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# Viscosity, Specific Gravity, and Equilibrium Concentration of Sodium Aluminate Solutions

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## INTRODUCTION

The properties of sodium aluminate solutions have been measured and reported by a large number of investigators, particularly because the varying conditions that prevail in individual Bayer plants preclude universal acceptance of published data. Also of great interest to chemists are the unique characteristics of sodium aluminate solutions, among which their instability ranks high.

Fulda and Ginsberg[1] published the results of extensive measurements on the solubility of $\alpha$-$Al_2O_3 \cdot 3H_2O$ (gibbsite) in caustic soda solution. They claim that at temperatures above 100°C the stable dispersed phase is $\alpha$-$Al_2O_3 \cdot H_2O$ (boehmite) and that the solubility at these temperatures is lower than that at lower temperatures as a result of the transformation of gibbsite to the less soluble boehmite. Russell et al.[2] determined the solubilities of gibbsite, boehmite, and $\beta$-$Al_2O_3 \cdot 3H_2O$ (bayerite) and also determined the specific gravities of the corresponding sodium aluminate solutions.

Many other authors[3–5] also studied the properties of aluminate solutions. While the data, as reported, are very important from a theoretical point of view, the literature contains very few papers that cover a sufficiently broad range of conditions to be of practical value to alumina plant engineers.

In the light of this shortcoming, the authors ran many series of tests for the purpose of obtaining data in a suitably convenient form for use in basic studies and in industrial analysis of various stages of the Bayer process (including bauxite digestion, sedimentation, filtration of red mud, crystallization and filtration of aluminum hydroxide, as well as engineering studies, e.g., of piping, pumps, etc.).

Since the plant with which the writers are connected uses exclusively a gibbsitic bauxite of tropical origin, the tests were limited to this type of material.

## PROCEDURE

### Materials

#### *Caustic Soda Solution*

First grade sodium hydroxide, as specified in Japanese Industrial Standard K-8576 was dissolved in distilled water.

Aluminum turnings (used to facilitate dissolution) were dissolved in this caustic solution, the impurities were filtered off, and the solution was adjusted to the desired concentration. Such solutions were then used in the specific gravity and viscosity measurements.

#### *Aluminum Hydroxide*

To a solution containing 160 g/liter NaOH and 123 g/liter $Al_2O_3$ (mole ratio $Na_2O/Al_2O_3 = 1.66$), prepared as described above, was added aluminum hydroxide solution in an amount corresponding to 5% by weight of $Al_2O_3$. The samples used in the experiments were obtained by stirring for 72 hr at 60°C, filtering, washing with water, and drying the crystallized product. Average grain size of the product was 20 $\mu$ (3% were less than 3 $\mu$ in size and 0.5% were less than 1 $\mu$).

### Analytical Method

The NaOH content in the sodium aluminate solutions was determined volumetrically using phenolphthalein indicator. The $Al_2O_3$ concentration was determined gravimetrically on igniting the product of an $NH_4OH$ precipitation.

### Measuring the Specific Gravity

An Ostwald-type pycnometer made in our laboratory (capacity about 50 ml) was used. The specific gravity of the solutions was related to distilled water. The thermostatted bath was controlled to within 0.1°C.

### Measuring the Viscosity

In measuring viscosity, the authors used a Cannon-Fenske type of viscometer, as specified in Japanese Industrial Standard K-2203. With this viscometer, viscosity is measured (as it is in the Ostwald viscometer) by clocking the time it takes for the solution to pass through a capillary tube. Since these viscometers come in various sizes, we selected that through which the solution would flow in 3–5 min. The viscometers were calibrated against distilled water.

### Measuring the Equilibrium Concentration

One of the prominent characteristics of sodium aluminate is its pronounced metastability. Consequently, if the concentration is assessed by measuring the amount of alumina dissolved, the result will be close to the actual value. By contrast, if the crystallization approach is used, equilibrium is not readily reached, particularly at low temperatures. In view of these facts, the authors used the following method.

One-hundred milliliters of the above-mentioned caustic soda solution were introduced into a 150-ml steel beaker, and aluminum hydroxide was added to a $Na_2O/Al_2O_3$ mole ratio of 0.5.

