

Calculation of the Ionic Composition of Aluminate Solutions

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Abstract

One of the difficulties in modelling aluminate solutions remains their ionic composition, which over time has been more completely described by systematic research in this area. The understanding of ionic composition allows physicochemical models capable of accurately describing production processes and providing reliable process indicators in automated control systems. To date, the ion composition of solutions in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system and its closest analogue, $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$, has been reliably established by Raman spectroscopy. This collective knowledge allows the calculation of solution equilibria using equilibrium concentration constants, making it dependent on the solution's ionic composition, but does not require calculated and/or empirical data for activity coefficients. By taking into account the material and charge balance, assuming the ions present, and where the $\text{Al}(\text{OH})_4^-$ equilibrium constant does not change, two equations for ionic composition can be derived. The assumption of a stable equilibrium constant is confirmed by the linear dependence of the equilibrium Al_2O_3 concentration on the Na_2O concentration, and a constant ratio of the activity coefficients of $\text{Al}(\text{OH})_4^-$ and OH^- with changes in solution ionic strength. Where there are departures from this relationship, a derivative function can be used to determine the ionic composition at any point on the isotherm, and in the case of a more complex equilibrium, the second concentration derivative can be used. Thus, the information embedded in the equilibrium isotherms allows quantification of the equilibrium composition of aluminate solutions where several anionic forms exist.

Keywords: aluminate solutions, ionic composition, physicochemical equilibria, thermodynamic modeling.

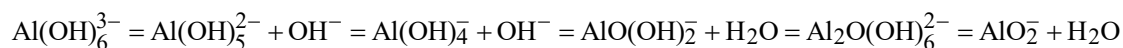
1. Introduction

The understanding of the structure and ionic composition of aluminate solutions is fundamental to efficient alumina production from alkaline solutions, allowing a scientific interpretation of the processes occurring in the different unit operations of an alumina refinery.

A fifty-year history of attempts to create a theory of aluminate solutions as a way to explain their behavior under various conditions was published as early as 1959 [1]. Analyzing the equilibrium constants of aluminate solutions, the researchers came to conclusions about their ionic nature, and the possible polymerization of $\text{Al}(\text{OH})_4^-$ at higher aluminum concentrations in alkaline solutions. At the same time, the development of colloidal theory took place. This theory provided an explanation for a number of properties of aluminate solutions which were difficult to characterize in terms of true ionic solutions. Some ideas about the presence of complex anions in aluminate solutions, consistent with the poly-ion theory, was developed at the same time [1].

By the end of the 1960s, the development of physicochemical research methods allowed the ionic nature of aluminate solutions to be unambiguously established, while their composition continued to be debated [2]. Since then, the determination of composition by various methods has allowed a better understanding of the complex ionic composition of aluminate solutions and its dependence on the parameters defining the state of the system [3-6].

The study of aluminate solutions by NMR and Raman spectroscopic methods have allowed to reliably establish the stability regions of hydrated monomers of $[\text{Al}(\text{OH})_4^-]$ and dimers of the meta-aluminate ion $[\text{Al}_2\text{O}(\text{OH})_6^{2-}]$ [7]. Later studies have shown that with increasing alkali and aluminum concentrations in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system, sequential dehydration of aluminum hydroxy-complexes occurs resulting in the formation of the AlO_2^- meta-aluminate ion in solutions containing at least 5 mole/kg alkali and at least 1 mole/kg aluminum according to the following scheme [8-11]:

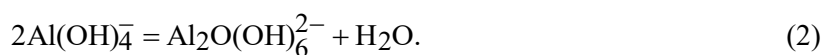


2. Steps for Calculation of Ionic Composition of Aluminate Solution

In general, a similar scheme describes the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system, and is maintained in the presence of a silicon impurity [7]. For the technology significant region of the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ and $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ systems, most researchers note the presence of two forms of complex aluminum anions, existing in the form of hydrated monomers and dimers of the meta-aluminate ion. This suggests the existence of the following equilibria in the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system, in contact with aluminum tri-hydroxide in the solid phase:



and formation of the dimeric form of the aluminum tetrahydroxy complex:



The thermodynamic equilibrium constant (in terms of activity) and concentration equilibrium constant (in terms of molar concentration) for reaction (1) are given by the following equation:

$$K_1 = \frac{a_{\text{Al}(\text{OH})_4^-}}{a_{\text{OH}^-}} = \frac{[\text{Al}(\text{OH})_4^-]}{[\text{OH}^-]} \cdot \frac{\gamma_{\text{Al}(\text{OH})_4^-}}{\gamma_{\text{OH}^-}} = Q_1 \cdot \Pi_{\gamma,1}, \quad (3)$$

Where:

K_1 and Q_1 thermodynamic and concentration equilibrium constants respectively
 $\gamma_{\text{Al}(\text{OH})_4^-}$ and γ_{OH^-} activity coefficients of the corresponding anions.

If the concentration of Al_2O_3 in an alkali solution is not more than 90 g/L and the molar ratio $n_{\text{Na}_2\text{O}}/n_{\text{Al}_2\text{O}_3}$ is 1.55 ± 0.05 [7], only reaction (1) takes place and it is possible to write the charge balance equation as follows:

$$[\text{Na}^+] = [\text{OH}^-] + [\text{Al}(\text{OH})_4^-] \quad (4)$$

where the concentration of components is expressed in terms of molarity or molality.

This equation represents the concentration equilibrium constant as:

$$Q_1 = \frac{[\text{Al}(\text{OH})_4^-]}{[\text{Na}^+] - [\text{Al}(\text{OH})_4^-]} \quad (5)$$

From equation (5), taking into account the ratios of molar concentrations:

$$[\text{Na}^+] = [\text{NaOH}] = 2[\text{Na}_2\text{O}] \text{ and } [\text{Al}(\text{OH})_4^-] = 2[\text{Al}_2\text{O}_3] \quad (6)$$

the following expression for the dependence of the equilibrium concentration of $[\text{Al}_2\text{O}_3]$ on the concentration of $[\text{Na}_2\text{O}]$ in solutions if equilibrium (1) exists was obtained:

$$[\text{Al}_2\text{O}_3] = \frac{Q_1}{1 + Q_1} [\text{Na}_2\text{O}] \quad (7)$$

Equation (7) is an expression of the simple observation that under the condition of a relatively constant equilibrium constant, for example in solutions with low ionic strength and a component concentration of 0.1 mole/L, the concentration of Al_2O_3 is a linear function of the concentration of Na_2O .

It can be assumed that if a linear dependence of $[\text{Al}_2\text{O}_3]$ on $[\text{Na}_2\text{O}]$ is observed, then this indicates not only the constancy of Q_1 , but also the constancy of the ratio of activities in equation (3) as the solution ionic strength changes, and that the equilibrium description is correct according to stoichiometry of equation (1). This type of dependence is explained by the uniformity of the Debye-Hückel equation for calculating the activity coefficients of singly charged ions, at least in a limited range of solution concentrations and ionic strength [12].

For solutions of relatively low concentration in the region where solubility isotherms are linear, this allows the calculation of both the concentration and thermodynamic equilibrium constant, as well as to extrapolate this dependence to the where deviation from the linearity is first observed. This is possible because changes in the linearity of the solubility isotherm are most likely not related to a dependence departure (7), but are a consequence of dimer formation according to equation (2). The equilibrium of dimers and monomers that is established in this case is determined by the following equilibrium constant:

$$K_2 = \frac{[\text{H}_2\text{O}] \cdot [\text{Al}_2\text{O}(\text{OH})_6^{2-}]}{[\text{Al}(\text{OH})_4^-]^2} \cdot \frac{\gamma_{\text{H}_2\text{O}} \cdot \gamma_{\text{Al}_2\text{O}(\text{OH})_6^{2-}}}{\gamma_{\text{Al}(\text{OH})_4^-}^2} = Q_2 \cdot \Pi_{\gamma,2} \quad (8)$$

Where:

K_2 and Q_2 : thermodynamic and concentration equilibrium constant (2), respectively;
 $\gamma_{\text{Al}_2\text{O}(\text{OH})_6^{2-}}$, $\gamma_{\text{Al}(\text{OH})_4^-}$ and $\gamma_{\text{H}_2\text{O}}$: activity coefficients of ionic forms of aluminum and water.

