

Investigation of the Buffering Function of Aluminum being in Equilibrium with the Mineral Kaolinite in Acidic Natural Water

Feng LIU, Shu Ping BI*, Ning GAN

Department of Chemistry, State Key Laboratory of Pollution Control & Resource Reuse,
Nanjing University, Nanjing 210093

Abstract: This paper presents a computer model to investigate the buffering function of aluminum being in equilibrium with mineral kaolinite in acidic natural water. Factors affecting the theoretical pH values are discussed. The model is verified by analyzing practical water samples.

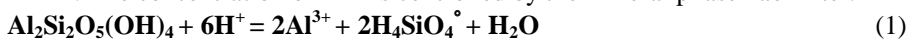
Keywords: Kaolinite, aluminum, buffering function.

Aluminum is not only claimed to be a potential threat to the health of many species including humans, but also demonstrated to be an important pH buffer under an acidic condition¹. For this reason, it has received considerable concerns these years². In surface waters where basic cations(C_B : K^+ , Ca^{2+} , Na^+ , Mg^{2+}) are barely released and/or strong acid anions(C_A : Cl^- , SO_4^{2-} , NO_3^-) are minimally retained, elevated concentrations of acidic cations such as H^+ or Al^{n+} are observed. The Al^{n+} undergoes a series of hydrolysis reactions and thus plays a substantial role in the regulation of the acid-base buffer status of acidic water. Models have investigated the buffering function of Al equilibria with gibbsite $Al(OH)_3$ in acidic natural water^{3,4}. However, as Al mainly occurs as aluminosilicate minerals within the earth's crust, and the concentration of the soluble Al in equilibrium is largely associated with the mineral phase the solution contacts with, it is meaningful to investigate the buffering function of Al in acidic natural water equilibria with the aluminosilicate minerals. The most common one is kaolinite $Al_2Si_2O_5(OH)_4$ and so far there has been little thorough investigation about it. In this paper, we develop a model utilizing thermodynamic relationships coupled with mass balance and electroneutrality constraints to illustrate the buffering function of Al equilibria with kaolinite by comparing the pH, acid neutralizing capacity(ANC) and buffering capacity(β) of acidic natural water in the presence of Al with those in the absence of it. Since pH is an important parameter influencing the speciation of metallic cations, we predict pH values of acidic natural waters by considering the buffering function of Al.

Theory

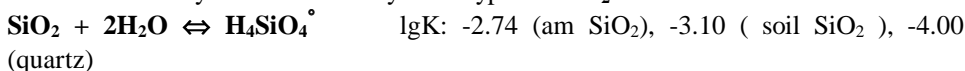
Assumptions have been suggested in previous study³. In case of kaolinite, two different assumptions are employed:

1. The concentration of Al^{3+} is controlled by the mineral phase kaolinite¹:



$$\lg K_{\text{sp}} = 6.87, [\text{Al}^{3+}] = K_{\text{sp}}^{1/2} / [\text{H}_4\text{SiO}_4^\circ][\text{H}^+]^3 \quad \text{let } K_{\text{sp}}' = K_{\text{sp}}^{1/2} / [\text{H}_4\text{SiO}_4^\circ]$$

2. The dissolved silica can be depicted as $\text{H}_4\text{SiO}_4^\circ$ in natural waters and its concentration may be determined by three types of SiO_2 ⁵:



As the average concentration of dissolved silica in natural waters is $300 \mu\text{mol/L}$ ⁶, we suggest that quartz controls its concentration¹.

Acid neutralizing capacity ANC and buffering capacity β are useful tools in assessing the acid-base status of acidic natural waters. ANC is calculated by Driscoll's definition⁷:

$$\text{ANC} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] + [\text{HOrg}^{2-}] + 2[\text{Org}^{3-}] - [\text{H}_3\text{Org}] + [\text{Al}(\text{OH})_2^+] + 3[\text{Al}(\text{OH})_4^-] + [\text{AlOrg}] - 2[\text{Al}^{3+}] \quad (2)$$

β is defined as the amount of strong acid or base required to produce an incremental change in pH ⁶.

