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## The Precipitation of Alumina Hydrate from Aluminate Solutions in the Presence of Some Higher Alcohols and Starch

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The effect of low concentrations of isopropyl alcohol, *n*-butyl alcohol, isovaleryl alcohol, glycol, glycerol, glucose and starch on the rate of precipitation of alumina hydrate from metastable aluminate solutions was studied. The changes of electric conductivity during the precipitation were also measured. Only glycol accelerated the precipitation of alumina hydrate at concentrations covered by the experiments; the other substances retarded the precipitation. Glycerol in a concentration of about 0.2 M/l., glucose in a concentration of 6.7 g./l., and starch in a concentration of 6.7 g/l. prevented the precipitation.

A previous paper by H. Iveković, T. Vrbaški and D. Pavlović<sup>1</sup> dealt with the effects of addition of methanol on the viscosity of aluminate solutions prior to the precipitation of alumina hydrate. In this connexion it seemed interesting to examine the effect of alcohols upon the rate of precipitation of alumina hydrate from metastable aluminate solutions. In the present paper, the results obtained with isopropyl alcohol, *n*-butyl alcohol, isovaleryl alcohol, glycol, glycerol, glucose and starch are reported, while the results with lower alcohols, as well as the conclusions which may be drawn from the experimental material as a whole, are left for a subsequent publication.

### EXPERIMENTAL

#### *Preparation of the aluminate solutions*

The solution of sodium aluminate was prepared in the way described in our previous paper<sup>1</sup>.

Stock solutions containing on the average 1.489 M/l.  $\text{Al}_2\text{O}_3$  and 2.195 M/l.  $\text{Na}_2\text{O}$  were used. The experiments were performed with solutions obtained from these stock solutions by diluting them with water and an alcohol to a final concentration of about 1.0 M/l.  $\text{Al}_2\text{O}_3$ . In the case of *n*-butyl alcohol and isopropyl alcohol smaller quantities were taken because of their lower solubility.

Measurements were started as soon as the solution of selected concentration was prepared, with addition of alcohol or otherwise, and were continued until about 60 mole per cent of the alumina hydrate contained in the solution had precipitated. This took about 40 or 45 hours.

The aluminate solutions were contained in stoppered Erlenmeyer flasks, shaken all the time by a mechanical device. All the experiments were carried out in a constant temperature water bath at  $30 \pm 0.1^\circ\text{C}$ .

The  $\text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  in the solution were determined by titration with 1 N HCl with tropaeolin 00 and phenolphthalein as indicators<sup>2</sup>. By continuing the addition of acid until the solution became reddish-onion coloured, results were obtained in close accordance with those obtained gravimetrically.

At appropriately spaced intervals of time samples were taken from the flasks. Only the supernatant liquid above the precipitate, which quickly settled when the shaking was discontinued, was taken for the analysis.

During the precipitation of alumina hydrate the electric conductivity of the clear solution was also determined.

*Precipitation of alumina hydrate from aluminate solutions in presence of isopropyl alcohol, n-butyl alcohol and isovaleryl alcohol*

For these experiments aluminate solution I was used, the composition of which is shown in Table I. This solution was obtained by dilution 100 ml. of the stock solution with water, or with water and an alcohol, to the volume of 150 ml.

TABLE I  
Composition of aluminate solutions

Solution	M Al <sub>2</sub> O <sub>3</sub> /l.	M Na <sub>2</sub> O/l.	Caustic ratio
I	0.984	1.510	1.532
II	1.007	1.510	1.500
III	0.984	1.368	1.390

Referring to Fig. 1, curves  $a_1$ — $a_3$  show the effect of isopropyl alcohol (10 ml.), *n*-butyl alcohol (1 ml.) and isovaleryl alcohol (1 ml.) respectively on the rate of precipitation of alumina hydrate from aluminate solutions I composed as shown in Table I. Curve  $a_0$  relates to the spontaneous precipitation of alumina hydrate.

