

## INVESTIGATION OF COMPLEX EQUILIBRIA BY WATER-ACTIVITY MEASUREMENT

THE ALUMINATE-SODIUM HYDROXIDE SYSTEM

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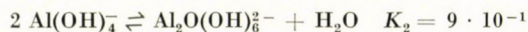
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A new method based on measurement of the water activity of the solutions was elaborated to study the complex equilibria in concentrated aqueous electrolyte solutions, and to determine the equilibrium constants.

Infrared study of solutions with various aluminium (1–6 *M*) and sodium hydroxide (6–14 *M*) concentrations, based on the earlier work by MOLENAAR *et al.* [12], confirmed that under the given conditions the two predominant aluminium-containing ions in the systems are the mononuclear  $\text{Al}(\text{OH})_4^-$ , and the binuclear ion  $\text{Al}_2\text{O}(\text{OH})_6^{2-}$ , formed from the mononuclear ion in a dehydration reaction.

On this basis, the equilibria of formation of these ions were studied *via* water-activity measurements. The water activities of the solutions are in close connection with the dehydration process resulting in dimer formation, and also with the effects of the individual ions which give rise to changes in the structure of the water and hence in the water activity, *i.e.* with the equilibrium ion concentrations. In this way, with certain simplifying conditions, the equilibrium constant was determined for the formation of  $\text{Al}_2\text{O}(\text{OH})_6^{2-}$ :



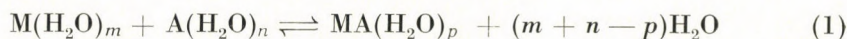
### Introduction

Study of the complex equilibria in concentrated aqueous electrolyte solutions, and determination of the complex stability constants, are in many cases not possible, or only with great difficulty, if the traditional methods are employed (potentiometric or spectrophotometric measurement of the equilibrium concentrations of the central atom, the ligand, or the complex ions).

In the aqueous electrolyte solution the formation of complexes in the solution has a considerable effect on the water activity, as the association or dissociation reactions are accompanied by changes in the hydration of the particles. Thus, it is to be expected that information on the complex-formation reactions in the solution can be obtained by following the water activity of the system.

In aqueous solution the ionic species taking part in complex formation, both cations and anions, are present in solvated form. Accordingly, dissolution of these ions decreases the activity of the water. Complex formation between the metal ions and ligands changes the solvation conditions in the system.

The customary stepwise complex-formation reactions can be written as follows, the changes occurring in the hydration of the reactants in the course of the process also being taken into account:



In accordance with this, in the equilibrium constants of these processes the free water activity of the solution figures as the corresponding power:

$$K_1 = \frac{[MA(H_2O)_p] [H_2O]^{m+n-p}}{[M(H_2O)_m] [A(H_2O)_n]}$$

$$K_2 = \frac{[MA_2(H_2O)_q] [H_2O]^{p+n-q}}{[MA(H_2O)_p] [A(H_2O)_n]}$$

where it is also taken into consideration that in the present system the water also figures as solvent, the free water activity being  $[H_2O]$ .

It should be noted that the water activity in the solution is further affected by the structure of the solvent itself, the formation of hydrogen-bonded associates, etc. Thus, in contrast with the situation for the other ligands the difference between the total water content of the solution and its measurable water activity cannot be regarded as the amount of coordinated water. The water activity change occurring during solvation and desolvation reactions can therefore be followed only in such a way that by definition the activity of pure distilled water in terms of mole fraction is taken as unity.

If the compositions (metal-ligand ratios) of the complexes formed in the reactions of the ions in solution are known, then if the water activity change is followed over a suitable, wide concentration interval, it is possible to determine the changes in water activity due to the individual species, and in the ideal case the equilibrium constant of the complex-formation process.

Accordingly, in systems in which for some reason the formation of the complex cannot be followed in the normal manner by measuring the change in concentration of the central atom, the ligand, or some complex, but on the other hand the compositions of at least the predominant complexes in the solution can be established by some structure-examination method, quantitative information on the complex equilibria can be obtained by means of measurement of the water activity.



