Solubility of Al_2O_3 in the $Na_2O-Al_2O_3-H_2O-CH_3OH$ System at (30 and 60) °C

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To realize the objective of high alumina yield and a high molar Na_2O/Al_2O_3 ratio in caustic solutions for Bayer plants, this paper presents the solubility of Al_2O_3 in methanol−water solvent mixtures with a fixed mass ratio of methanol to water of 1:1 at (30 and 60)°C and containing various Na_2O concentrations. The Al_2O_3 solubility in the $Na_2O-Al_2O_3-H_2O-CH_3OH$ quaternary system increases with an increase of Na_2O concentration, reaching maximum values of 1.70 % and 2.48 % by weight at (30 and 60) °C, respectively. Then, the solubility decreases with a further increase in the Na_2O concentration. The equilibrium solids are aluminum hydroxide $Al(OH)_3$ and mono-sodium aluminate hydrate $Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ in the different alkali concentration regions. The data show that the solubility of Al_2O_3 in the $Na_2O-Al_2O_3-H_2O-CH_3OH$ quaternary system is much lower than that in the $Na_2O-Al_2O_3-H_2O$ ternary system.

Introduction

The properties of sodium aluminate solutions play a key role in the production of $Al(OH)_3$ in Bayer plants, as has been reported by a large number of investigators.[1−7] Precipitation of $Al(OH)_3$ from the supersaturated sodium aluminate solution, which takes place in the low-alkali concentration region,[8] shows that the precipitation is limited by the solubility of $Al(OH)_3$ in the caustic solution, especially for a fixed sodium aluminate component of about 170 $g \cdot L^{-1}$ Na_2O and 1.5 molar ratio (MR) of Na_2O to Al_2O_3 in industrial production and that, because of kinetic tardiness, less than 55 % precipitation occurs after (56 to 72) h. Even though many studies have been done and measures, including seed activation,[9] adding surfactants,[10,11] and introducing ultrasound and magnetic fields,[12] have been carried out to intensify the precipitation process, the effects are not so satisfying.

Andrija[13] and Wilhelmy[14] pointed out that methanol could promote crystallization of $A1(OH)_3$ from the sodium aluminate solution, but the volume ratio of methanol in the CH_3OH-H_2O solvent was less than 20 %. To break the thermodynamic equilibrium of the $Na_2O-Al_2O_3-H_2O$ system, Wang et al.[15−17] also added methanol to the sodium aluminate solution and studied the solubility of Al_2O_3 for various Na_2O concentrations with different mass ratios of methanol to water at 30 °C, indicating that the equilibrium Al_2O_3 concentration is only 13 $g \cdot L^{-1}$ with a mass ratio of about 16 when the MR of methanol to water is 1:1 and the Na_2O concentration is 120 $g \cdot L^{-1}$, as compared to that of about 33 $g \cdot L^{-1}$ Al_2O_3 and 6.0 MR with 120 $g \cdot L^{-1}$ Na_2O without methanol.[18] Adding methanol to sodium aluminate solution can thus result in a high $Al(OH)_3$ precipitation yield, and the relevant research has been carried out.[19,20] The solubility of Al_2O_3 in various Na_2O concentrations with a mass ratio of methanol to water of 1:1 at (30 and 60) °C is therefore investigated in this paper.

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Experimental Procedures

All reagents, including methanol (≥ 99.5 %, manufactured by Beijing Chemical Works), sodium hydroxide (≥ 98 %, from Alfa Aesar), and aluminum hydroxide (with water content between 32.0 % and 35.0 %, produced by Beijing Chemical Reagents Company), were of analytical grade. High-purity Milli-Q water, with a resistivity of above 18.2 $M\Omega \cdot cm$ at ambient temperature, was used for the preparation of the solutions.

