

The Solubility and Hydrolysis of Aqueous Aluminium Hydroxides in Dilute Fresh Waters at Different Temperatures

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This study is mainly focusing on the effect of temperature and pH on the chemistry of $\text{Al}(\text{OH})_3(\text{s})$ using available thermodynamic data.

The calculations show that a doubling of the $[\text{H}^+]$ or a decrease in temperature by 15°C , approximately yields the same solubility increase of the various $\text{Al}(\text{OH})_3(\text{s})$ presented.

The relative concentration of aqueous aluminium hydrolysis complexes is also highly temperature dependent. At 25°C and pH 5, the calculated distribution of dissolved, inorganic aluminium hydroxides corresponds to about 36 % of Al^{3+} , 37 % of $\text{Al}(\text{OH})^{2+}$, 26 % of $\text{Al}(\text{OH})_2^+$ and 1 % of $\text{Al}(\text{OH})_3^0$. At the same pH but at 0°C , about 84 %, 13 %, 2 % and 0 % are present as Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_3^0$, respectively. This temperature effect is of major importance as the hydroxide species are supposed to be the most toxic species to aquatic biota.

Literature reports on the equilibrium constants $\text{Al}(\text{OH})_3(\text{s})$, \log^*K_s , vary from about 8 to 11, a variation in the product by a factor of 1000. In natural soil/water systems the solubility products of crystalline and amorphous solid aluminium sources are unknown and the solubility may also be coupled to combined weathering/ion exchange processes. In addition substantial amount of aluminium may be present as organic complexes where aluminium by cation exchange reactions may enter the solution as monomeric inorganic species. Thus, if a low value for the equilibrium constants of $\text{Al}(\text{OH})_3(\text{s})$ is used as reference when calculating the degree of aluminium saturation, an apparent oversaturation will often be demonstrated. To estimate the degree of aluminium saturation in natural waters would therefore only be of theoretical interest.

Introduction

Acidification of soil systems may cause a mobilization of inorganic, dissolved aluminium species from edaphic reservoirs to surface waters (Cronan and Schofield 1979; Dickson 1980). These mainly inorganic monomeric species, have been shown to be toxic to fish and other aquatic organisms (Muniz and Leivestad 1980; Schofield and Trojnar 1980; Baker and Schofield 1982). Organic aluminium complexes, however, have never been shown to have any acute harmful effects on aquatic biota.

Al^{3+} and its hydrolysis products are probably the most toxic aluminium species in natural waters (Helliwell *et al.* 1983; Leivestad *et al.* 1987). This paper presents solubility changes of different $\text{Al}(\text{OH})_3(\text{s})$ and changes in hydrolysis due to pH and temperature variations.

In nature, presence of other ligands but hydroxide, *i.e.* silicic acid, fluoride, sulfate and humic substances, generally may increase the amount of dissolved aluminium. The amounts of dissolved aluminium will therefore often exceed the equilibrium concentration predicted with respect to the solubility product (\log^*K_s) chosen.

In order to cover most of the reported \log^*K_s values of $\text{Al}(\text{OH})_3(\text{s})$, this work includes 3 different $\text{Al}(\text{OH})_3(\text{s})$, from a slightly soluble well crystallized gibbsite to a highly soluble amorphous phase.

Based on the theoretical data present, the discussion is dealing with some examples demonstrating how temperature and pH may effect the chemistry of aqueous aluminium hydroxides.

Materials and Methods

In this paper, solubility and hydrolysis constants are written in terms of H^+ and H_2O , rather than OH^- . Thus, the equilibrium constants are written *K instead of K . Subscript «s» refers to solubility product for a solid phase.

Theoretically it is more correct to estimate the ion activity instead of ion concentration and activity product instead of solubility product. For work with reasonably dilute solutions ($I < 0.1$ mol/l) where great accuracy is not important, activity coefficients can be estimated on the basis of a theoretical treatment formulated by Debye and Hückel where the activity coefficient (γ) of an ion is

$$-\log \gamma = Az^2 I^{\frac{1}{2}} \quad (1)$$

where z is the charge of the ion, I is the ionic strength of the solution and A is a constant depending of temperature and the dielectric constant of the solvent, equal approximately to 0.51 in water at 25°C. Because the presented paper mainly is focusing on the aluminium chemistry in dilute fresh waters ($I < 0.001$ mol/l) the activity coefficients are close to 1; this means that activity is practical equal to

concentration. Thus, the term concentration is used instead of activity in the further presentation.

