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Studies on recrystallised aluminium mono-hydroxide precipitates. Kinetics of dissolution by sodium hydroxide solutions

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With 3 figures and 1 table

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1. Introduction

Amorphous aluminium hydroxide precipitates and their recrystallisation products may be characterised by their rate of dissolution by sodium hydroxide solutions (1, 2, 3). This work extends previous studies on the kinetics of dissolution of recrystallised aluminium tri-hydroxide precipitates. Aluminium mono-hydroxide gels were recrystallised under controlled conditions to give Boehmite powders of different particle size and their dissolution by well-stired sodium hydroxide solutions was studied at 35 ° to 65 °C. Reaction mechanisms were discussed.

2. Experimental

2.1 Materials

2.1.1 Boehmite P5/30 m powder

2.5 percent benzene solution of aluminium isopropoxide (supplied by Honeywell and Stein Ltd.) was hydrolysed by shaking with 200 cm^3 hot distilled water at 80 °C. The amorphous aluminium hydroxide gel was then aged in hot water for 30 min (4). This recrystallised material was then centrifuged free of solution, washed three times with distilled water, dried by resuspension in anhydrous acetone and then outgassed at room temperature for 24 hr with a mercury vapour pump.

Boehmite P5/2 and P5/8 powders

Two other batches of amorphous aluminium hydroxide gel were prepared as above and recrystallised for 2 and 8 hr in hot distilled water. The precipitates were then washed and dried in the same manner.

The chemical and physical properties of these powders were investigated by the techniques described in our previous paper (3) and were as follows:
particle shape; fibres (cylinders) – $l_0/w_0 =$ 4–6 (Cf. ref 4): particle length (l_0); $P5/30$ m 0.07 μm, $P5/2$ 0.10 μm, $P5/8$ 0.10 μm:
chemical and thermogravimetric analysis; 0.995 $A100H$:
X-ray diffraction; >0.95 Boehmite:
i.r. spectrophotometry; >0.98 Boehmite.

2.1.2 Sodium hydroxide solutions (concentrations $C = 1$ to 8 M) were prepared from A.R. material in double-distilled CO_2-free water.

2.2 Reaction kinetics

Boehmite powder (0.6 g) was completely redispersed in large excess (100 cm^3) aqueous sodium hydroxide solution in a 'Quickfit' flask. The reaction flask was shaken at 240 vibrations per min in a Dubnoff Shaker – Water Bath thermostatted to ±1 °C. 1 cm^3 reaction solution was withdrawn after different times and analysed for aluminate anion by the modified Waenninen's method (3). The aluminate concentrations $(W_{sol})_t$ were determined.

3. Results

3.1 Physical and chemical changes

Boehmite powders (cylindrical fibres of initial length $l_0 = 0.06$ to 0.10 μm) were prepared by controlled hydrolysis of aluminium

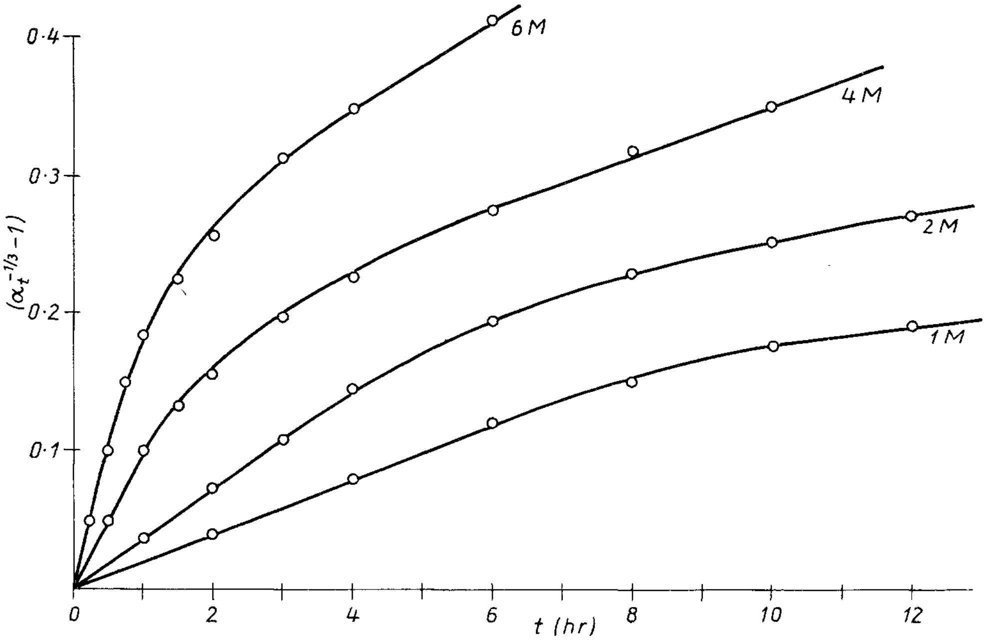

Fig. 1A. Dissolution of Boehmite *P*5/2 by sodium hydroxide solutions at 50 °C. Variation of $(\alpha_t^{-1/3} - 1)$ with time.