To avoid silica contamination from glass induced by sodium hydroxide, the equilibration experiments in this study were conducted in polyethylene plastic bottles. The supersaturated sodium aluminate solutions were prepared by dissolving aluminum hydroxide in hot caustic solutions in a polytetrafluoroethylene (PTFE) vessel, which were first prepared by dissolving sodium hydroxide in super purified water. The hot solution was rapidly filtered through a 0.22 μm pore-size membrane and preserved in PTFE bottles in an oven at 80 °C. After the Na_2O and Al_2O_3 concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES), the mass of water in the caustic solution of a certain volume was calculated. Then methanol with the same mass as the water was added to the plastic bottle containing the sodium aluminate solution. These plastic bottles were sealed and placed in a shaking water bath rotating at 200 rpm and at a temperature of (30 or 60) °C.

After shaking for two weeks and standing for one week, the supernatants were sampled for analyzing the concentrations of Na_2O and Al_2O_3. Then shaking was continued for another two weeks and standing for another one week. The relative deviations between the first and the second samplings were small, which are all less than ± 1.0 %. Here, the system was considered to be in equilibrium. Experimental results showed that two weeks was sufficient for the system to reach equilibrium. The wet solid of each sample was washed by ethanol and dried at 100 °C for at least 24 h. The structure of the solid was identified

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Table 1. Equilibrium Data of the $Na_2O-Al_2O_3-H_2O-CH_3OH$ ($CH_3OH:H_2O$ = 1 g/g) Quaternary System at 30 °C

sample no.	composition of liquid phase				MR of liquid phase	equilibrium crystalline phases
	g·L^{-1}		wt %			
	Na_2O	Al_2O_3	Na_2O	Al_2O_3		
1	20.76	0.53	2.30	0.06	64.80	A
2	30.70	0.88	3.35	0.10	57.14	A
3	43.32	1.55	4.66	0.17	46.01	A
4	52.12	2.10	5.61	0.23	40.82	A
5	64.22	2.88	6.75	0.30	36.70	A
6	71.80	3.56	7.54	0.37	33.21	A
7	85.63	5.02	8.75	0.51	28.07	A
8	93.88	6.43	9.69	0.66	24.03	A
9	109.92	11.33	11.13	1.15	15.96	A
10	121.91	13.52	12.24	1.36	14.83	A
11	132.96	17.31	13.04	1.70	12.64	A + B[a]
12	142.94	15.33	13.69	1.47	15.34	B
13	150.52	13.00	14.68	1.27	19.05	B
14	162.18	9.25	15.61	0.89	28.84	B
15	170.67	9.39	16.32	0.90	29.91	B

[a] A and B represent the solids $Al(OH)_3$ and $Na_2O\cdot Al_2O_3\cdot 2.5H_2O$, respectively; A + B means that the compounds coexist.

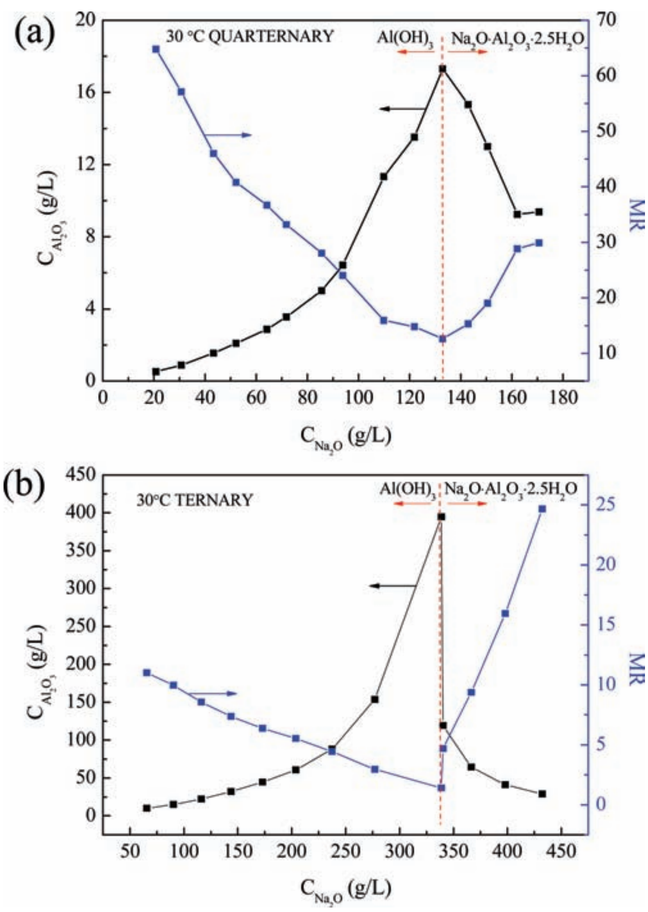

Figure 1. Solubility relations at 30 °C: (a) for the $Na_2O-Al_2O_3-H_2O-CH_3OH$ quaternary system; (b) for the $Na_2O-Al_2O_3-H_2O$ ternary system.