The solubility and hydrolysis constants (at 298.15 K = 25°C) used in this paper are those recommended by Nordstrom *et al.* (1984). In this referred paper partial compilation and revision of basic data of aluminium in the WATEQ-programs have been carried out. In addition the density and dielectrical constants of water and their temperature dependence are evaluated for the purpose of updating the Derbye-Hückel solvent parameters in the activity coefficient equations. Uncertainties reported by the original authors are given in parantheses following the reported value. These numbers usually represent one standard deviation.

The \log^*K_s of $\text{Al}(\text{OH})_3(\text{s})$ and the hydrolysis constants (\log^*K_{1-4}) reported in the literature are varying considerably, but the discrepancies are rarely explained. As far as the variation in the solubility products of $\text{Al}(\text{OH})_3(\text{s})$ is concerned, this paper covers most of the reported values:

- A) Well crystallized gibbsite, aging time about 4 years, no difference in particles, 0.05-50 μm in size. \log^*K_s : 7.97 (.05) (Kittrick 1966)
- B) Microcrystalline gibbsite, aged for 2-20 weeks. \log^*K_s : 9.35 (.3) (Hem and Roberson 1967)
- C) Amorphous $\text{Al}(\text{OH})_3(\text{s})$, aged for 24 hours. \log^*K_s : 10.4 (Hayden and Rubin 1974)

The \log^*K_s values are adjusted with respect to temperature by the Van't Hoff relation

$$\log^*K_s = \log^*K_s(T_r) = \frac{H_r^\circ(T_r)}{2.303 \cdot R} \left(\frac{1}{T} - \frac{1}{T_r} \right) \quad (2)$$

in which T_r is the reference temperature (298.15 K = 25°C) H_r° : - 22.8 kcal/mol (Nordstrom *et al.* 1984).

This enthalpy change ($H_r^\circ = - 22.8$ kcal/mol) used in the Van't Hoff relation should only be used for crystalline gibbsites but is often used for both crystalline and amorphous forms of $\text{Al}(\text{OH})_3(\text{s})$. In handbook of chemistry and physics (Weast and Astle 1982) the H° value for amorphous $\text{Al}(\text{OH})_3(\text{s})$ is - 27.0 kcal/mol. Thus, the increase in \log^*K_s by lowering temperature from 25°C to 0°C is 1.81 for amorphous $\text{Al}(\text{OH})_3(\text{s})$ (10.4 at 25°C to 12.21 at 0°C), *i.e.* the solubility of an amorphous $\text{Al}(\text{OH})_3(\text{s})$ is more temperature sensitive than a crystalline gibbsite. However, we have only used the H_r° value of - 22.9 kcal/mol in the further presentation.

The hydrolysis constants (\log^*K_{1-4}) used are those recommended by Nordstrom *et al.* 1984 (at 298.15 K):

$$\begin{aligned} \log^*K_1 &= -4.987(.08) \text{ (May } et al. \text{ 1979; Ball } et al. \text{ 1980)} \\ H_r^\circ &= 11.9(0.5) \text{ kcal/mol (Baes and Mesmer 1976; Ball } et al. \text{ 1980)} \end{aligned}$$

$$\log^* K_2 = -10.13(.08) \text{ (May } et al. \text{ 1979; Ball } et al. \text{ 1980)}$$

$$H_r^\circ = 22.0 \text{ kcal/mol (This value was obtained by a correlation made by Nordstrom } et al. \text{ 1984 based on data from Baes and Mesmer 1976)}$$

$$\log^* K_3 = -16.76(.09) \text{ (May } et al. \text{ 1979)}$$

$$H_r^\circ = 33.0 \text{ kcal/mol (This value is obtained by Nordstrom } et al. \text{ 1984 by assuming a linear increase).}$$

$$\log^* K_4 = -22.07 \text{ (Hem } et al. \text{ 1973)}$$

$$H_r^\circ = 44.06 \text{ kcal/mol (Ball } et al. \text{ 1980; Truesdell and Jones 1974)}$$

The temperature dependence of the $\log^* K_{1-4}$ values is calculated using the already presented Van't Hoff relation Eq. (2).

