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Phase Diagram for the System $Na_2O-Al_2O_3-H_2O$ at High Alkali Concentration

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The high alkali concentration regions of the phase diagrams for the system $Na_2O-Al_2O_3-H_2O$ were studied at 95 °C and 110 °C, to provide a chemical database for producing monosodium aluminate hydrate ($Na_2O\cdot Al_2O_3\cdot 2.5H_2O$). In the phase diagram at 95 °C, the solid phases of $4Na_2O\cdot Al_2O_3\cdot 12H_2O$ and $6Na_2O\cdot Al_2O_3\cdot 12H_2O$, besides $Na_2O\cdot H_2O$, $Al_2O_3\cdot 3H_2O$, and $Na_2O\cdot Al_2O_3\cdot 2.5H_2O$, were discovered. In the phase diagram at 110 °C, $4Na_2O\cdot Al_2O_3\cdot 12H_2O$ was found missing. These phase diagrams show that all these sodium aluminate hydrates decompose in the presence of water and that the higher the temperature, the larger the region with $Na_2O\cdot Al_2O_3\cdot 2.5H_2O$ as the equilibrium solid.

Sodium aluminate, mainly used in effective subacid water purification, can thoroughly precipitate iron, manganese, and organic matter and remove phosphorus as well out of water. It is also extensively used in the manufacture of paper, paint pigments, alumina-containing catalysts, dishwasher detergents, ingot molds, molecular sieves, and concrete as well as in drilling mud preparations for plug bore holes in oil exploration. The crystallization of monosodium aluminate hydrate ($Na_2O\cdot Al_2O_3\cdot 2.5H_2O$) with low Na_2O/Al_2O_3 molar ratio from concentrated alkaline sodium aluminate solution is the most important unit operation in the sodium aluminate process including the alkali digestion technology. And it is also the key step in the production of alumina through either the high-pressure hydrothermal chemical method or the atmospheric pressure digestion process using concentrated alkali solution.[1] The high alkali content region of the phase diagram of the $Na_2O-Al_2O_3-H_2O$ system is the key database for the crystallization of monosodium aluminate hydrate ($Na_2O\cdot Al_2O_3\cdot 2.5H_2O$).

The alkaline method, especially the Bayer process, has been used to produce alumina for over a hundred years, and the study of the phase diagram for the system $Na_2O-Al_2O_3-H_2O$ started just as early. But, because the traditional alumina-producing systems always dealt with dilute alkali solutions, almost all published studies on the phase diagram for the system $Na_2O-Al_2O_3-H_2O$ were confined to the dilute alkali region of the diagram.

Using Schreinemaker's method, Fricke and Jucaitis[2] first studied the composition of sodium aluminate hydrate and its crystallization from sodium aluminate solutions, and they verified the solid phase as $Na_2O\cdot Al_2O_3\cdot 2.5H_2O$. Although dissent about the composition of the sodium aluminate hydrate emerged subsequently, through several decades of argument, it was finally confirmed that the crystal was $Na_2[Al_2O_3(OH)_2]\cdot 1.5H_2O$, that is, $Na_2O\cdot Al_2O_3\cdot 2.5H_2O$, belonging to the cubic system, and the crystal lattice parameters were also determined.[3] Recently, Kaduk and Pei[4] studied the crystal structure in detail.

Also using Schreinemaker's method, Jucaitis[5] started to study the higher alkali concentration region of the diagram and inferred the existence of an equilibrium solid with the composition $3Na_2O\cdot Al_2O_3\cdot 6H_2O$. Using X-ray diffraction, Kuznetsov[6] considered, however, that the solid was a mixture of $Na_2O\cdot Al_2O_3\cdot 2.5H_2O$ and $Na_2O\cdot H_2O$. But Gessner[7] proposed a variable chemical composition for the solid of (4.6 to 4.9)$Na_2O\cdot Al_2O_3\cdot$(12.9 to 13.8)H_2O. Qiu and Chen[8] used an iodide ion tracing method to determine the amount of the mother liquor carried between crystals, arriving at an exact composition of the equilibrium solid of $4Na_2O\cdot Al_2O_3\cdot 12H_2O$.