by X-ray diffraction (XRD) with a Japan Rigaku D/max-2400 X-ray diffractometer with Cu Kα radiation. All samples were scanned over a 10° to 90° 2θ range.

Results and Discussion

Al_2O_3 Solubility in the $Na_2O-Al_2O_3-H_2O-CH_3OH$ ($CH_3OH:H_2O$ = 1 g/g) System at 30 °C. The experimental results at 30 °C are summarized in Table 1 and shown graphically in Figure 1. Compared to the ternary system $Na_2O-Al_2O_3-H_2O$, the maximum equilibrium concentration of Al_2O_3 for the new quaternary system (1.70 % by weight) is only about one-tenth of that for the ternary system (25.59 % by weight), and the corresponding minimum equilibrium MR (12.64) is about ten times of that (1.41) of Figure 1b.[18]

Table 2. Equilibrium Data of the $Na_2O-Al_2O_3-H_2O-CH_3OH$ ($CH_3OH:H_2O$ = 1g/g) Quaternary System at 60 °C

sample no.	composition of liquid phase				MR of liquid phase	equilibrium crystalline phases
	g·L^{-1}		wt %			
	Na_2O	Al_2O_3	Na_2O	Al_2O_3		
1	22.39	1.29	2.44	0.14	28.51	A
2	34.09	3.12	3.69	0.34	17.98	A
3	43.13	4.17	4.59	0.44	17.00	A
4	50.31	5.47	5.29	0.57	15.14	A
5	61.38	7.44	6.35	0.77	13.57	A
6	73.81	9.28	7.56	0.95	13.08	A
7	76.44	9.85	7.75	1.00	12.76	A
8	88.19	13.14	8.85	1.32	11.04	A
9	94.31	14.08	9.24	1.38	11.02	A
10	99.07	17.45	9.66	1.70	9.34	A
11	100.17	18.09	9.75	1.76	9.11	A
12	114.77	25.11	11.13	2.44	7.52	A
13	116.05	25.75	11.20	2.48	7.42	A + B[a]
14	121.17	12.51	11.76	1.21	15.94	B
15	124.17	10.89	12.01	1.05	18.76	B
16	130.60	8.50	12.91	0.84	25.28	B
17	135.69	6.47	13.41	0.64	34.51	B
18	143.68	6.44	14.08	0.63	36.69	B

[a] A and B represent the solids of $Al(OH)_3$ and $Na_2O\cdot Al_2O_3\cdot 2.5H_2O$, respectively; A + B means that the compounds coexist.