Results and Discussion

The influence of temperature on the solubility of $\text{Al}(\text{OH})_3(\text{s})$ and on the hydrolysis of aluminium, is often ignored. Based on the theoretical data presented, some examples demonstrating how pH and temperature may affect the aqueous aluminium chemistry are discussed.

– At pH 5, 10°C, 28 $\mu\text{g Al/l}$ should exist in solution at equilibrium with respect to well crystallized gibbsite. At the same pH and temperature, theoretically 670 and 7,770 $\mu\text{g Al/l}$ should be present in solution at equilibrium with microcrystalline gibbsite and amorphous $\text{Al}(\text{OH})_3(\text{s})$, respectively. In natural water systems, the solubility products of the aluminium pool are unknown and have to represent an average solubility product for all solid aluminium sources present. Consequently, when evaluating the degree of aluminium saturation, one has to pick out a suitable solubility product from the literature. Many water/soil acidification models (ILWAS; Chen *et al.* 1983, MAGIC; Cosby *et al.* 1985 a,b, BIRKENES; Christophersen *et al.* 1982 and PROFILE; Sverdrup and Warfinge 1988.) have incorporated several gibbsite equilibrium coefficient values. But the aluminium concentrations in surface waters do not seem to be controlled by dissolution reactions of a single aluminium mineral. Aluminium chemistry appears to require some more complex descriptions than the gibbsite equilibrium hypothesis (Seip *et al.* 1986).

Studies so far shows that the kinetics of $\text{Al}(\text{OH})_3(\text{s})$ formation is a very fast process compared with the $\text{Al}(\text{OH})_3(\text{s})$ dissolution process (Lydersen *et al.* in prep). In this work aluminium solutions (100 to 800 $\mu\text{g Al/l}$) were titrated from pH 4.5 to pH about 5.5 (by NaOH) to study the formation kinetics of $\text{Al}(\text{OH})_3(\text{s})$. Correspondingly identical aluminium solutions were titrated from

pH 4.5 to 5.5, before pH was lowered by NaOH (NaOH addition equivalent to the HCl addition) to achieve the initial pH 4.5 in order to study the dissolution kinetics. Since the dissolution kinetics of aluminium was found to be a generally slow process, *undersaturation* and *not oversaturation* of aluminium with respect to the true solid aluminium pool will occur in most natural water/soil systems during pH-depression periods if the amount of dissolved aluminium only is dependant of the solubility of a solid pool(s). If a very slightly soluble $\text{Al}(\text{OH})_3(\text{s})$ is used as reference for the calculations, however, an apparent oversaturation will often be demonstrated. In contrast to the cited work, Dahlgren *et al.* (1989) found that the dissolution of natural gibbsite in two forest soils has been shown to be a rather rapid process, less than 0.3 h. Despite the slow dissolution kinetics of different forms of $\text{Al}(\text{OH})_3(\text{s})$ the dissolution may very well be a relatively fast process if substantial amounts of solid aluminium forms are present. However, the fast elevation of dissolved inorganic aluminium often observed during pH-depression periods can probably very seldom be explained by dissolution of crystalline and amorphous forms of $\text{Al}(\text{OH})_3(\text{s})$ alone. Fast processes as ion-exchange reactions should therefore be evaluated and quantified in more detail. A model for aluminium-humic complexes is tested out by Tipping *et al.* (1988) and this work is continuously progressing.