The above studies on the system $Na_2O-Al_2O_3-H_2O$ were all performed at 30 °C. And because of the high viscosity of the aluminate solution and the impossibility of obtaining the pure solid phase, study on the equilibrium solid phase at even higher alkali concentrations encountered considerable difficulty. Published research on the phase diagram for the system $Na_2O-Al_2O_3-H_2O$ at other temperatures significant for sodium aluminate hydrate crystallization has, however, been lacking. The present work focused on the concentrated alkali regions of the phase diagram at 95 °C and 110 °C. In particular, the area inclusive of the equilibrium solid phase $Na_2O\cdot Al_2O_3\cdot 2.5H_2O$ was investigated in detail, because of its significance in sodium aluminate hydrate crystallization. Schreinemaker's method combined with X-ray diffraction was used in the present study.

Experimental Procedure

A supersaturated solution containing 30% Na_2O and 20% Al_2O_3 (all the content data in the present paper are in mass percent) was first prepared at 70 °C from analytical-grade aluminum hydroxide and sodium hydroxide and ion-free water. Sodium aluminate hydrate was crystallized from this supersaturated solution, recovered by filtration, washed with absolute alcohol, and then dried.

The sodium aluminate solution of a known composition, obtained through alternately dissolving a calculated amount of the prepared sodium aluminate hydrate and analytical-grade sodium hydroxide in a given amount of water, was stored in sealed polyethylene bottles which were kept in a thermostat maintained at 95 ± 0.5 °C and 110 ± 0.5 °C for 2 months in order to make the system reach thorough equilibrium. At the experimental temperature, the viscosity

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Table 1. Equilibrium Data of the $Na_2O-Al_2O_3-H_2O$ System at 95 °C

composition of equil solution[a]		
Na_2O	Al_2O_3	equilibrium solid phase
20.93	27.21	$Al_2O_3 \cdot 3H_2O$ (A) + $Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
22.85	17.22	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
26.14	9.75	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
27.95	8.41	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
33.83	4.43	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
37.31	2.66	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
40.15	2.23	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
42.12	2.1	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B) + $4Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (C)
42.73	2.06	$4Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (C)
44.95	1.54	$4Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (C)
47.09	0.63	$4Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (C)
51.10	0.33	$4Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (C)
51.27	0.31	$4Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (C) + $6Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (D)
53.87	0.24	$6Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (D)
56.80	0.15	$6Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (D)
59.70	0.11	$6Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (D) + NaOH (E)
59.58	0.00	$Na_2O \cdot H_2O$ (E)

[a] Mass %.

Table 2. Equilibrium Data of the $Na_2O-Al_2O_3-H_2O$ System at 110 °C

composition of equil solution[a]		
Na_2O	Al_2O_3	equilibrium solid phase
23.72	29.37	$Al_2O_3 \cdot 3H_2O$ (A) + $Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
24.94	22.53	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
28.78	13.92	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
35.75	6.84	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
40.81	4.18	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
43.60	2.78	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
45.00	2.03	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
47.61	1.27	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
53.19	0.55	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
54.06	0.51	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B)
55.23	0.46	$Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (B) + $6Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (D)
55.85	0.39	$6Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (D)
58.76	0.28	$6Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (D)
60.80	0.20	$6Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (D) + NaOH (E)
60.62	0.00	$Na_2O \cdot H_2O$ (E)

[a] Mass %.

of the saturated sodium aluminate solution was still low enough to easily obtain clear liquid through sedimentation, and the supersaturated solution reached equilibrium readily easily within 3 weeks. Sodium oxide and alumina contents in the samples were respectively analyzed by a titrimetric method and ICP-AES.

The corresponding equilibrium liquid composition and a series of the total compositions of equilibrium mixtures with different relative amounts of the liquid and the solid were analyzed, and the equilibrium solid was further rechecked through X-ray diffraction.[7] According to the lever rule, all the composition points of the samples from identical total composition should lie on a common straight line (coupling-line) containing the total composition point in the phase diagram for the system $Na_2O-Al_2O_3-H_2O$. Obviously, more sampling points used in the present work would make the coupling-line more precise as compared to that for only sampling the saturated liquid and the equilibrium solid alone, as for the traditional Schreinemaker's method.