The solution was then divided into two parts. The aluminum hydroxide concentration in one vessel was increased to a point above the equilibrium concentration by the simple device of preheating this solution to a temperature above that used in that particular test. The solution in the other vessel was not changed. Both vessels were then placed in a tumbling shaker immersed in a controlled-temperature glycerin bath. The vessels were removed from the shaker at periodic intervals, cooled, and small samples of the contents were withdrawn for analysis. The vessels were then returned to the shaker and tumbling was resumed. This operation was repeated until the mole ratio $Na_2O/Al_2O_3$ became stable. Data obtained at 130°C reveal that where boehmite was the dispersed phase, the alumina concentration in solution rose at one point and then decreased gradually. Therefore, the maximum concentration obtained was taken as the practical equilibrium concentration of gibbsite.

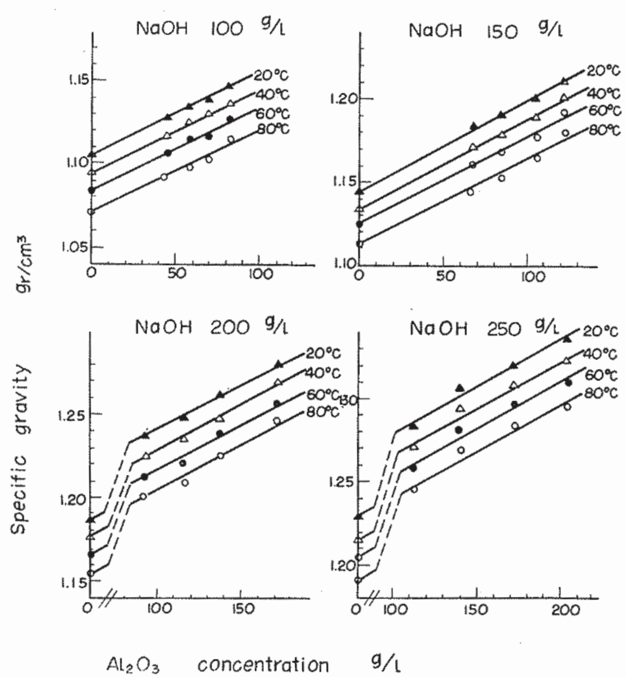


Fig. 1. Specific gravity of sodium aluminate solutions.

## EXPERIMENTAL RESULTS

### Specific Gravity and Viscosity of Sodium Aluminate Solutions

The experimental data are given in Figures 1 and 2 and Table I.

TABLE I
Specific Gravity and Viscosity of Sodium Aluminate Solutions[a]

| NaOH g/liter | $Al_2O_3$ g/liter | 20°C sp. g. | 20°C v | 40°C sp. g. | 40°C v | 60°C sp. g. | 60°C v | 80°C sp. g. | 80°C v |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0.998 | 1.005 | 0.992 | 0.653 | 0.983 | 0.470 | 0.972 | 0.356 |
| 100.0 | 0 | 1.105 | 1.84 | 1.095 | 1.14 | 1.085 | 0.81 | 1.071 | 0.58 |
| | 45.3 | 1.125 | 2.12 | 1.115 | 1.29 | 1.105 | 1.90 | 1.092 | 0.65 |
| | 58.9 | 1.132 | 2.25 | 1.122 | 1.36 | 1.112 | 0.92 | 1.097 | 0.66 |
| | 69.9 | 1.138 | 2.32 | 1.128 | 1.39 | 1.116 | 0.95 | 1.103 | 0.68 |
| | 83.1 | 1.146 | 2.46 | 1.136 | 1.49 | 1.124 | 1.01 | 1.112 | 0.71 |
| 150.0 | 0 | 1.147 | 2.52 | 1.136 | 1.47 | 1.126 | 1.02 | 1.111 | 0.73 |
| | 67.6 | 1.183 | 3.34 | 1.172 | 1.87 | 1.160 | 1.25 | 1.146 | 0.88 |
| | 86.4 | 1.190 | 3.54 | 1.179 | 2.00 | 1.168 | 1.31 | 1.153 | 0.91 |
| | 106.4 | 1.200 | 3.87 | 1.189 | 2.14 | 1.177 | 1.40 | 1.166 | 0.95 |
| | 124.4 | 1.212 | 4.28 | 1.201 | 2.35 | 1.190 | 1.48 | 1.179 | 1.03 |
| 200.0 | 0 | 1.189 | 3.52 | 1.178 | 1.99 | 1.166 | 1.33 | 1.154 | 0.90 |
| | 91.5 | 1.238 | 5.40 | 1.226 | 2.75 | 1.213 | 1.74 | 1.200 | 1.19 |
| | 115.6 | 1.248 | 5.90 | 1.236 | 3.07 | 1.224 | 1.88 | 1.210 | 1.25 |
| | 139.2 | 1.262 | 6.84 | 1.249 | 3.41 | 1.238 | 2.07 | 1.225 | 1.35 |
| | 171.0 | 1.280 | 8.42 | 1.270 | 4.03 | 1.257 | 2.32 | 1.246 | 1.54 |
| 250.0 | 0 | 1.229 | 5.05 | 1.217 | 2.59 | 1.205 | 1.67 | 1.190 | 1.10 |
| | 113.0 | 1.284 | 8.59 | 1.272 | 4.02 | 1.259 | 2.40 | 1.245 | 1.57 |
| | 141.6 | 1.306 | 10.63 | 1.294 | 4.74 | 1.280 | 2.77 | 1.270 | 1.81 |
| | 173.0 | 1.319 | 12.43 | 1.307 | 5.46 | 1.294 | 3.11 | 1.282 | 1.94 |
| | 206.0 | 1.334 | 15.24 | 1.321 | 6.33 | 1.309 | 3.48 | 1.294 | 2.13 |

