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 Na_2O-Al_2O_3-H_2O system and its closest analogue, K_2O-Al_2O_3-H_2O, 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 $Al(OH)_4^-$ 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 $Al(OH)_4^-$ 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 $Al(OH)_4^-$ 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 a 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 $[Al(OH)_4^-]$ and dimers of the meta-aluminate ion $[Al_2O(OH)_6^{2-}]$ [7]. Later studies have shown that with increasing alkali and aluminum concentrations in the $Na_2O-Al_2O_3-H_2O$ 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]:

$$Al(OH)_6^{3-} = Al(OH)_5^{2-} + OH^- = Al(OH)_4^- + OH^- = AlO(OH)_2^- + H_2O = Al_2O(OH)_6^{2-} = AlO_2^- + H_2O$$
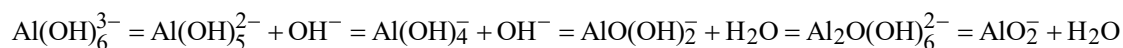
2.   Steps for Calculation of Ionic Composition of Aluminate Solution

In general, a similar scheme describes the $K_2O-Al_2O_3-H_2O$ system, and is maintained in the presence of a silicon impurity [7]. For the technology significant region of the $Na_2O-Al_2O_3-H_2O$ and $K_2O-Al_2O_3-H_2O$ 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 $Na_2O-K_2O-Al_2O_3-H_2O$ system, in contact with aluminum tri-hydroxide in the solid phase:

$$Al(OH)_3 + OH^- = Al(OH)_4^- \tag{1}$$
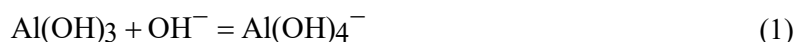
and formation of the dimeric form of the aluminum tetrahydroxy complex:

$$2Al(OH)_4^- = Al_2O(OH)_6^{2-} + H_2O. \tag{2}$$
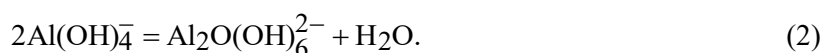
The thermodynamic equilibrium constant (in terms of activity) and concentration equilibrium constant (in terms of molar concentration) for reaction (1) are given by the following equation:

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

Where:
K_1 and Q_1 thermodynamic and concentration equilibrium constants respectively
$\gamma_{Al(OH)_4^-}$ 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 $n_{Na_2O}/n_{Al_2O_3}$ is 1.55 ± 0.05 [7], only reaction (1) takes place and it is possible to write the charge balance equation as follows:

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

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

This equation represents the concentration equilibrium constant as:

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

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

4.   Acknowledgements

5.   References

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