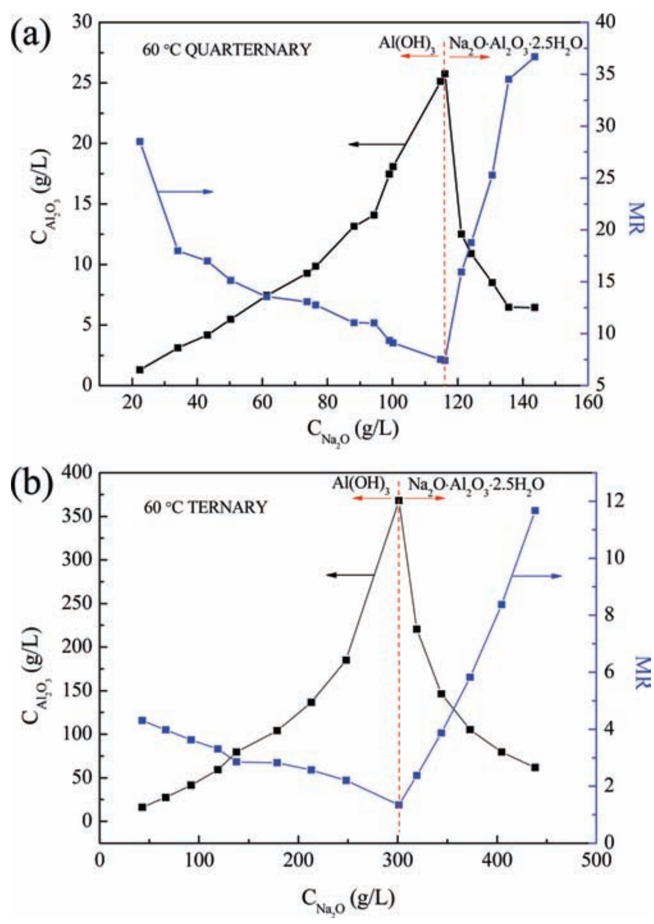

Figure 2. Solubility relations at 60 °C: (a) for the $Na_2O-Al_2O_3-H_2O-CH_3OH$ quaternary system; (b) for the ternary $Na_2O-Al_2O_3-H_2O$ system.

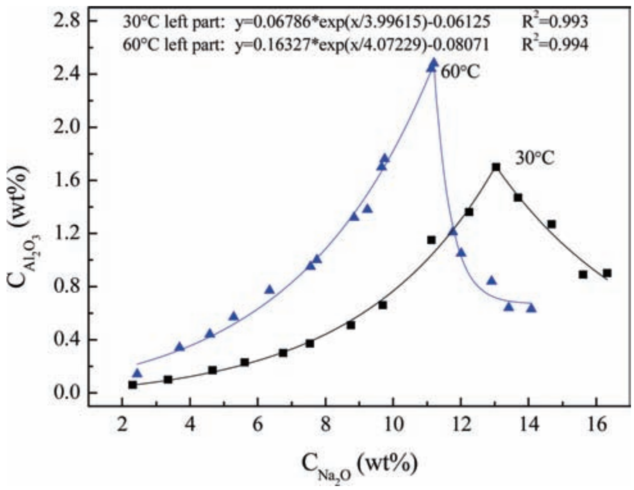

Figure 3. Fitting curves for the $Na_2O-Al_2O_3-H_2O-CH_3OH$ ($CH_3OH:H_2O$ = 1 g/g) system at (30 and 60) °C.

However, the trends for both the quaternary and the ternary systems share the common feature of $Al(OH)_3$ for the left region and $Na_2O\cdot Al_2O_3\cdot 2.5H_2O$ for the right region, as determined by the XRD pattern of Figure 4, especially, which shows a typical gibbsite type of aluminum hydroxide for the quaternary system. Consequently, when methanol is added to the system, more aluminum will be separated from the sodium aluminate solution in the form of $Al(OH)_3$, thus realizing the objective of obtaining a high MR caustic solution and high alumina yield at the same time.

Particularly, the fitting curve for the left region at 30 °C (Figure 3) indicates that the relationship between the concentrations of Na_2O and Al_2O_3 can be expressed as

$$C_{Na_2O} = 0.06786 \exp\left(\frac{C_{Al_2O_3}}{3.99615}\right) - 0.06125 \qquad (1)$$

in which C_{Na_2O} and $C_{Al_2O_3}$ are the mass fractions of the two components.

Al_2O_3 Solubility in the $Na_2O-Al_2O_3-H_2O-CH_3OH$ ($CH_3OH:H_2O$ = 1 g/g) System at 60 °C. Corresponding experimental results at 60 °C are summarized in Table 2, indicating almost the same as those at 30 °C: in the quaternary system at 60 °C, the maximum equilibrium concentration of Al_2O_3 (2.48 % by weight) is approximately one-tenth of that (24.45 % by weight) for the ternary system, and the minimum equilibrium MR (7.42) is five times more than that (1.34) for the ternary system of Figure 2b.[18] For both (30 and 60) °C, the equilibrium solid compositions are $Al(OH)_3$ of gibbsite type for the left region and $Na_2O\cdot Al_2O_3\cdot 2.5H_2O$ for the right region.