[a] Specific gravity (sp. g.) is in g/cm³ and viscosity (v) is in centipoises.

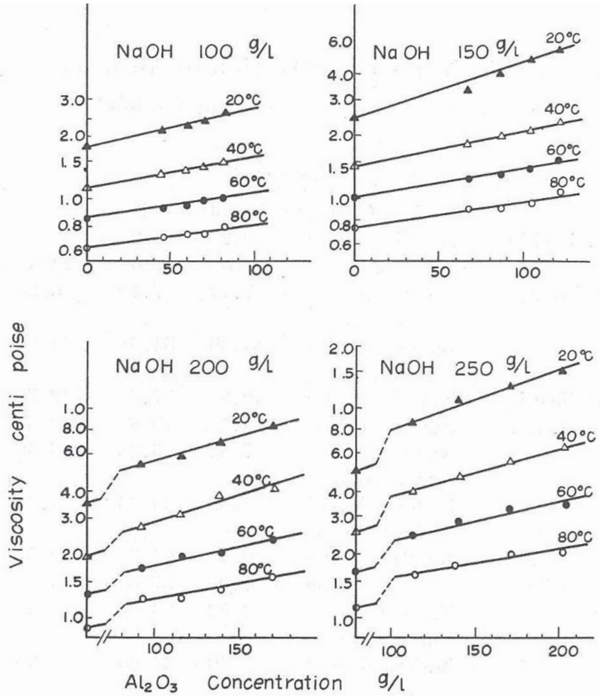


Fig. 2. Viscosity of sodium aluminate solutions.

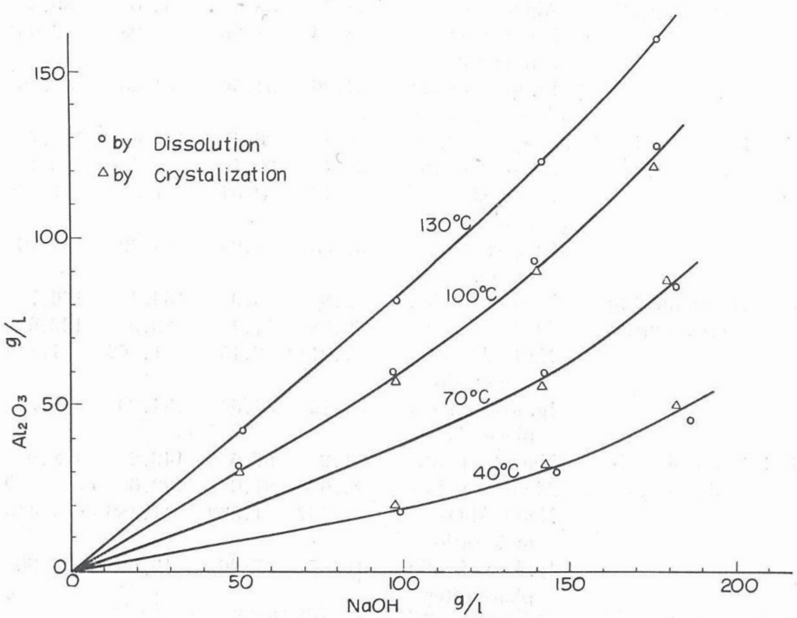


Fig. 3. Equilibrium concentration of alumina.

**Equilibrium Concentration of Alumina**

The concentrations are given in Figure 3 and Table II.