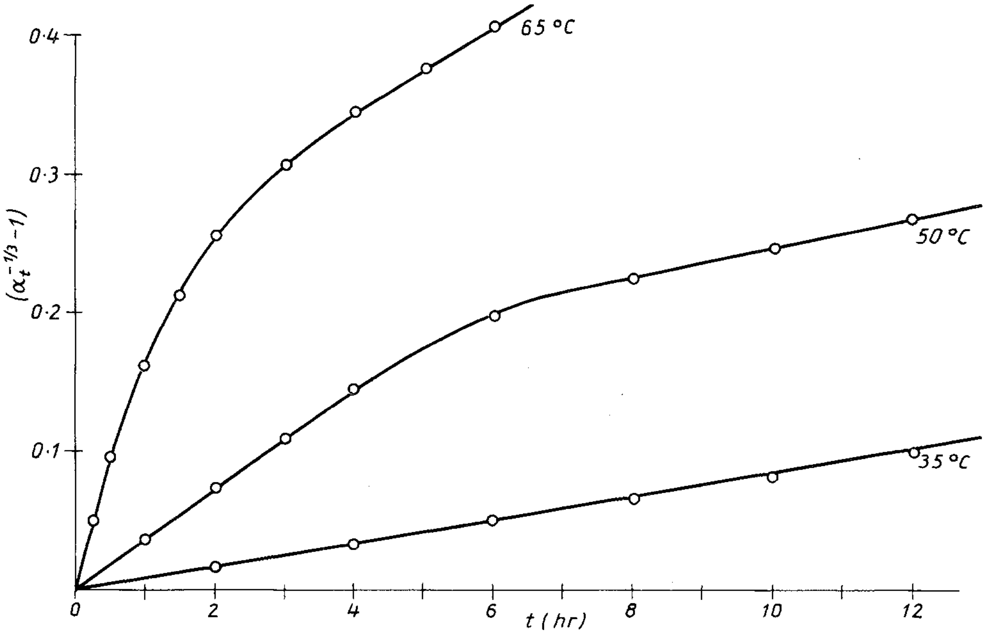

Fig. 1B. Dissolution of Boehmite *P*5/2 by sodium hydroxide solution ($C = 2$ *M*) at different temperatures. Variation of $(\alpha_t^{-1/3} - 1)$ with time.

isopropoxide and recrystallisation of the aluminium hydroxide precipitates in hot water (80 °C). These powders were dispersed in sodium hydroxide solutions ($C = 1$–8 *M*) and their dissolution was studied at 35 ° to 65 °C. The suspension concentration was 0.6 g per 100 cm^3 and the hydroxyl ion was in large excess; this eliminated any variation in reaction rate with hydroxyl ion concentration during a run and simplified the kinetic studies (3).

The Boehmite powders first adsorbed rapidly 1 to 3 monolayers of hydroxyl ion and then dissolved to form aluminate anion. The crystals retained their cylindrical form for over 60 percent reaction and so the dissolution was three-directional. The X-ray diffraction pattern and the i.r. spectra were not modified after prolonged contact with hydroxide solution; that is, the solid retained the composition AlOOH. The aluminate concentrations $(W_{sol})_t$ in solution were found equivalent to the weight losses ΔW_t of the boehmite solids.

3.2 Kinetics

3.2.1 Reaction order

Residual weights (W_t) after different times were determined by analysis of the reaction solutions for aluminate anion;

then, $W_t = [W_0 - (W_{sol})_t]$.

Some typical $\left[\left(\frac{W_t}{W_0}\right)^{-1/3} - 1\right]$ vs t plots for reactions with Boehmite $P5/2$ are presented in figs. 1A, 1B. For the first thirty percent dissolution, the recrystallised Boehmites reacted quite rapidly with sodium hydroxide solutions; then, the rates of reaction slowed down. Over the range of rapid dissolation, the function $[(W_t/W_0)^{-1/3} - 1] = (\alpha_t^{-1/3} - 1)$ varied linearly with reaction time t. That is, at any time t (5),

$$\frac{dW}{dt} = -k_w\, W_t^{4/3}\ \mathrm{g\,h^{-1}} \qquad [1]$$

where k_w is the rate constant w.r.t. powder weight.