Correspondingly, the fitting curve for the left region at 60 °C (Figure 3) can be expressed as

$$C_{Na_2O} = 0.16327 \exp\left(\frac{C_{Al_2O_3}}{4.07229}\right) - 0.08071 \qquad (2)$$

in which C_{Na_2O} and $C_{Al_2O_3}$ are the mass fractions of the two components.

Conclusion

The solubility for the $Na_2O-Al_2O_3-H_2O-CH_3OH$ system with a fixed mass ratio of methanol to water of 1:1 at (30 and 60) °C was investigated.

At (30 and 60) °C, the quaternary system $Na_2O-Al_2O_3-H_2O-CH_3OH$ shows the same trend as the ternary system $Na_2O-Al_2O_3-H_2O$, with $Al(OH)_3$ and $Na_2O\cdot Al_2O_3\cdot 2.5H_2O$ as the only solid phases. The solubility of Al_2O_3 in the $Na_2O-Al_2O_3-H_2O-CH_3OH$ quaternary system increases with an increase in the Na_2O concentration reaching a maximum of 1.70 % by weight and 2.48 % by weight at (30 and 60) °C, respectively. Thereafter, the equilibrium solid changes from $Al(OH)_3$ to $Na_2O\cdot Al_2O_3\cdot 2.5H_2O$, and solubility declines rapidly.

These diagrams show that the precipitation of $Al(OH)_3$ can be enhanced by adding methanol into the $Na_2O-Al_2O_3-H_2O$ ternary system and a high MR sodium aluminate solution can be obtained after methanol is distilled off, as is beneficial for the digestion of bauxite ore and red mud.

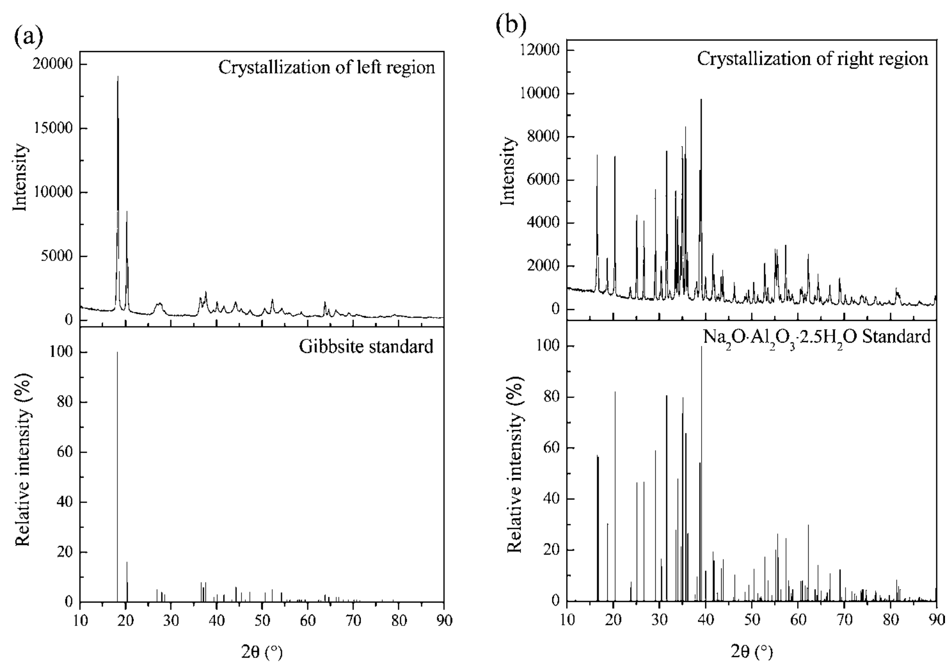

Figure 4. XRD pattern of the equilibrium solids: (a) XRD pattern of $Al(OH)_3$ left region; (b) XRD pattern of $Na_2O\cdot Al_2O_3\cdot 2.5H_2O$ right region.

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