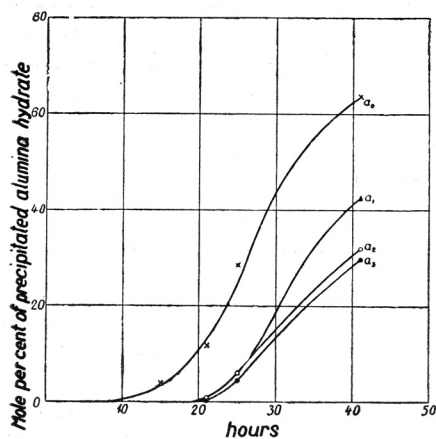


Fig. 1.

Figure 1. The effect of isopropyl alcohol, *n*-butyl alcohol and isovaleryl alcohol on the rate of precipitation of alumina hydrate from aluminate solution. Curve  $a_0$  — 10 ml. = 0.868 M of isopropyl alcohol per liter;  $a_1$  — 1 ml. = 0.0726 M of *n*-butyl alcohol per liter and  $a_3$  — 1 ml. = 0.0610 M of isovaleryl alcohol per liter at 30°C. Curve  $a_0$  relates to the spontaneous precipitation of alumina hydrate from the same solution. Volume of the aluminate solution was 150 ml.

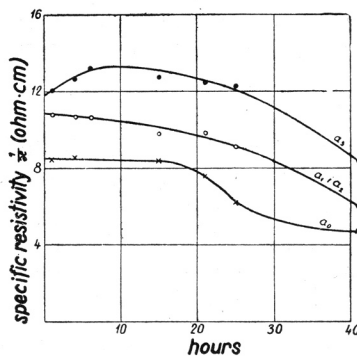


Fig. 2.

Figure 2. Changes of electric resistivity of aluminate solutions during precipitations of alumina hydrate in presence of different alcohols at 30°C. Curve  $a_0$  — without addition;  $a_1$  — with 10 ml. = 0.862 M of isopropyl alcohol per liter;  $a_2$  — with 1 ml. = 0.073 M of *n*-butyl alcohol per liter, and  $a_3$  — with 1 ml. = 0.061 M of isovaleryl alcohol per liter.

In the spontaneous process (curve  $a_0$ ), 10.0 mole per cent of the alumina hydrate originally present in the solution was precipitated in 20 hours. After 41 hours of precipitation this quantity amounted to 63.6 mole per cent.

In the presence of the above mentioned alcohols the rate of precipitation decreased markedly (curves  $a_1 - a_3$ ).

This, as an example, addition of 10 ml. of isopropyl alcohol resulted in a reduction of the amount of alumina hydrate precipitated in a reduction of the amount of alumina hydrate precipitated after 41 hours to 42.0 mole per cent, addition of 1 ml. of *n*-butyl alcohol to 32.0 mole per cent, of 1 ml. of isovaleryl alcohol to 28.8 mole per cent.

Fig. 2 shows the changes of specific electric resistivity ( $1/\kappa$ ) of aluminate solutions, in presence of the above mentioned alcohols.

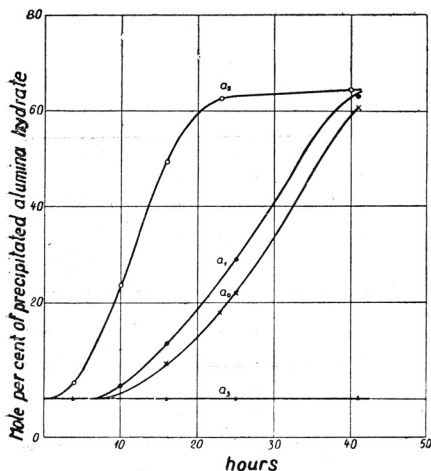


Fig. 3.

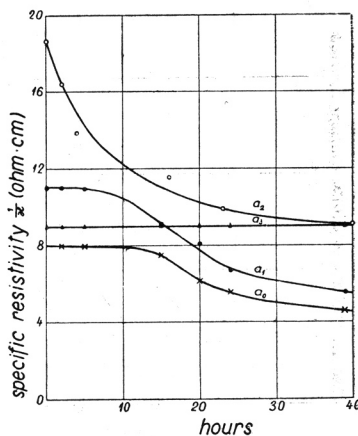


Fig. 4.