The concentration ratio of monomers and dimers for a specific equilibrium composition in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system and its closest analogue, $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$, can be determined as a new concentration equilibrium constant:

$$Q_2' = \frac{Q_2}{[\text{H}_2\text{O}]} = \frac{[\text{Al}_2\text{O}(\text{OH})_6^{2-}]}{[\text{Al}(\text{OH})_4^-]^2} \quad (9)$$

$[\text{H}_2\text{O}]$ is unambiguously determined by the total concentration of the components and ionic composition of solution in accordance with the material balance by water, taking into account the amount of hydroxyl ions and all aluminum hydroxy-complexes:

$$\begin{aligned}
 [\text{H}_2\text{O}]_{\Sigma} &= [\text{H}_2\text{O}] + [\text{H}_2\text{O}]_{\text{OH}^-} + [\text{H}_2\text{O}]_{\text{Al}(\text{OH})_4^-} + [\text{H}_2\text{O}]_{\text{Al}_2\text{O}(\text{OH})_6^{2-}} = \\
 &= [\text{H}_2\text{O}] + 0,5[\text{OH}^-] + 2[\text{Al}(\text{OH})_4^-] + 3[\text{Al}_2\text{O}(\text{OH})_6^{2-}],
 \end{aligned}
 \tag{10}$$

Where:

$[\text{H}_2\text{O}]_{\Sigma}$: total concentration of water in the aluminate solution, mole/L;
 $[\text{H}_2\text{O}]$: equilibrium concentration of free water, i.e. not associated with chemical compounds, mole/L;
 $[\text{H}_2\text{O}]_{\text{An}}$: concentration of water in the composition of the corresponding anions and anionic complexes (OH^- , $\text{Al}(\text{OH})_4^-$, $\text{Al}_2\text{O}(\text{OH})_6^{2-}$), mole/L.

In this case, the total concentration of H_2O in the system is uniquely determined by its equilibrium composition according to the equation:

$$[\text{H}_2\text{O}]_{\Sigma} = (\rho \cdot 1000 - 102 \cdot [\text{Al}_2\text{O}_3] - 62 \cdot [\text{Na}_2\text{O}]) / 18 \tag{11}$$

Where:

ρ : density of the equilibrium aluminate solution, $\text{g} \cdot \text{cm}^{-3}$; 102, 62 and 18, respectively, molar mass of Al_2O_3 , Na_2O and H_2O , g/mol.

Since in equation (9) the concentration constant Q_2' contains two unknowns, the constant itself and the concentration of dimers, equation (9) must be supplemented by another to determine them, which is the mass balance equation for aluminum:

$$[\text{Al}^{3+}] = [\text{Al}(\text{OH})_4^-] + 2[\text{Al}_2\text{O}(\text{OH})_6^{2-}] \tag{12}$$

where $[\text{Al}^{3+}]$ is the total concentration of aluminum in solution, mole/L.

At the same time, with the participation of two ionic forms of aluminum, the concentration of hydroxyl ions in equation (3) changes and the charge balance equation (4) should be replaced by an equation involving all forms of anions:

$$[\text{Na}^+] = [\text{OH}^-] + [\text{Al}(\text{OH})_4^-] + 2[\text{Al}_2\text{O}(\text{OH})_6^{2-}] \tag{13}$$

where $[\text{Na}^+]$ is the total concentration of sodium ions in solution, mole/L.