TABLE II

Equilibrium Concentration of Alumina

| | | | | | | |
|---|---|---|---|---|---|---|
| | Determined by dissolution | NaOH g/liter | 50.2 | 98.0 | 145.3 | 186.1 |
| | | $Al_2O_3$ g/liter | 9.0 | 17.6 | 29.6 | 45.2 |
| | | $Na_2O/Al_2O_3$ mole ratio | 7.12 | 7.10 | 6.26 | 5.24 |
| | | Ig. loss of solid phase, % | 34.30 | 34.58 | 34.62 | 34.26 |
| 40°C | Determined by crystallization | NaOH g/liter | 49.8 | 97.6 | 142.7 | 180.9 |
| | | $Al_2O_3$ g/liter | 8.1 | 19.8 | 32.0 | 49.9 |
| | | $Na_2O/Al_2O_3$ mole ratio | 7.84 | 6.28 | 5.68 | 4.62 |
| | | Ig. loss of solid phase, % | 34.82 | 34.33 | 34.60 | 34.42 |
| | Determined by dissolution | NaOH g/liter | 49.4 | 95.7 | 142.6 | 183.2 |
| | | $Al_2O_3$ g/liter | 17.9 | 37.6 | 59.2 | 86.2 |
| | | $Na_2O/Al_2O_3$ mole ratio | 3.52 | 3.24 | 3.07 | 2.71 |
| | | Ig. loss of solid phase, % | 34.40 | 34.60 | 34.30 | 34.60 |
| 70°C | Determined by crystallization | NaOH g/liter | 50.4 | 97.1 | 141.5 | 180.3 |
| | | $Al_2O_3$ g/liter | 18.7 | 38.0 | 55.0 | 86.8 |
| | | $Na_2O/Al_2O_3$ mole ratio | 3.44 | 3.26 | 3.28 | 2.65 |
| | | Ig. loss of solid phase, % | 34.20 | 34.56 | 34.23 | 34.48 |
| | Determined by dissolution | NaOH g/liter | 50.4 | 96.4 | 139.4 | 177.7 |
| | | $Al_2O_3$ g/liter | 30.4 | 60.1 | 93.4 | 128.1 |
| | | $Na_2O/Al_2O_3$ mole ratio | 2.12 | 2.04 | 1.905 | 1.768 |
| | | Ig. loss of solid phase, % | 34.35 | 33.98 | 34.49 | 34.10 |
| 100°C | Determined by crystallization | NaOH g/liter | 50.6 | 96.9 | 139.4 | 176.7 |
| | | $Al_2O_3$ g/liter | 29.3 | 57.4 | 89.9 | 122.0 |
| | | $Na_2O/Al_2O_3$ mole ratio | 2.21 | 2.15 | 1.962 | 1.845 |
| | | Ig. loss of solid phase, % | 34.42 | 34.64 | 34.20 | 34.34 |
| 130°C | Determined by dissolution | NaOH g/liter | 51.2 | 97.6 | 142.2 | 178.0 |
| | | $Al_2O_3$ g/liter | 42.6 | 81.0 | 122.6 | |
| | | $Na_2O/Al_2O_3$ mole ratio | 1.532 | 1.539 | 1.480 | 1.415 |
| | | Ig. loss of solid phase after reaction, % | 19.87 | 17.06 | 16.60 | 16.90 |

## DEVELOPMENT OF EXPERIMENTAL FORMULA

### Specific Gravity

As shown in Figure 1, the specific gravity of sodium aluminate solutions increases linearly with the $Al_2O_3$ concentration. This rate is the same at all NaOH concentrations and temperatures.

The ratio of $D$ (difference between the specific gravities $D_{Al}$ of sodium aluminate and $D_{Na}$ of the caustic soda solution) to $Al_2O_3$ concentration may be computed as follows:

$$D/Al_2O_3 \text{ (g/liter)} = 0.00049 \text{ (g/cm}^3\text{)/(g/liter)} \quad (1)$$

On the other hand, the specific gravity of the caustic soda solution $D_{Na}$ is given by a binary equation for NaOH concentration and temperature, as shown in Figure 4.

$$D_{Na} = 1.027 + 0.0008985N - 0.0000025N^2 - 0.000395T - 0.000002T^2 \quad (2)$$

From eqs. (1) and (2)

$$D_{Al} = 1.027 + 0.0008985N - 0.0000025N^2 - 0.000395T - 0.000002T^2 + 0.00049A \quad (3)$$