Figure 3. The effect of glycol and glycerol on the rate of precipitation of alumina hydrate from aluminate solution. Curve  $a_1$  — with 10 ml. = 1.19 M of glycol per liter;  $a_2$  — with 30 ml. = 3.58 M of glycol per liter and  $a_3$  — with 2 ml. = 0.182 M of glycerol per liter, at 30° C. Curve  $a_0$  relates to the spontaneous precipitation of alumina hydrate from the same solution. Volume of the aluminate solution was 150 ml.

Figure 4. Changes of electric resistivity of aluminate solutions during the precipitation of alumina hydrate in presence of different quantities of glycol or glycerol at 30°. Curve  $a_0$  — without addition;  $a_1$  — with 10 ml. = 1.18 M of glycol per liter;  $a_2$  — with 30 ml. = 3.58 M of glycol per liter and  $a_3$  — with 2 ml. = 0.182 M of glycerol per liter.

### Precipitation of alumina hydrate from aluminate solutions in presence of glycol and glycerol

For this run of experiments aluminate solution II was used, the composition of which is shown in Table I.

Referring to Fig. 3, curves  $a_1$  and  $a_2$  show the effect of glycol (10 and 30 ml.) on the rate of precipitation of alumina hydrate from aluminate solution II composed as shown in Table I. Curve  $a_0$  relates to the spontaneous precipitation of alumina hydrate from aluminate solution.

In the spontaneous process (curve  $a_0$ ), 12.8 mole per cent of the alumina hydrate originally present in the solution was precipitated in 20 hours. After 40 hours of precipitation this quantity amounted to 59.4 mole per cent.

The presence of glycol gradually increased the rates of precipitation. On addition of 3.58 moles per liter (curve  $a_2$ ), the quantity of alumina hydrate precipitated after 20 hours is 59.6 mole per cent. After 40 hours this quantity amounts to 64.4 mole per cent.

It is apparent that glycol accelerates considerably the precipitation of alumina hydrate in the first part of the process.

The difference between the quantity of hydrate precipitated in presence of 3.58 moles of glycol per liter and the quantity precipitated spontaneously amounted to 46.8 mole per cent after 20 hours, as compared with 5.0 mole per cent after 40 hours.

The shape of the curves of precipitation in these cases disclosed an autocatalytic process.

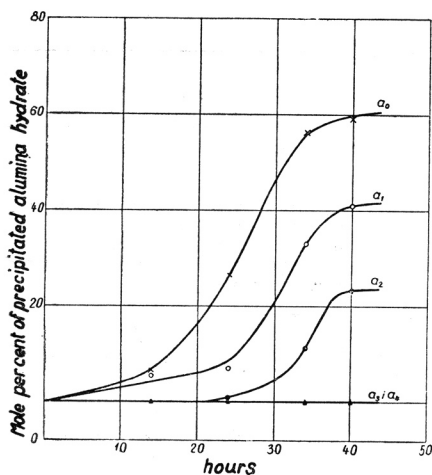


Fig. 5.

Figure 5. The effect of glucose and starch on the rate of precipitation of alumina hydrate from aluminate solutions. Curve  $a_1$  — 0.67 g. glucose per liter;  $a_2$  — 0.67 g. starch per liter;  $a_3$  — 6.7 g. glucose per liter and  $a_4$  — 6.7 g. starch per liter, at 30°C. Curve  $a_0$  relates to the spontaneous precipitation of alumina hydrate from aluminate solutions at 30°C. Volume of the aluminate solution was 150 ml.

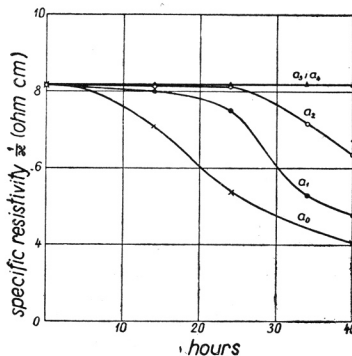


Fig. 6.