**Equilibrium measurements in the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$  systems  
by the isopiestic water-activity measurement method**

On the basis of the above considerations, an equilibrium study by means of water-activity measurement was first attempted on the aluminate-sodium hydroxide system: in concentrated alkali solutions direct measurement of either the free ligand activity or the free metal ion activity involves great difficulties, whereas there is no obstacle to follow the change in water activity by the isopiestic method (Table I).

**Table I**

*Values of water activity of aqueous sodium hydroxide solutions,  
determined by the isopiestic method*

NaOH molality	$a_w$ [17]	$a_w$ measd.	$\Delta a_w$
11.45	0.489	0.4110	+0.002
11.47	0.403	0.4030	0.000
12.40	0.363	0.365	+0.002
12.65	0.350	0.351	+0.001

$a_w$  = water activity in mole fraction.  
 $\Delta a_w = a_w \text{ measd.} - a_w \text{ [17].}$

Quantitative evaluation of the data obtained with this method is possible if the structures of the dominant complex ions in solution can be assumed as known from data acquired with the aid of independent structure-examination methods [1-12].

Although contradictions too can be found among some of the literature data, on the basis of the Raman and infrared spectroscopic and NMR investigations of MOLENAAR *et al.* [12], and also taking into account the X-ray studies by JOHANSSON [13], we set out in our work from the following two equilibria:



With the aim of the determination of the equilibrium constants of these reactions, the isopiestic method was used to measure the water activities ( $a_w$ ) of solutions with different sodium hydroxide and aluminium concentrations (Table II).

Table II

Experimental data regarding isopiestic equilibrium study  
of the aluminate-sodium hydroxide system

A	B	$a_w$
0.1955	0	0.3072
0.2074	0.032	0.3072
0.2161	0.0501	0.3072
0.1940	0	0.3118
0.2077	0.0321	0.3118
0.2124	0.0493	0.3118
0.1759	0	0.3842
0.1951	0.0780	0.3842
0.2087	0.1004	0.3842
0.2146	0.12056	0.3842
0.1755	0	0.3863
0.1956	0.0782	0.3863
0.2093	0.1006	0.3863
0.2143	0.1204	0.3863
0.2426	0.035	0.2020
0.2432	0.053	0.2045
0.2497	0.0725	0.217
0.2280	0.0344	0.2767
0.2314	0.0522	0.2835
0.2380	0.0719	0.2970
0.1976	0.0359	0.4162
0.2036	0.0555	0.4278
0.2053	0.0746	0.4313
0.1600	0.032	0.4898
0.1695	0.0509	0.5036
0.1815	0.0729	0.5387
0.1586	0.0351	0.5383
0.1616	0.0538	0.5440
0.1358	0.0344	0.6239
0.1385	0.0534	0.6352
0.1253	0.0357	0.6438
0.10565	0.0352	0.7205
0.09105	0.02625	0.7753

A = total alkali concentration, in mole fraction.  
B = total aluminium concentration, in mole fraction.  
 $a_w$  = measured water activity, in mole fraction.



If it is assumed that only the two equilibria described by Eqs (3) and (4) are involved in the reaction between  $\text{Al}(\text{OH})_3$  and sodium hydroxide, the complex formation affects the water activity of the solution in two ways:

(1) stoichiometrically, in the dehydration process of formation of the dimer;

(2) as a consequence of the differing dehydrations of the various ions.