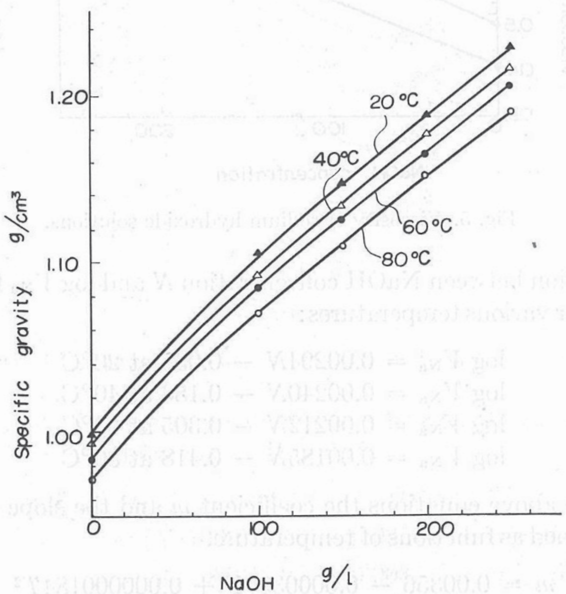

Fig. 4. Specific gravity of sodium hydroxide solutions.

where $N$ is the caustic soda solution, g/liter; $T$ is the temperature, °C; and $A$ is the alumina concentration, g/liter.

### Viscosity

As seen from Figure 5, the plot of log viscosity versus sodium hydroxide concentration is linear:

$$\log V_{Na} = m\,N - n \quad (4)$$

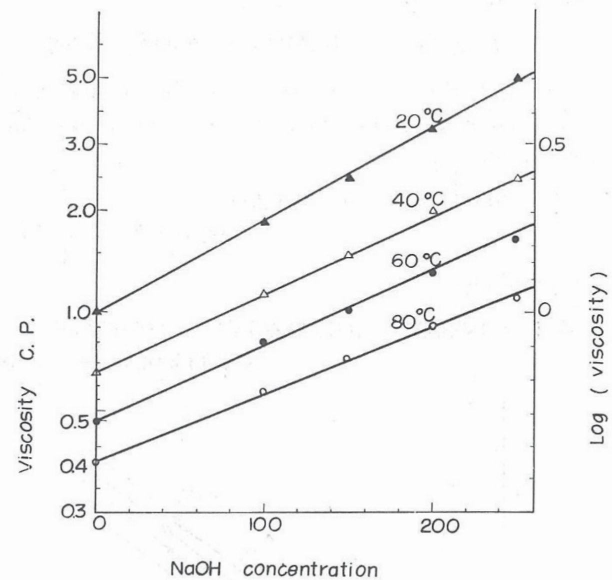

Fig. 5. Viscosity of sodium hydroxide solutions.

The relation between NaOH concentration $N$ and log $V_{Na}$ from Figure 5 is given for various temperatures:

$$\begin{aligned} \log V_{Na} &= 0.00294N - 0.035 \text{ at } 20°C \\ \log V_{Na} &= 0.00240N - 0.186 \text{ at } 40°C \\ \log V_{Na} &= 0.00212N - 0.305 \text{ at } 60°C \\ \log V_{Na} &= 0.00185N - 0.418 \text{ at } 80°C \end{aligned} \quad (5)$$

From the above equations the coefficient $m$ and the slope $n$ of eq. (4) are determined as functions of temperature.

$$\begin{aligned} m &= 0.00356 - 0.0000357T + 0.000000184T^2 \\ n &= 0.0857 - 0.00658T - 0.0000023T^2 \end{aligned} \quad (6)$$

The viscosity $V_{Na}$ of the caustic soda solutions can then be calculated

$$\log V_{Na} = (0.00356 - 0.0000357T + 0.000000184T^2)N + 0.0857 - 0.00658T + 0.0000023T^2 \quad (7)$$

The per cent increase in viscosity of $V_{Al}$ per g/liter of $Al_2O_3$ is computed by determining the difference between $V_{Al}$ and $V_{Na}$ following the functional transformation, as shown above. The results are given in Figure 6.

$$\Delta V = (3.23 + 0.0034N - 0.1246T + 0.00204T^2 - 0.00001107T^3)/1000 \quad (8)$$

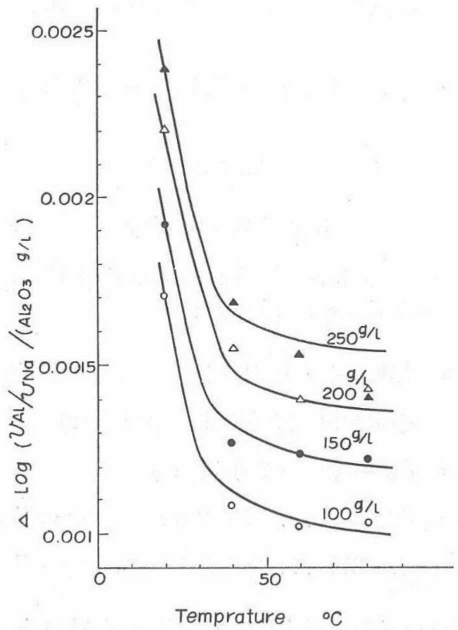


Fig. 6. Relation between log $(V_{Al}/V_{Na})$ and alumina concentration.