Then, taking into account the conserved constancy of the equilibrium constant Q_1 , the independent equations (3, 9, 11, 12) contain four unknowns $[\text{OH}^-]$, $[\text{Al}(\text{OH})_4^-]$, $[\text{Al}_2\text{O}(\text{OH})_6^{2-}]$ and Q_2' that can be determined by jointly solving equations. When solving the system using the substitution method, and expressing the unknown concentrations of dimers and monomers through known values of Q_1 , $[\text{Na}^+]$ and $[\text{Al}^{3+}]$, we obtain the equation for Q_2' , which includes only known values:

$$Q_2' = \frac{[\text{Al}^{3+}] - Q_1 \cdot ([\text{Na}^+] - [\text{Al}^{3+}])}{2 \cdot Q_1^2 \cdot ([\text{Na}^+] - [\text{Al}^{3+}])^2} \tag{14}$$

In the transition to a total equilibrium concentration of sodium and aluminum in terms of oxides, we obtain the calculated equation for determining Q_2' :

$$Q_2' = \frac{[Al_2O_3] - Q_1 \cdot ([Na_2O] - [Al_2O_3])}{4 \cdot Q_1^2 \cdot ([Na_2O] - [Al_2O_3])^2} \quad (15)$$

Given the condition of Q_1 being constant, this expression represents the first approximation of the ionic composition for the transition region of solutions. A more general solution or a second approximation is to determine the ionic composition, subject to a change in Q_1 with a change in the concentration and ionic strength of the aluminate solution. Then equation (15) contains two variables, and for their correct determination, one more independent equation is needed. Since $[Al^{3+}]$ is a complex function of the ionic composition and concentration of the aluminate solution according to (12) and (13), we express it through the known and unknown values, i.e. Q_1 and Q_2' :

$$[Al^{3+}] = Q_1 \cdot ([Na^+] - [Al^{3+}]) + 2 \cdot Q_2' \cdot Q_1^2 \cdot ([Na^+] - [Al^{3+}])^2 \quad (16)$$

After replacing the known aluminum and sodium equilibrium concentration values by oxides equivalents, we obtain the following expression:

$$[Al_2O_3] = Q_1 \cdot ([Na_2O] - [Al_2O_3]) + 4 \cdot Q_2' \cdot Q_1^2 \cdot ([Na_2O] - [Al_2O_3])^2 \quad (17)$$

From equation (17) it follows that the equilibrium concentration $[Al_2O_3]$ is a function of the new variable $([Na_2O] - [Al_2O_3])$. This allows us to obtain an independent equation as a derivative of the function $[Al_2O_3]$ with respect to this variable:

$$\frac{d([Al_2O_3])}{d([Na_2O] - [Al_2O_3])} = Q_1 + 8 \cdot Q_2' \cdot Q_1^2 \cdot ([Na_2O] - [Al_2O_3]) \quad (18)$$

Finding the value of the derivative of a function for given equilibrium conditions does not cause significant difficulties. It is done by building an equilibrium concentration of Al_2O_3 using the accepted variable as an argument, a mathematical description of the resulting relationship, followed by finding the derivative of the function and calculating its value for the given conditions from the concentration of Al_2O_3 and Na_2O . Then a joint solution of equation (17) and (18) is performed. Given that the derivative function is the tangent of the slope of the dependence in the coordinates $[Al_2O_3] = f([Na_2O] - [Al_2O_3])$, for approximate calculations, the graphical estimation method can be used.

Thus, the degree of nonlinearity of the solubility isotherms of Al_2O_3 in the $Na_2O-Al_2O_3-H_2O$ and $K_2O-Al_2O_3-H_2O$ system is a measure of the change in ionic forms in an equilibrium aluminate solution, and serves as a source of information for calculating their concentration.

3. Conclusion

When establishing equilibrium in the system $Na_2O-Al_2O_3-H_2O$ and $K_2O-Al_2O_3-H_2O$ with one ionic form of aluminum (a tetra-hydroxy complex), a linear dependence of the Al_2O_3 concentration on the concentration of caustic alkali $[Na_2O]$ (or $[K_2O]$) should be observed. The distortion of this dependence with an increase in the aluminate concentration is most likely due to the formation of the dimeric form of the hydroxy complex.

Equilibrium with $Al(OH)_3$ in the solid phase and two ionic forms (monomers and dimers) of the meta-aluminate ion (AlO_2^-) in the aluminate solution is characterized by a parabolic dependence of the equilibrium Al_2O_3 concentration on $([Na_2O] - [Al_2O_3])$, which is a measure of the change in

the concentration of ionic forms in an equilibrium aluminate solution and serves as a source of information for calculating their concentration.

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