The following symbols have been used:

$$\left. \begin{array}{l} A = \text{initial OH}^- \text{ concentration} \\ B = \text{initial Al concentration} \\ D = \text{initial H}_2\text{O concentration} \end{array} \right\} \text{expressed in mole fractions}$$

For alkaline aluminate solutions various relations hold between the equilibrium and initial concentrations of the species. Thus:

$$A = [\text{OH}^-] + [\text{Al}(\text{OH})_4^-] + 2 [\text{Al}_2\text{O}(\text{OH})_6^{2-}]$$

(The OH introduced by dissolution of  $\text{Al}(\text{OH})_3$  has not been included.)

$$\begin{aligned} B &= [\text{Al}(\text{OH})_3] + [\text{Al}(\text{OH})_4^-] + 2 [\text{Al}_2\text{O}(\text{OH})_6^{2-}] \\ D &= [\text{H}_2\text{O}]_{\text{tot.}} - [\text{Al}_2\text{O}(\text{OH})_6^{2-}] \end{aligned}$$

where  $[\text{H}_2\text{O}]_{\text{tot.}}$  is the total water concentration, which is larger than the initial water concentration as a consequence of the dehydration.

A relation was sought between the selected parameter ( $a_w$ ) and the equilibrium concentrations of the species, the following assumptions being made:

(1) The changes in water activity due to the ions are directly proportional to their equilibrium concentrations. This assumption is supported, for example, by known data from the literature, relating to pure NaOH solutions.

(2) In the given solution (our sample) the changes in water activity due to the different ions  $[\text{Na}^+, \text{OH}^-, \text{Al}(\text{OH})_4^-, \text{Al}_2\text{O}(\text{OH})_6^{2-}]$  vary additively with their concentrations.

On the above basis, if  $a_w$  is the water activity of the aluminate solution, then

$$a_w = [\text{H}_2\text{O}]_{\text{tot.}} - x_1[\text{Al}(\text{OH})_4^-] - x_2[\text{Al}_2\text{O}(\text{OH})_6^{2-}] - x_3[\text{Al}(\text{OH})_3] - x_4[\text{NaOH}]$$

where, according to our assumption,  $x_1, x_2, x_3$  and  $x_4$  are constants and measures of the effects of the species on the water activity.

Our aim was to determine the following  $K_1$  and  $K_2$  values, and also  $x_1, x_2, x_3$  and  $x_4$ .  $K_1$  is the equilibrium constant of process (3):

$$K_1 = \frac{[\text{Al}(\text{OH})_4^-]}{[\text{Al}(\text{OH})_3][\text{OH}^-]}$$

while  $K_2$  is that of process (4):

$$K_2 = \frac{[\text{H}_2\text{O}] [\text{Al}_2\text{O}(\text{OH})_6^{2-}]}{[\text{Al}(\text{OH})_4^-]^2}$$

Based on a computer programme, the correct values of  $K_1$  and  $K_2$  can be determined from  $K_1$ ,  $K_2$  value pairs by a critical selection of the  $x$  values.

Aspects of the selection:

(1) The value determined by computer is compared with the value of  $x_4$  calculated from the previously reported concentration dependence of the water activity of pure sodium hydroxide ( $x_4 \sim 2.25$ ).

(2) The values of  $x_1$ ,  $x_2$  and  $x_3$  are presumably of the same or nearly the same order of magnitude.

(3)  $K_1 \gg 10$ , since the transformation of the  $\text{Al}(\text{OH})_3$  to  $\text{Al}(\text{OH})_4^-$  is very considerable.

It turns out from Table III that on the above basis  $K_1 = 10^5$  and  $K_2 = 9 \cdot 10^{-1}$ . In the range under examination the equilibrium concentration of the dimer,  $\text{Al}_2\text{O}(\text{OH})_6^{2-}$ , is more than 5%, and at times attains 20%, of the concentration of  $\text{Al}(\text{OH})_4^-$ .

It should be noted that this method is primarily suitable for the exact determination of the equilibrium constants, the components of which are present in significant amounts and ionically in the solution. Thus, since the dissolved  $\text{Al}(\text{OH})_3$  concentration in the solution is very small, the value of  $K_1$  suffers from a large error. However, as this value (if large enough) causes only a small change in  $K_2$ , the value found for  $K_2$  can be regarded as realistic.