In a region of the three-component phase diagram for the system $Na_2O-Al_2O_3-H_2O$, if there is only one solid phase in the equilibrium mixture with the solid and the liquid, the saturated solution has three degrees of freedom, whose composition can change while the temperature and the pressure are fixed, then the different coupling-lines, in the region, cross at the identical equilibrium solid point. But if there are two equilibrium solids in a region of the diagram, the saturated solution composition is unique at a given temperature and pressure, with the different coupling-lines in the region crossing at the identical saturated solution, the invariant point in the phase diagram.

Results and Discussion

Phase Diagram for the System $Na_2O-Al_2O_3-H_2O$ at 95 °C. The experimental results for 95 °C are summarized in Table 1 and shown graphically in Figure 1. In the figure, points A, B, C, D, and E represent respectively the solids $Al_2O_3 \cdot 3H_2O$, $Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (SAH-1), $4Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (SAH-2), $6Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (SAH-3), and $Na_2O \cdot H_2O$ (NaOH). Points O, K, J, I, F, and G are all located on the saturated liquid line. Point O on the ordinate of the diagram represents the solubility of alumina in pure water at the given temperature, and point G on the abscissa shows the solubility of Na_2O in pure water at 95 °C, with 59.58 Na_2O (mass percent).

Curves OK, KJ, JI, IF, and FG indicate the compositions of saturated ternary solutions that are in equilibrium respectively with the solids alumina hydrate (A), SAH-1 (B), SAH-2 (C), SAH-3 (D), and sodium hydroxide (E). The data of curve OK have been published.[9]

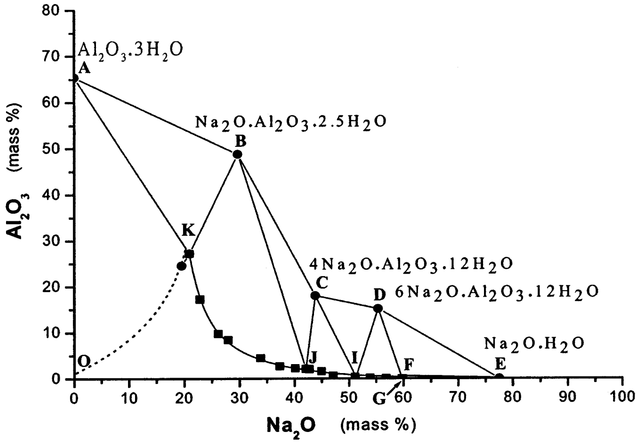

Figure 1. Phase diagram for the system $Na_2O-Al_2O_3-H_2O$ at 95 °C.

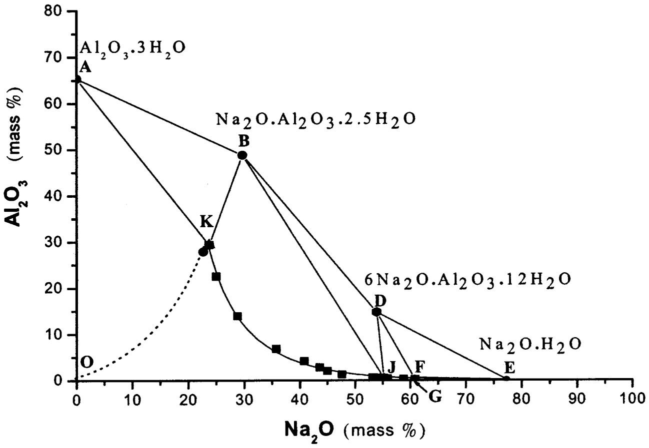

Figure 2. Phase diagram for the system $Na_2O-Al_2O_3-H_2O$ at 110 °C.

Areas ABKA, BCJB, CDIC, and DEFD are four triple-phase regions of coexisting respective alumina hydrate (A), SAH-1 (B), and saturated solution (K); SAH-1 (B), SAH-2 (C), and saturated solution (J); SAH-2 (C), SAH-3 (D), and saturated solution (I); and SAH-3 (D), sodium hydroxide (E), and saturated solution (F). And K, J, I, and F are four invariant points, whose compositions are shown in Table 1.