- When estimating the solubility of a $\text{Al}(\text{OH})_3(\text{s})$, pH and temperature measurements are required, since the solubility is highly sensitive to both parameters. At 5°C, the concentration of dissolved aluminium at equilibrium with well crystallized gibbsite, is changed from 190 $\mu\text{g Al/l}$ to 360 $\mu\text{g Al/l}$ as pH is changed from 4.8 to 4.7. The importance of accurate pH measurements when estimating a \log^*K_s value, or the degree of aluminium saturation, should therefore be obvious. *In situ* measurements of pH in soil and lake water are often difficult, because CO_2 equilibrium seldom exists. This problem is even more serious if samples are stored prior to the pH measurement.
- A temperature reduction by 15°C or a doubling of the $[\text{H}^+]$, theoretically yields about the same solubility increase. This pH/temperature relationship is directly a consequence of the Van't Hoff relation (Fig. 1). In natural waters, a temperature variation of 15°C throughout a year, occurs many places. At several of these sites, soil acidification and aluminium mobilization from edaphic to aquatic milieu is a serious problem. Freshwater systems of pH 5 and 15°C should therefore be a common summer situation. Theoretically, the amount of dissolved aluminium at equilibrium with well crystallized gibbsite, should be 16 $\mu\text{g Al/l}$ in the autumn and in the springtime, however, a water temperature of 5°C is normal, and pH may easily decrease to about 4.7. Then the equilibrium concentration with respect to well crystallized gibbsite will increase to 360 $\mu\text{g Al/l}$. The pH reduction alone (from 5.0 to 4.7) increases the equilibrium concentration

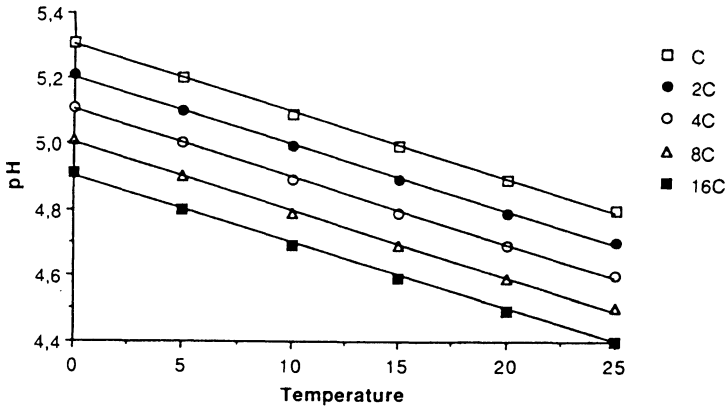


Fig. 1. The solubility concentration (C) at equilibrium with crystalline gibbsite in relation to pH and temperature (°C).

from 16 to 100 $\mu\text{g Al/l}$, while the remaining solubility increase of 260 $\mu\text{g Al/l}$ is a result of the temperature reduction from 15°C to 5°C.

- Dissolved, inorganic monomeric aluminium is thought to contain the most toxic aluminium species with $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$ as the most toxic (Helliwell *et al.* 1983; Leivestad *et al.* 1987). The presence of these species (hydrolysis products) are very sensitive to pH and temperature (Fig. 2), but temperature, however, has never been seriously evaluated in aluminium toxicological studies so far. At 25°C, pH 5, theoretically 37% and 26% of dissolved, inorganic aluminium should be present as $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$, respectively (*i.e.* 37 $\mu\text{g Al/l}$ and 26 $\mu\text{g Al/l}$ when the concentration of dissolved inorganic aluminium is 100 $\mu\text{g/l}$). At same pH, but at 5°C, the amounts of $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$ are reduced to 17% (17 $\mu\text{g Al/l}$) and 4% (4 $\mu\text{g Al/l}$).
- In several acidified regions of the world, 100-300 $\mu\text{g/l}$ of inorganic monomeric aluminium is often present in natural surface water systems. These concentrations may very well exist without being oversaturated with respect to the actual solid aluminium pool(s) present. By making the following pH/temperature combinations, 300, 200 and 100 $\mu\text{g Al/l}$ (dissolved inorganic aluminium species) contains about the same total amounts of $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$:

300 $\mu\text{g Al/l}$ (pH 5.1, 2°C).
 200 $\mu\text{g Al/l}$ (pH 5.0, 10°C).
 100 $\mu\text{g Al/l}$ (pH 5.1, 20°C).