The value of  $x_4$  was found to be 2.48, which agrees acceptably with the value of 2.25 calculated from the literature data.

$x_1 = 0.7275$ . This is a measure of the effect of  $\text{Al}(\text{OH})_4^-$  on the water activity.

$x_2 = 0.2237$ , which indicates that the complex ion  $\text{Al}_2\text{O}(\text{OH})_6^{2-}$  decreases the water activity of the solution to a smaller extent than does the monomer.

Our investigations clearly prove that, albeit to a limited extent, water-activity measurement is suitable for following complex equilibria in concentrated alkali solutions. A condition of the application of the method is that the compositions of the ionic species in the solution, or the equations of the equilibria describing their formation, be known from independent structure investigations.

The restricted value of the results of our investigations similarly follows from the above. The values of the equilibrium constants found can be regarded as definite only if, apart from the two ions assumed, no others are formed in the concentration range in question.



Table III

Equilibrium concentrations, in mole fraction,  
relating to the equilibrium constants  $K_1 = 10^5$  and  $K_2 = 9 \cdot 10^{-1}$

$[\text{Al}(\text{OH})_4^-]$	$[\text{Al}_2\text{O}(\text{OH})_2^-]$	Dissolved $[\text{Al}(\text{OH})_3]$	$[\text{OH}^-]$	$\alpha_w$	$[\text{H}_2\text{O}]$
$2.80 \cdot 10^{-2}$	$3.52 \cdot 10^{-3}$	$1.31 \cdot 10^{-6}$	0.214	0.213	0.760
$3.93 \cdot 10^{-2}$	$6.80 \cdot 10^{-3}$	$1.92 \cdot 10^{-6}$	0.203	0.241	0.763
$5.09 \cdot 10^{-2}$	$1.07 \cdot 10^{-2}$	$2.56 \cdot 10^{-6}$	0.198	0.250	0.761
$2.89 \cdot 10^{-2}$	$2.73 \cdot 10^{-3}$	$1.45 \cdot 10^{-6}$	0.199	0.266	0.774
$4.13 \cdot 10^{-2}$	$5.42 \cdot 10^{-3}$	$2.17 \cdot 10^{-6}$	0.190	0.286	0.772
$5.41 \cdot 10^{-2}$	$8.87 \cdot 10^{-3}$	$2.94 \cdot 10^{-6}$	0.183	0.299	0.770
$3.15 \cdot 10^{-2}$	$2.16 \cdot 10^{-3}$	$1.90 \cdot 10^{-6}$	0.166	0.381	0.804
$4.64 \cdot 10^{-2}$	$4.53 \cdot 10^{-3}$	$2.95 \cdot 10^{-6}$	0.157	0.401	0.800
$5.97 \cdot 10^{-2}$	$7.44 \cdot 10^{-3}$	$4.10 \cdot 10^{-6}$	0.145	0.436	0.802
$2.89 \cdot 10^{-2}$	$1.53 \cdot 10^{-3}$	$2.20 \cdot 10^{-6}$	0.131	0.506	0.836
$4.39 \cdot 10^{-2}$	$3.45 \cdot 10^{-3}$	$3.50 \cdot 10^{-6}$	0.125	0.521	0.833
$6.06 \cdot 10^{-2}$	$6.14 \cdot 10^{-3}$	$5.01 \cdot 10^{-6}$	0.120	0.530	0.824
$3.17 \cdot 10^{-2}$	$1.68 \cdot 10^{-3}$	$2.50 \cdot 10^{-6}$	0.126	0.524	0.842
$4.66 \cdot 10^{-2}$	$3.59 \cdot 10^{-3}$	$4.05 \cdot 10^{-6}$	0.114	0.561	0.841
$3.15 \cdot 10^{-2}$	$1.43 \cdot 10^{-3}$	$3.02 \cdot 10^{-6}$	0.104	0.609	0.865
$4.71 \cdot 10^{-2}$	$3.14 \cdot 10^{-3}$	$5.15 \cdot 10^{-6}$	0.009	0.654	0.863
$3.27 \cdot 10^{-2}$	$1.49 \cdot 10^{-3}$	$3.53 \cdot 10^{-6}$	0.009	0.654	0.875
$3.25 \cdot 10^{-2}$	$1.32 \cdot 10^{-3}$	$4.45 \cdot 10^{-6}$	0.007	0.733	0.895
$2.48 \cdot 10^{-2}$	$7.14 \cdot 10^{-4}$	$3.74 \cdot 10^{-6}$	0.6	0.76	0.909
$2.75 \cdot 10^{-2}$	$2.22 \cdot 10^{-3}$	$1.53 \cdot 10^{-6}$	0.179	0.304	0.762
$4.05 \cdot 10^{-2}$	$4.80 \cdot 10^{-3}$	$2.30 \cdot 10^{-6}$	0.175	0.291	0.738
$2.76 \cdot 10^{-2}$	$2.20 \cdot 10^{-3}$	$1.53 \cdot 10^{-6}$	0.180	0.303	0.762
$4.00 \cdot 10^{-2}$	$4.62 \cdot 10^{-3}$	$2.32 \cdot 10^{-6}$	0.172	0.304	0.743
$6.07 \cdot 10^{-2}$	$8.64 \cdot 10^{-3}$	$4.52 \cdot 10^{-6}$	0.134	0.402	0.735
$7.44 \cdot 10^{-2}$	$1.29 \cdot 10^{-2}$	$5.54 \cdot 10^{-6}$	0.134	0.373	0.703
$8.59 \cdot 10^{-2}$	$1.73 \cdot 10^{-2}$	$6.68 \cdot 10^{-6}$	0.128	0.371	0.682
$6.09 \cdot 10^{-2}$	$8.60 \cdot 10^{-3}$	$4.52 \cdot 10^{-6}$	0.134	0.401	0.734
$7.46 \cdot 10^{-2}$	$1.29 \cdot 10^{-2}$	$5.54 \cdot 10^{-6}$	0.134	0.371	0.703
$8.59 \cdot 10^{-2}$	$1.72 \cdot 10^{-2}$	$6.69 \cdot 10^{-6}$	0.128	0.372	0.682