The area above line ABCDE is the all solids phase region, and that below the saturated liquid line OKJIFG is the unsaturated sodium aluminate solution region.

Phase Diagram for the System $Na_2O-Al_2O_3-H_2O$ at 110 °C. The experimental results for 110 °C are summarized in Table 2 and shown graphically in Figure 2. In Figure 2, compared to Figure 1, point C (SAH-2) is missing and point G has the different composition of 60.62Na_2O (mass percent).

Curves OK, KJ, JF, and FG indicate the compositions of saturated ternary solutions that are in equilibrium respectively with the solids alumina hydrate (A), SAH-1 (B), SAH-3 (D), and sodium hydroxide (E). The data of curve OK have also been published.[9]

Triple-phase region BDJB is of coexisting SAH-1 (B), SAH-3 (D), and saturated sodium aluminate solution (J). And the compositions of the three invariant points K, J, and F are shown in Table 2.

These diagrams show the unique feature that the area for precipitating SAH-1 broadens with increasing temperature, which provides a significant foundation for the monosodium aluminate hydrate crystallization at higher alkali concentrations. At 110 °C, the alkali concentration of the liquid in equilibrium with sodium aluminate hydrate can be as high as 55.23% Na_2O, while the SAH-2 is missing. It should be noted that, for both 95 °C and 110 °C, the alumina content in the saturated aluminate solution in equilibrium with sodium hydroxide (E) is extremely low. Obviously, in both diagrams, all straight lines respectively connecting the SAH-1 (B), SAH-2 (C), and SAH-3 (D) with the water point (original point in these diagrams) do not cut their corresponding saturation curves, which indicates that all these sodium aluminate hydrates decompose in the presence of water.

In our experiments, the sodium-rich aluminate hydrates, SAH-2 and SAH-3, crystallized relatively slowly from the solution to form very fine particles. Furthermore, since the alkali concentration of the equilibrium liquid was high, it was difficult to obtain pure crystals. As the temperature of a sample fell rapidly after sampling, sodium hydroxide in the solution carried between the crystals of the samples precipitated immediately, resulting in sodium-rich aluminate hydrate samples; that is, both SAH-2 and SAH-3, are contaminated by free solid sodium hydroxide, as reflected by strong sodium hydroxide diffraction peaks in their XRD patterns. On the other hand, SAH-1 crystals could freely grow to several millimeters in size. Washed with a 400 g/L alkali solution at 70 to 80 °C, these crystals become very pure, with the same XRD patterns as those reported in ref 4.

Conclusion

The high alkaline concentration regions of the phase diagrams for the system $Na_2O-Al_2O_3-H_2O$ at 95 °C and 110 °C were investigated.

At 95 °C, in addition to the known solid phases of $Al_2O_3 \cdot 3H_2O$, $Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$ (SAH-1), and $Na_2O \cdot H_2O$, two solids were found with the compositions $4Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (SAH-2) and $6Na_2O \cdot Al_2O_3 \cdot 12H_2O$ (SAH-3), and the latter was not reported earlier. Four invariant points, with their corresponding pairs of equilibrium solids ($Al_2O_3 \cdot 3H_2O$ and SAH-1; SAH-1 and SAH-2; SAH-2 and SAH-3; and SAH-3 and $Na_2O \cdot H_2O$) were identified with their compositions.

At 110 °C, the solid-phase SAH-2 was found missing, and therefore, there were only three invariant points, with their corresponding pairs of equilibrium solids ($Al_2O_3 \cdot 3H_2O$ and SAH-1; SAH-1 and SAH-3; and SAH-3 and $Na_2O \cdot H_2O$).

These diagrams show that the area for precipitating SAH-1 broadens with increasing temperature. And all straight lines respectively connecting the points SAH-1 (B), SAH-2 (C), and SAH-3 (D) with the water point do not cut their corresponding saturation curves, which indicates that all these sodium aluminate hydrates decompose in the presence of water.

These findings provide a significant database for monosodium aluminate hydrate crystallization at high alkaline concentrations.

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