were investigated.

- (1) Precipitation ratio of sodium aluminate solution with ethanol-water solvent increased with mass ratio of ethanol to ethanol-water solution (W) increasing, and decreased with temperature rising. When W was 1.0, ethanol-water solvent improved precipitation ratio of sodium aluminate solution remarkably. The precipitation process of sodium aluminate solution can be divided into three regions: rapid precipitation region, slow precipitation region, precipitation equilibrium region.
- (2) The ratio of $AlOOH$ in the product increased significantly with mass ratio of methanol increased. Under the experimental conditions: $C(Al_2O_3)=110$ g/L, $MR=1.53$, $SR=0.4$, $30^\circ C$, the volume ratio of ethanol-water solution to sodium aluminate solution (VR)= 1:1, the ratio of boehmite in product reached 90%.
- (3) Kinetics of boehmite precipitation from supersaturated sodium aluminates solutions with ethanol-water solvent showed it followed second order kinetic model, and the activity energy was 13.7 kJ, indicating it was controlled by diffusion process.

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