$$x_1 = -0.7275, x_2 = -0.2237.$$

### Infrared spectroscopic study of sodium aluminate solutions

Since the correctness of the evaluation of the water-activity measurements depends on a knowledge of the compositions of the complexes formed in the system, infrared spectroscopic examinations were carried out to confirm that the species demonstrated by MOLENAAR *et al.* actually are present in the concentration range studied in our work.

Evaluation of the infrared examinations is made difficult by the fact that the solvent possesses a broad absorption band in the interval 400—1000  $\text{cm}^{-1}$  (Fig. 1). The absorption of the solvent was compensated with a NaOH solution. In this way, well-evaluatable spectra were obtained.

In the infrared spectra of aqueous sodium aluminate solutions a strong band can be observed at  $745 \pm 5 \text{ cm}^{-1}$ . At higher aluminium concentrations a new band also appears, at  $900 \pm 5 \text{ cm}^{-1}$  (Figs 2—4). The results are listed in Table IV.

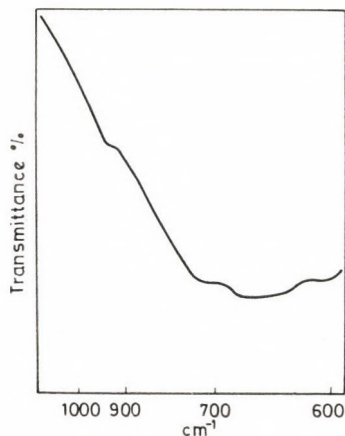


Fig. 1. Infrared spectrum of an aqueous 12.95 M solution of NaOH from 600 to 1000  $\text{cm}^{-1}$ .