Initial rate constants (k_{wi}) were then determined from the gradients of the $(\alpha_t^{-1/3} - 1)$ v t plots according to the relation,

$$k_{wi} = \frac{3}{W_0^{1/3}} \text{ grad } [(\alpha_t^{-1/3} - 1) \text{ v } t \text{ plot}]\ \mathrm{g^{-1/3}\,h^{-1}}. \qquad [3A]$$

Average rate constants (k_{wav}) were determined from the half-lifes ($t_{0.5}$) according to the relation,

$$k_{wav} = \frac{0.78}{W_0^{1/3}\, t_{0.5}}\ \mathrm{g^{-1/3}\,h^{-1}}. \qquad [3B]$$

Typical results for the reactions of different recrystallised Boehmite powders with 1–8 M sodium hydroxide solutions at 50 °C are presented in tab. I.

3.2.2 Sodium hydroxide concentration

Rates of dissolution at any temperature increased with increasing (excess) hydroxyl ion concentration. Generally, the rate constants (k_w) increased linearly with the mean ionic activity ($a_\pm$) of the hydroxide solutions; refer to fig. 2.

Then,

$$k_w = k_{wi}\, a_\pm \qquad [3]$$

where $k_w = k_{wi}$ at $a_\pm = 1$ M.

Tab. 1. Rate constants k_{wi} and k_{wav} ($\mathrm{g^{-1/3}\,h^{-1}}$) for the reactions of Boehmite powders with well-stirred sodium hydroxide solutions at 50 °C; $W_0 = 0.6$ g per 100 cm

C	$a_\pm$	$P5/30$ m ($S_0^* = 10$ m^{2}g^{-1})		$P5/2$ ($S_0 = 7$ m^{2}g^{-1})		$P5/8$ ($S_0 = 7$ m^{2}g^{-1})	
(M)	(M)	100 k_{wi}	100 k_{wav}	100 k_{wi}	100 k_{wav}	100 k_{wi}	100 k_{wav}
1	0.68	15	9	7.5	4.5	4.5	2.5
2	1.35	28	16	15	9	8.8	5.3
3	2.31	46	25	24	14	14.5	8.0
4	3.52	75	45	37	20	22	12
5	5.2	110	65	55	33	33	20
6	7.4	155	90	80	45	48	28
7	12.0	240	145	120	70	70	40
8	15.5	330	190	160	95	100	60
	$a_\pm = 1$	21		10.5		6.4	

*) $S_0 = \frac{2.2}{\varrho l_0}$ (see discussion)

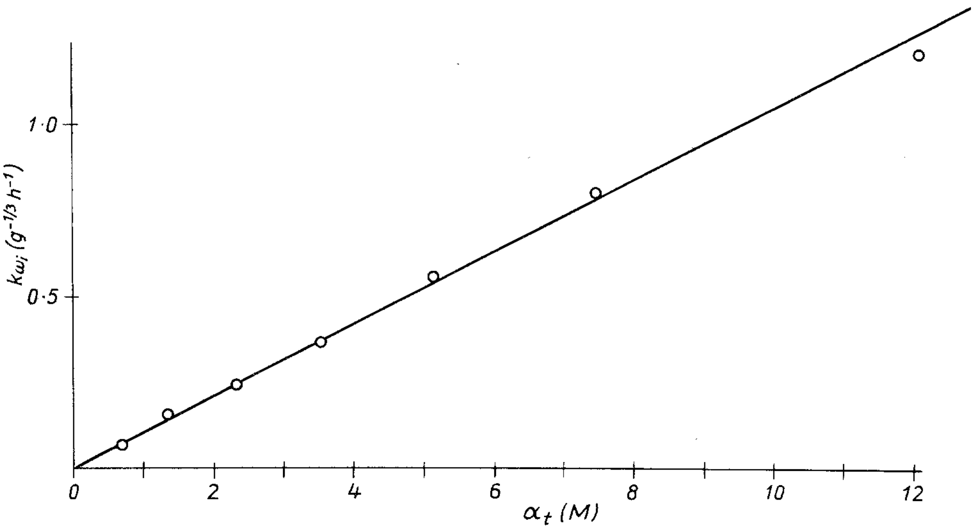

Fig. 2. Dissolution of Boehmite *P*5/2 by sodium hydroxide solutions at 50 °C. Variation of rate constants with mean ionic activity of reaction solution.