All combinations should therefore theoretically yield the same toxic response, as far as the hydrolysis products are concerned. This experiment has never been

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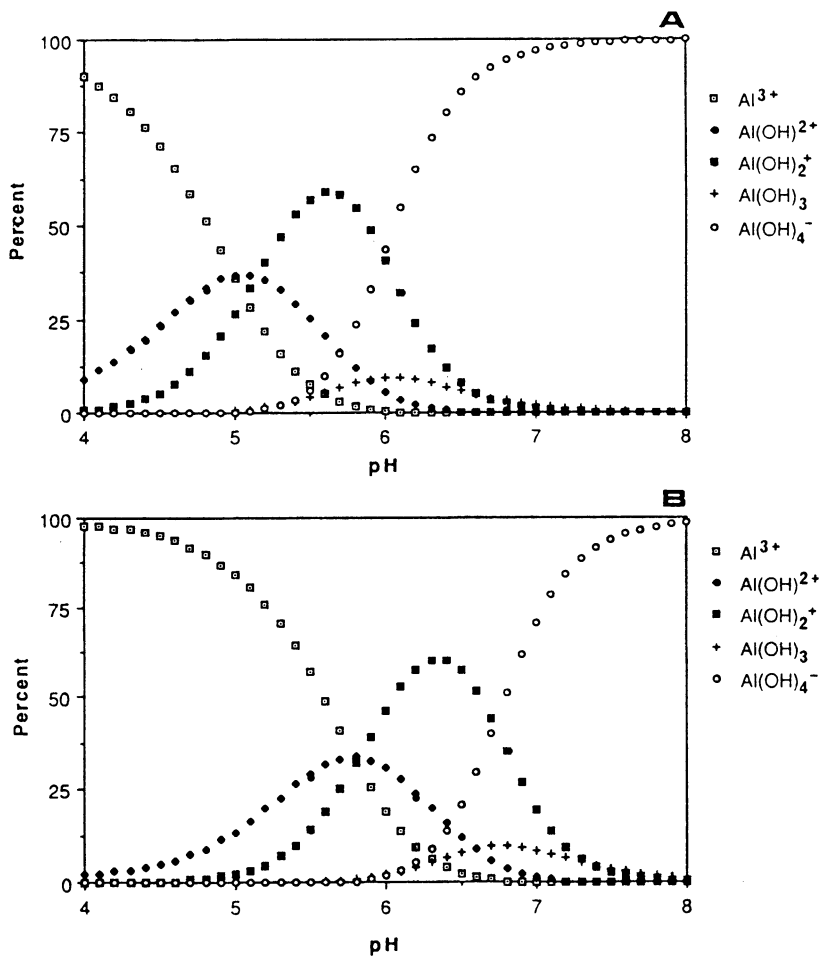


Fig. 2. The distribution of aqueous monomeric hydrolysis products in the pH range: 4.0 - 8.0. A: At 2°C. B: At 25°C.

performed so far. It is impossible to make a thorough evaluation of the toxicity of different aluminium species, without investigating various pH/temperature combinations.

Conclusion

This paper is only focusing on $\text{Al}(\text{OH})_3(\text{s})$ and does not incorporate other ligands. In natural aquatic systems several ligand competitors are present, making the aqueous aluminium chemistry even more complicated.

The solubility of $\text{Al}(\text{OH})_3(\text{s})$ and its hydrolysis are highly sensitive to pH and temperature. Ignoring temperature is absurd, if estimating solubility, hydrolysis, saturation and toxicity of inorganic aluminium species.

The aluminium hydroxide system is thought to be the main source of aluminium toxicity. The solubility and hydrolysis constants give no information about kinetics, *i.e.* how fast an equilibrium is established. It is therefore of major importance to increase our knowledge particularly concerning dissolution and formation kinetics of different solid aluminium pools and improve our knowledge concerning the hydrolysis and polymerization of the hydrolysis products at different pH and temperature.

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