Table IV

*Infrared spectroscopic data on sodium aluminate solutions*

Aluminium concentration M	Sodium hydroxide concentration M	Absorption bands $\text{cm}^{-1}$
1	8	$745 \pm 5$
1	12.95	$745 \pm 5$
3.5	8	$745 \pm 5$ $900 \pm 5$
5	12.95	$745 \pm 5$ $900 \pm 5$
6.0	13.0	$745 \pm 5$ $900 \pm 5$



These infrared bands correspond to the bands found and assigned by MOLENAAR *et al.* [12].

The high-intensity band at  $745 \pm 5 \text{ cm}^{-1}$  is due to the Al-O antisymmetric stretching vibration of the complex ion  $\text{Al}(\text{OH})_4^-$ , which is of tetrahedral symmetry. The new band appearing at higher aluminium concentrations ( $900 \pm 5 \text{ cm}^{-1}$ ) can be assigned as the Al-O stretching vibration of  $\text{Al}_2\text{O}(\text{OH})_6^{2-}$ .

Figure 2 reveals that increase of the aluminium concentration favours formation of  $\text{Al}_2\text{O}(\text{OH})_6^{2-}$ , but even at an aluminium concentration of 3.5 M the intensity of the new band at  $900 \text{ cm}^{-1}$  is still quite small.

Figures 3 and 4 confirm the above findings.

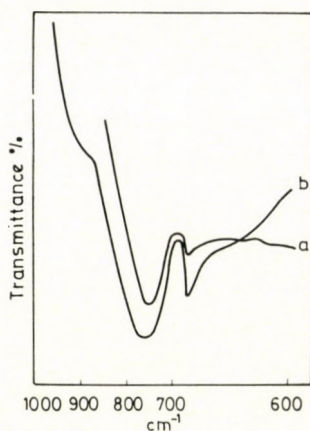


Fig. 2. Infrared spectra of sodium aluminate solutions from 600 to  $1000 \text{ cm}^{-1}$

- (a) 8 M NaOH, 1 M Al } compensated  
 (b) 8 M NaOH, 3.5 M Al } with 12.95 M NaOH

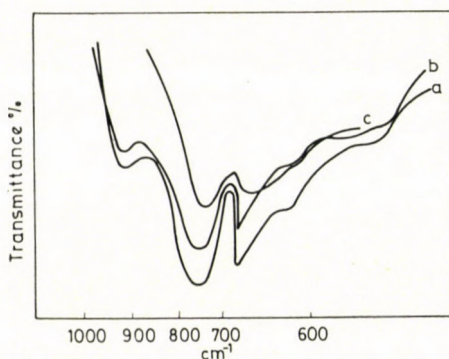


Fig. 3. Infrared spectra of sodium aluminate solutions from 600 to  $1000 \text{ cm}^{-1}$

- (a) 13.00 M NaOH, 6 M Al } compensated  
 (b) 12.95 M NaOH, 5 M Al } with 12.95 M NaOH  
 (c) 12.95 M NaOH, 1 M Al }

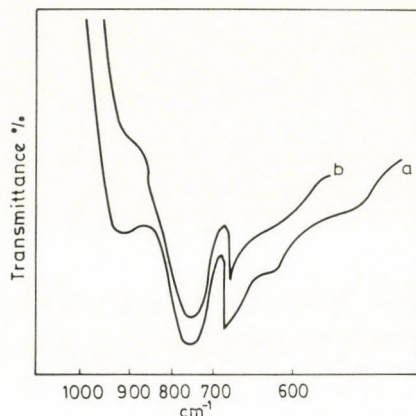


Fig. 4. Infrared spectra of sodium aluminate solutions from 600 to 1000  $\text{cm}^{-1}$ .  
 (a) 13 M NaOH, 6.0 M Al } compensated with  
 (b) 8 M NaOH, 3.5 M Al } 12.95 M NaOH

## Experimental

### Preparation and control of the materials and solutions used in the course of the measurements

Reagents used: NaOH (Reanal) of analytical purity; bayerite prepared in our laboratory.