Figure 6. Changes of electric resistivity of aluminate solutions during precipitation of alumina hydrate in presence of glucose and starch at 30°C. Curve  $a_0$  — without addition;  $a_1$  — 0.67 g. glucose per liter;  $a_2$  — 0.67 g. starch per liter and  $a_3$ — $a_4$  — 6.7 g. starch and glucose respectively per liter. Volume of the aluminate solution was 150 ml.

Moreover, it was found that glycerol in a concentration as low as 0.182 M/l. completely inhibited the precipitation of alumina hydrate from aluminate solutions.

Figure 4 shows the change in specific electric resistivity ( $1/\kappa$ ) of aluminate solutions in presence of glycol and glycerol.

#### *Precipitation of alumina hydrate from aluminate solutions in presence of glucose and starch*

For this run of experiments aluminate solution III was used (Table I).

Referring to Fig. 5, curves  $a_1$  and  $a_2$  show the influence of glucose (0.67 g./l.) and starch (0.67 g./l.) on the rate of precipitation of alumina hydrate

from aluminate solution III having a composition shown in Table I. Curve  $a_0$  relates to the spontaneous precipitation.

In the spontaneous process (curve  $a_0$ ), 12.8 mole per cent of the alumina hydrate originally present in the solution was precipitated in 20 hours. After 40 hours this quantity amounted to 40.8 mole per cent.

In the presence of glucose and starch, the rate of precipitation of alumina hydrate from aluminate solutions was considerably diminished (curves  $a_1$  and  $a_2$ ). On addition of 0.1 g. of glucose to the aluminate solution (curve  $a_1$ ), the quantity of alumina hydrate precipitated after 20 hours was 6.2 mole per cent; after 40 hours of precipitation this quantity amounted to 40.8 mole per cent.

On addition of 0.67 g. of starch per liter to the aluminate solution (curve  $a_2$ ) the quantity of alumina hydrate precipitated after 40 hours was 23.4 mole per cent only, whereas after 20 hours no precipitation took place.

The differences between the quantity of alumina hydrate precipitated in presence of glucose and starch, and the quantity precipitated spontaneously was, after 20 hours, 6.6 mole per cent in presence of starch. After 40 hours of precipitation this difference amounted to 18.8 mole per cent in the presence of glucose and 36.2 mole per cent in the presence of starch.

The shape of the curves reveals, as in the previous cases, an autocatalytic process.

Concentrations of glucose or starch superior to 0.1 g. per 150 ml. of aluminate solution corresponding to 0.67 g./l. stabilized the aluminate solution to such an extent, that no precipitation took place even after 600 hours (cf. curves  $a_3$  and  $a_4$ , Fig. 5).

These experiments may have some significance for the alumina production by the Bayer's process if starch is added before or after the extraction of bauxite to accelerate the settling up of the red mud.

Figure 6 shows the changes of specific electric resistivity (1%) of aluminate solutions in presence of glucose and starch.

#### REFERENCES

1. H. Iveković, T. Vrbaški and D. Pavlović, *Croat. Chem. Acta* **28** (1956) 41.
2. E. Herrmann, *Arhiv kem.* **21** (1949) 218.

#### IZVOD

#### Izlučivanje aluminijevog oksihidrata iz aluminatnih lužina u prisutnosti nekih viših alkohola i škroba

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Ispitano je djelovanje malih koncentracija izo-propanola, *n*-butanola, izo-pentanola, glikola, glicerola, glukoze i škroba na izlučivanje aluminijevog oksihidrata iz metastabilnih aluminatnih lužina. Za vrijeme taloženja mjerena je i električna vodljivost. Kod koncentracija upotrebljenih u pokusima samo glikol ubrzava izlučivanje aluminijevog oksihidrata, dok ostale navedene tvari usporavaju izlučivanje. Glicerol u koncentraciji od cca 0.2 M/l., glukoza u koncentraciji od 6.7 g./l. i škrob u koncentraciji od 6.7 g./l. potpuno sprečavaju izlučivanje.

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