The viscosity $V_{Al}$ of sodium aluminate solutions can then be obtained by eq. (9), developed from eqs. (7) and (8).

$$\log V_{Al} = (0.0857 - 0.00658T + 0.0000023T^2) + (N/1000)(3.56 - 0.0357T + 0.000184T^2) + (A/1000)(3.23 - 0.0034N - 0.1246T + 0.00204T^2 - 0.00001107T^3) \quad (9)$$

### Equilibrium Concentration of Alumina

The equilibrium concentration $A$ at 40°C is related to NaOH concentration, as based on 8 measurements at 40°C.

$$\log A \sim 40 = 1.3032 \log N - 1.2984 \quad (10)$$

At temperatures in excess of 70°C, the incremental equilibrium concentration per °C varies with $N$ as follows:

$$A = -0.0617 + 0.007549N \quad (11)$$

From this the equilibrium concentration can be determined at various temperatures.

$$A = N^{1.3032}/19.88 + (0.007549N - 0.0617)(T - 40) \quad (12)$$

## DISCUSSION

### Specific Gravity

Russell et al.[2] gave a formula for calculating the specific gravity of sodium aluminate solutions, as follows:

$$d = 1.002 + 0.00125 \times (\text{g } Na_2O \text{ per liter}) + 0.0005 \times (\text{g } Al_2O_3 \text{ per liter})$$

$$d_t = d_{25} - (T - 25) \times \alpha \quad (13)$$

$$\alpha = 0.00075 \ldots \quad 75\text{–}100 \text{ g } Na_2O \text{ per liter}$$

$$= 0.00077 \ldots \quad 100\text{–}125 \text{ g } Na_2O \text{ per liter}$$

The increase in specific gravity per g/liter of $Al_2O_3$ is 0.0005 according to Russell et al. Sato[4] measured the specific gravity and viscosity at 30 and 50°C and claimed that the specific gravity is primarily a function of $Al_2O_3$ concentration. While Sato did not specify the value of the incremental factor, the authors have computed this from Sato's data as 0.0006 on the average. These values may be considered to be in good agreement. The specific gravity values for NaOH solutions obtained by the authors are in good agreement with the data reported in Gmelin.[6]

The data obtained and the equations developed by the authors conform to previous data and are sufficiently simplified to permit ready use.

## Viscosity

In his paper, Sato also proposed an equation for the viscosity of sodium aluminate solutions:

$$\log \eta/\eta_0 = kx$$

where $\eta$ and $\eta_0$ are the viscosity of caustic soda and sodium aluminate solutions, respectively; $x$ is the alumina concentration; and $k$ is constant.

Sato found this to agree with Arrhenius's experimental equation for viscosity. Speaking of the viscosity of caustic soda and sodium aluminate solutions at 25°C, Pearson[7] noted a sharp rise in viscosity with decreasing $Na_2O/Al_2O_3$ mole ratio leading in extreme cases to a liquor as viscous as water glass or glycerin. Apart from these studies, the authors could find no comprehensive date on the viscosity of sodium aluminate solutions.