*Preparation and analysis of bayerite:* Bayerite was prepared from high-purity aluminium turnings by the amalgam procedure [14]. Its thermal behaviour was investigated on a MOM derivatograph [15].

*Preparation of carbonate-free sodium hydroxide:* 50% sodium hydroxide solution was prepared from NaOH of analytical purity with boiled distilled water. Sodium carbonate impurity was separated from the pure solution by sedimentation and centrifugation. The concentration of NaOH solutions was determined by titration with hydrochloric acid.

*Preparation of aluminium-containing sodium hydroxide:* The calculated quantity of bayerite was added in small portions to a solution of sodium hydroxide of known concentration on a water-bath, and was completely dissolved. The concentration change occurring during the evaporation was corrected for on the basis of weight measurement, and the ready solution was thermostated for 30 min at the temperature of a boiling water-bath. If necessary (e.g. in the preparation of a saturated solution), the solution was centrifuged.

### Water-activity measurement method

Isopiestic water-activity measurement [16] can primarily be used to determine the water-activity of more concentrated solutions. The principle of the determination: two solutions of known weight and known concentration, prepared with the same solvent, and at the same temperature, are placed in nickel or platinum crucibles on an aluminium disc containing suitably prepared depressions, in a vacuum desiccator in a closed space. (The metal disc ensures good thermal conduction.) The desiccator is evacuated by vacuum-pump to a value close to the vapour pressure of the solutions, and is then thermostated at 25 °C. The solvent from the solution with higher vapour pressure distils over by isothermal distillation into the solution with lower vapour pressure until their vapour pressures become uniform. 24 hours later the desiccator is refilled with dry air, and the crucibles are removed and weighed. The concentration change is calculated from the weight change. For the direct determination of the water activity, it is necessary to know the concentration dependence of the water activity of a standard solution with vapour pressure similar to that of the solution to be measured. As standard solution, NaOH or  $\text{H}_2\text{SO}_4$  solutions were used, the water activities of which have been reported in the literature [17–21].



### Infrared spectroscopic study of sodium aluminate solutions

Spectra were recorded on a Zeiss UR 10 infrared spectrophotometer in the range 400–1000  $\text{cm}^{-1}$ . KRS 5 cells were employed in the measurement, and the absorption of the solvent was compensated against a NaOH solution [22].

### Equilibrium measurements in aluminate solutions with the isopiestic method

Four nickel or platinum crucibles each containing 3 ml of aluminate solution and pure sodium hydroxide solution of known weight and composition were placed in a vacuum desiccator, and the water activities were determined in 2 parallel measurements as described above. When a pure sodium hydroxide solution with the same concentration as the initial sodium hydroxide concentration of the aluminate solution was used as standard, equilibrium was established within a relatively short time (24 hours).

### Computer evaluation of the data

On the basis of the least squares principle, the programme determines the coefficients,  $x$ , of the hypothetical correlation of the form

$$a_{ij} = x_0 Y_0 + x_1 Y_1 + x_2 Y_2 + x_3 Y_3 + x_4 Y_4 \quad (5)$$

The  $Y$  values are the equilibrium concentrations, calculated by the programme from the two equilibrium constants ( $K_1$ ,  $K_2$ ) and three initial concentrations (A, B, D). Negative values are expected for  $x_1$ ,  $x_2$ ,  $x_3$  and  $x_4$ . The coefficients  $x$  are obtained as the solution of a linear equation system. For numerical reasons, the determinant of this for the  $Y$  values occurring is frequently zero. Expression (5) is therefore transformed from the insolvable region to the solvable one. The programme is also capable of leaving the individual equilibrium constants unchanged, and of calculating via the variation of the other constants.

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