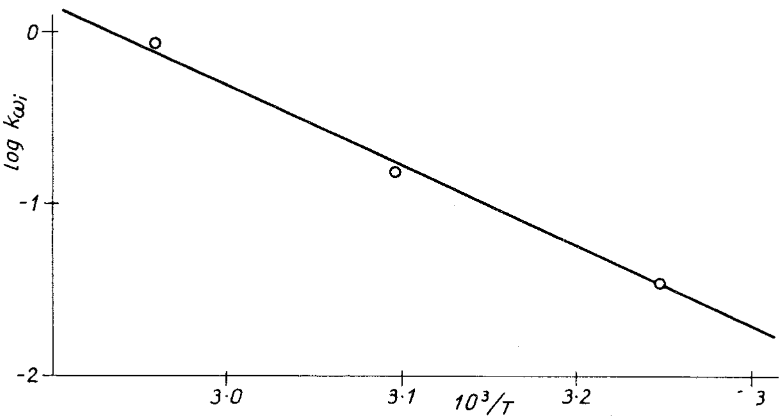

Fig. 3. Dissolution of Boehmite *P*5/2 by sodium hydroxide solution ($C=2$ *M*) at different temperatures. Variation of rate constants with temperature.

Equation [1] then becomes more generally,

$$\frac{dW}{dt} = -k_{wi}\,W_t^{4/3}\,a_{\pm}\ \text{g h}^{-1}. \qquad [4]$$

3.2.3 Powder surface area

Rate constants for dissolution by any hydroxide solution (at any temperature) increased with increasing initial surface area. The k_{wi} values for reactions with the finer Boehmite *P*5/30 m were about six times the k_{wi} values for reactions with the well-crystallised Boehmite *P*5/8: however, the rates of dissolution even of powder *P*5/30 m were markedly lower than the rates of reaction of amorphous pseudo-boehmite powders (2).

3.2.4 Temperature

The rates of dissolution by any hydroxide solution increased five-six times for a 15 °C rise in temperature. Generally, the rate constants increased exponentially with reciprocal temperature; refer to fig. 3. Energies of activation were then determined from the relation,

$$E_{act} = \frac{R\partial \ln k_{wi}}{\partial(^1/_T)}\ \text{kJ mole}^{-1} \qquad [5]$$

The E_{act} values were 115, 125 and 125 kJ mole^{-1} for the dissolution of powders *P*5/30m, *P*5/2 and *P*5/8 respectively.

4. *Discussion*

The experimental studies showed that the dissolution of recrystallised aluminium monohydroxide (Boehmite) precipitates takes place by a three-directional attack on the cylindrical particles; the rate of dissolution is controlled by a bimolecular reaction between hydroxyl ions adsorbed on the crystal surface and adjacent sites on the $-(\mathrm{Al\ O\ OH})-$ lattice (3, 5).

As a working model for the reactions studied in this work, we have considered the three-directional dissolution of W_0 g powder containing N_0 cylinders of initial length l_0 and thickness b_0 (where $b_0 = pl_0$). After time t there would be N_0 cylinders of length l_t and thickness b_t.

Then the powder weights at times $t = 0, t$ would be

$$W_0 = \pi N_0 \varrho b_0^2 l_0 = \pi N_0 \varrho p^2 l_0^3 \text{ g} \qquad [7A]$$

$$W_t = \pi N_0 \varrho b_t^2 l_t = \pi N_0 \varrho p^2 l_t^3 \text{ g} \qquad [7B]$$

The effective surface areas for three-directional dissolution at times $t = 0, t$ would be

$$\begin{aligned} A_{\mathrm{eff}0} &= eA_0 = (2\pi e N_0 k_0^2 + 2\pi e N_0 b_0 l_0) \\ &= 2\pi e N_0 (p^2 + p) l_0^2 \text{ m}^2 \qquad [8A] \end{aligned}$$

$$A_{\mathrm{eff}t} = eA_t = 2\pi e N_0 (p^2 + p) l_t^2 \text{ m}^2 \qquad [8B]$$

the initial specific surface areas would be

$$S_0 = \frac{A_0}{W_0} = \frac{2(p+1)}{\varrho p l_0} \text{ m}^2 \text{ g}^{-1} \qquad [9]$$

while the initial effective specific surface areas would be

$$S_{\mathrm{eff}0} = \frac{A_{\mathrm{eff}0}}{W_0} = \frac{2e(p+1)}{\varrho p l_0} \text{ m}^2 \text{ g}^{-1} \qquad [10]$$