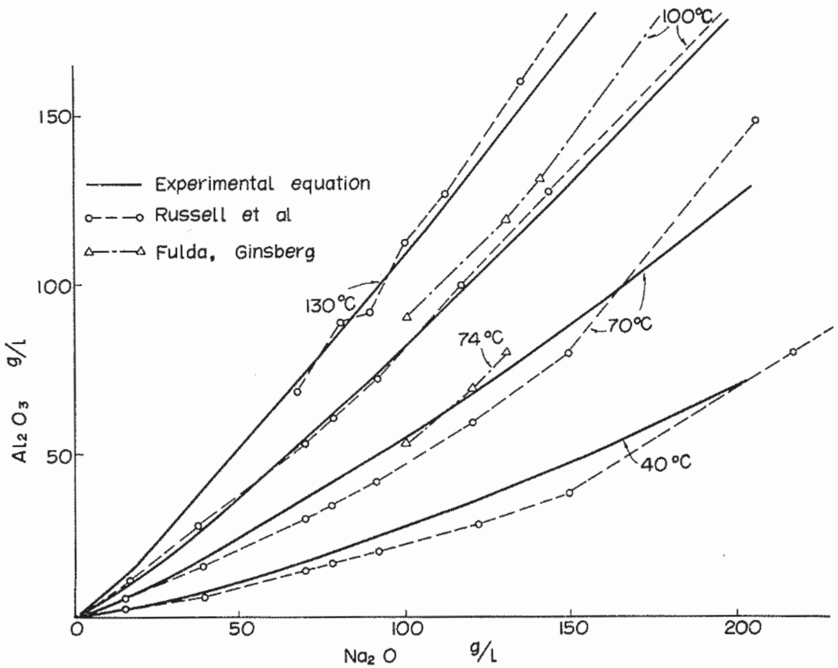


Fig. 7. Equilibrium concentration of alumina by some authors.

## Equilibrium Concentration of Alumina

A large body of information is available on the solubility of aluminum hydroxide in caustic soda solutions. Fulda and Ginsberg[1] reported experimental data in the range of 100–190 g/liter $Na_2O$ at 74–100°C. Russell et al.[2] investigated a wider range, 15–260 g/liter $Na_2O$ at 40–170°C.

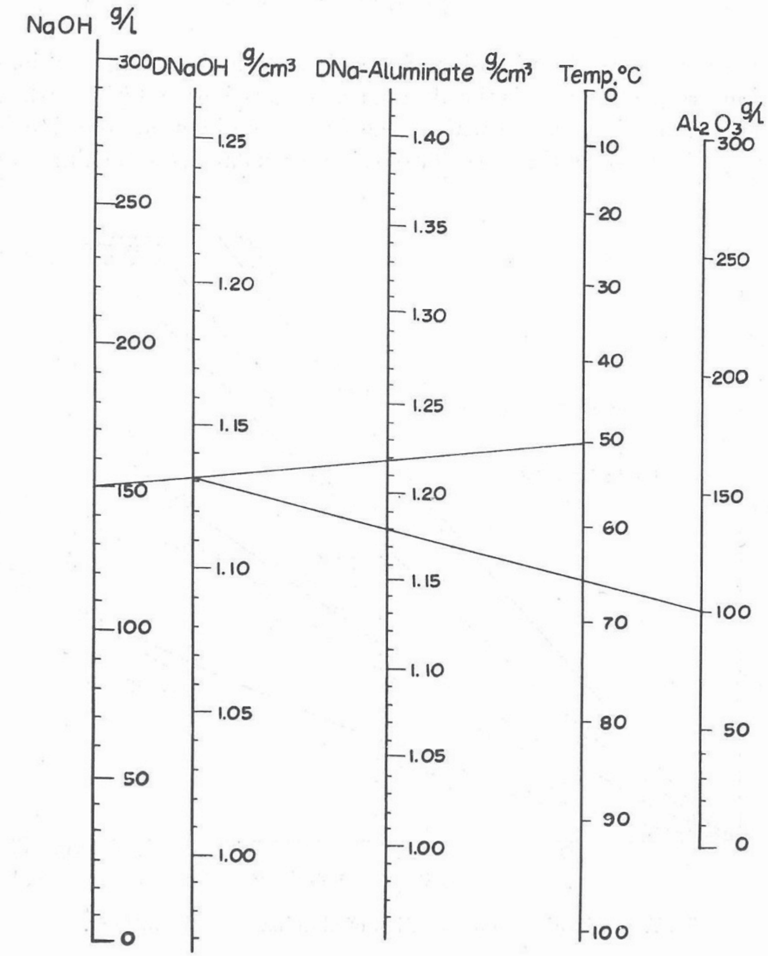


Fig. 8. Nomograph. Specific gravity of NaOH and sodium aluminate solutions.

It is interesting to note that there is good agreement between all the results, including those obtained by the authors, although some variances do exist (Fig. 7).

## REPRESENTATION IN NOMOGRAPH FORM

The experimental equations developed by the authors cover a broad range of conditions. However, since the desired data can be obtained

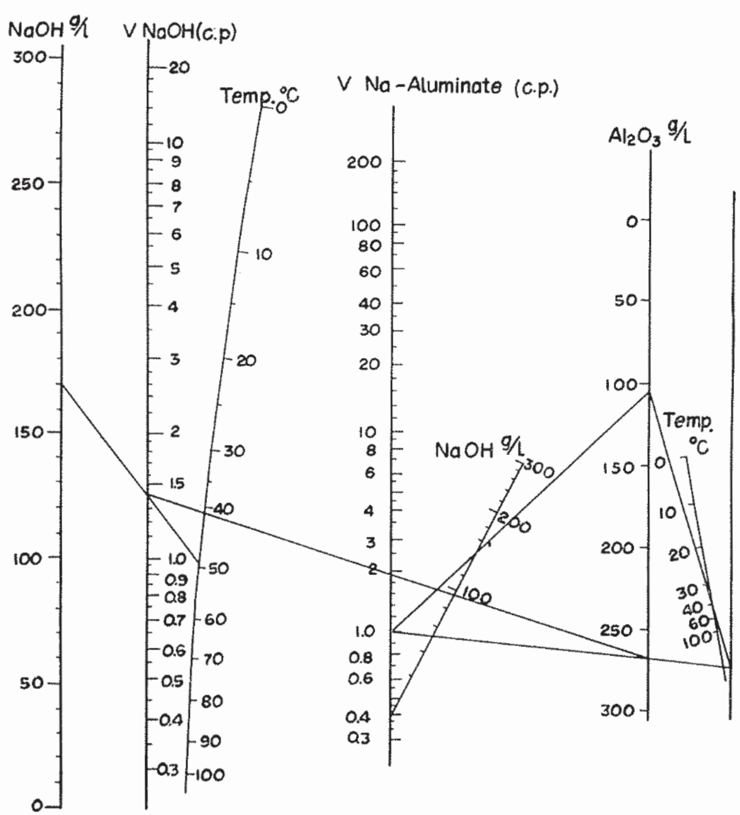


Fig. 9. Nomograph. Viscosity of NaOH and sodium aluminate solutions.

only by fairly complex calculations, the equations are inconvenient for practical use. Consequently, the authors have prepared graphic representations (nomographs) of these systems, as shown in Figures 8, 9, and 10.



## CONCLUSION

Measurements were made within the range of conditions of an operation using gibbsitic bauxite to determine the specific gravity, viscosity, and equilibrium concentration of alumina of sodium aluminate solutions.

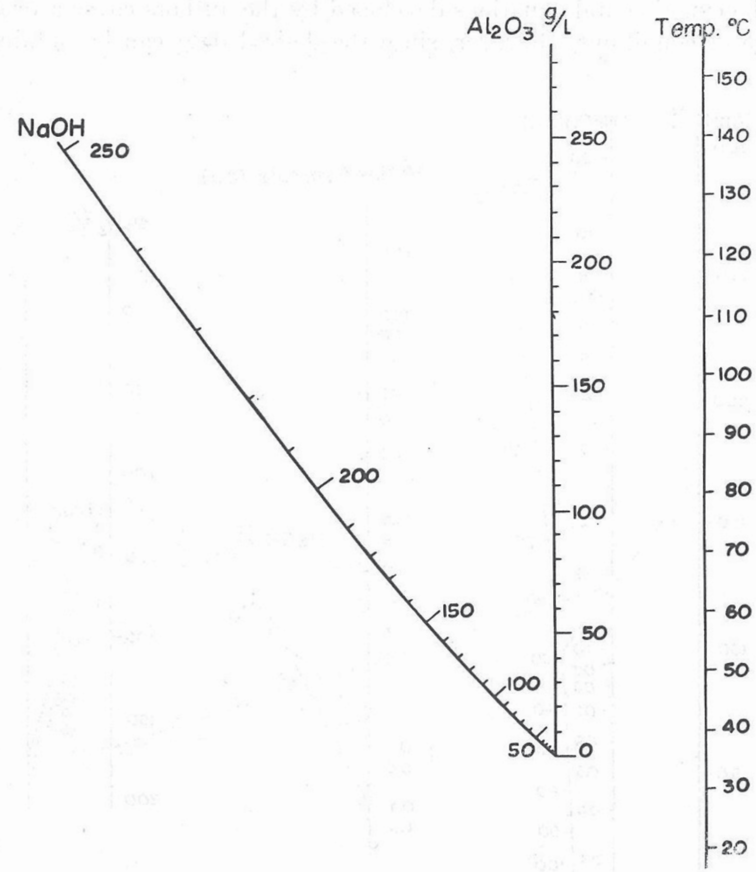


Fig. 10. Nomograph. Equilibrium $Al_2O_3$ concentration as a function of NaOH and temperature.

The results obtained were organized into equations and further simplified into nomographs. The data are in good accord with previously reported values and, moreover, are now available in a sufficiently convenient form for practical use.

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