Then at any time t,

$$A_{\mathrm{eff}t} = e\bar{A}\ W_t^{2/3} \text{ m}^2,$$

$$\text{where } \bar{A} = \frac{A_{\mathrm{eff}0}}{W_0^{2/3}}:$$

So equation [4] may be expressed as,

$$\begin{aligned} \frac{dW}{dt} &= -k_{wi} W_t^{4/3} a_{\pm} \\ &= -k_{Ai} A_{\mathrm{eff}t}^2 a_{\pm} \text{ g h}^{-1} \qquad [11] \end{aligned}$$

where $k_{Ai} \left(= \dfrac{k_{wi}}{e^2 \bar{A}^2}\right)$ is the rate constant w.r.t. powder effective surface area.

k_{wi} values in fact depend on k_{Ai} and $A_{\mathrm{eff}0}$ according to the relation,

$$k_{wi} = \frac{k_{Ai} A_{\mathrm{eff}0}^2}{W_0^{4/3}}.$$

Crystal structure defects would be minimal for the Boehmite $P5/8$ prepared by prolonged recrystallisation; for this material, it was assumed that $(S_{\mathrm{eff}0})_x$ equalled $(S_0)_x$; then for the other Boehmites, $S_{\mathrm{eff}0}$ would equal $\sqrt{\dfrac{k_{wi}}{(k_{wi})_x}} \cdot (S_0)_x$ [3].

The effective surface areas for the rapid dissolution of the first thirty percent of the finer powders were estimated from the above relation; these were in fact eighty to one hundred percent the overall surface areas (S_0) estimated from crystal lengths; so, these materials were also highly crystalline.

The effective surface areas for the whole dissolutions were in turn about seventy-eighty percent of the initial values: the Boehmite powders then probably contained appreciable amounts of aggregated material.

Summary

Boehmite powders were prepared by controlled hydrolysis of aluminium isopropoxide solution and recrystallisation in hot water; these were cylinders (fibres) of lengths (l_0) = 0.06 to 0.10 μm. The dissolution of dilute suspensions of these powders in well-stirred sodium hydroxide solutions was studied at 35 ° to 65 °C. Reaction solid and solution were analysed after different times by chemical and physical methods.

Reaction occurred by three-directional dissolution of the cylinders: the reactions of the first (non-aggregated) thirty percent material were four-third order w.r.t. powder weight (and second order w.r.t. powder surface area). The initial rate constants k_{wi} ($\mathrm{g}^{-1/3}\ \mathrm{hr}^{-1}$) for reactions with sodium hydroxide of unit mean ionic activity at 20 °C varied from 0.012 to 0.040. Rate constants increased linearly with the mean ionic activity of the hydroxide solution and exponentially with reciprocal temperature, five-six times for 15 °C temperature rise. Energies of activation varied from 115–125 kJ mole^{-1}.

Zusammenfassung

Boehmit-Pulver wurden durch kontrollierte Hydrolyse von Aluminiumisopropoxid-Lösungen hergestellt und in heißem Wasser rekristallisiert. Die Kristalle bildeten Zylinder (Fasern) mit einer Länge von 0,06–0,10 μm. Die Auflösung dieser Präparate in ver-

dünnten Suspensionen in Natriumhydroxidlösungen wurde bei 35–65 °C untersucht. Festkörper und Lösung wurden nach vorgegebenen Zeiten analysiert.

Die Lösung erfolgt in einer 3dimensionalen Reaktion der Zylinder. Die Anfangsgeschwindigkeitskonstanten für Reaktionen mit Natriumhydroxidlösungen bei 20 °C variierte von 0,012 bis 0,040 ($g^{-1/3}$ h^{-1}). Die Geschwindigkeitskonstanten steigen linear mit der Ionenaktivität der Hydroxidlösungen und exponentiell mit der reziproken Temperatur. Aktivierungsenergien liegen zwischen 115 und 125 kJ mol^{-1}.

References

1) *Souza Santos, P.*, Kolloid Z. Z. Polymere **133**, 101 (1953).

2) *Packter, A.* and *H. S. Dhillon*, Kolloid Z. Z. Polymere **239**, 598 (1970).

3) *Packter, A.* and *H. S. Dhillon*, Colloid & Polymer Sci. **252**, 249 (1974).

4) *Yoldas, B. E.*, J. appl. Chem. **23**, 803 (1973).

5) *Packter, A.* and *H. S. Dhillon*, Z. Physikal. Chem., in print.

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