$$\begin{aligned} \beta = d\text{ANC}/d\text{pH} = & -2.303 [\text{H}^+] d\text{ANC}/d\text{H} = \\ & -2.303 [\text{H}^+] \left([\text{CO}_3^{2-}] / K_{\text{c}2} + [\text{H}^+] / K_{\text{c}2} \partial \text{CO}_3^{2-} / \partial \text{H} + 2 \partial \text{CO}_3^{2-} / \partial \text{H} - K_{\text{w}} / [\text{H}^+]^2 - 1 + \right. \\ & [\text{Org}^{3-}] / K_{\text{g}3} + [\text{H}^+] / K_{\text{g}3} \partial \text{Org}^{3-} / \partial \text{H} + 2 \partial \text{Org}^{3-} / \partial \text{H} - 3 [\text{H}^+]^2 / (K_{\text{g}1} K_{\text{g}2} K_{\text{g}3}) [\text{Org}^{3-}] - \\ & \left. [\text{H}^+]^3 / (K_{\text{g}1} K_{\text{g}2} K_{\text{g}3}) \partial \text{Org}^{3-} / \partial \text{H} + K_{\text{OH}2} K_{\text{sp}}' - 3 K_{\text{OH}4} K_{\text{sp}}' / [\text{H}^+]^2 + 3 K_{\text{g}1} K_{\text{sp}}' [\text{H}^+]^2 [\text{Org}^{3-}] + \right. \\ & \left. K_{\text{g}1} K_{\text{sp}}' [\text{H}^+]^3 \partial \text{Org}^{3-} / \partial \text{H} - 6 K_{\text{sp}}' [\text{H}^+]^2 \right) \end{aligned} \quad (3)$$

The computer program is performed by using QBASIC on a Pentium II computer.

Results and Discussion

1. Aluminum's buffering function in natural water equilibria with kaolinite

Figure 1 illustrates concentration of soluble aluminum, pH, ANC and β as function of $C_{\text{B}}-C_{\text{A}}$ in the presence and absence of Al in acidic water equilibria with kaolinite.

Figure 1(a) shows that in the region of low values of $C_{\text{B}}-C_{\text{A}}$ ($< 200 \mu\text{eq/L}$), the concentration of soluble Al is relatively high. **Figure 1(b)** indicates that pH values are quite different in cases of Al present compared to those without it. Predicated pH values are low and change little with the decrease of the $C_{\text{B}}-C_{\text{A}}$ due to the high buffering capacities of H^+ and Al^{3+} . In the presence of Al, pH values are much larger. It is clarified by **Figure 1(c)** and (d) that the ANC and β are larger in the presence of Al compared to those in the absence of it. It indicates that Al does play a significant role in regulating the pH values of acidic natural waters.

In the vicinity of $C_{\text{B}}-C_{\text{A}}$ near zero (-200 to $200 \mu\text{eq/L}$), the pH values increase markedly from 4 to 6.3 because of the low concentration of Al and low buffering capacity near the $\text{H}^+ - \text{HCO}_3^-$ equilibrium. At higher values of $C_{\text{B}}-C_{\text{A}}$ ($> 200 \mu\text{eq/L}$), the

concentration of aqueous Al is extremely low and the water is simply buffered by the $\text{HCO}_3^- \text{---} \text{H}_2\text{CO}_3$ inorganic carbon equilibrium, then the pH, ANC and β are the same whether considering the buffering function of Al or not.

2. Factors affecting the theoretical predictions of pH values

Figure 2(a) illustrates the effect of the concentration of dissolved inorganic carbon(DIC) on the pH calculated. In the region of $C_B-C_A < -200 \mu\text{eq/L}$, the solution is acidic with pH about 4. The changes of the concentration of DIC have nearly no effect on the pH. In this region, as the concentrations of acid anions greatly exceed those of the basic cations and the H_2CO_3 is the prevalent form of DIC which facilitates the leaching of Al, the high buffering capacities of H^+ and Al maintain a constant pH. When the C_B-C_A is in the region of -200 to $200 \mu\text{eq/L}$, the concentration of soluble Al is significantly

Figure 1 Concentration of soluble aluminum(a), pH(b), ANC(c), $-\lg\beta$ (d) as function of C_B-C_A . (1)in the presence, (2)in the absence, of Al. $t = 25^\circ\text{C}$, $\text{DOC}=100$, $\text{DIC}=1000$, $C_F^*=5$, $\mu\text{mol/L}$.

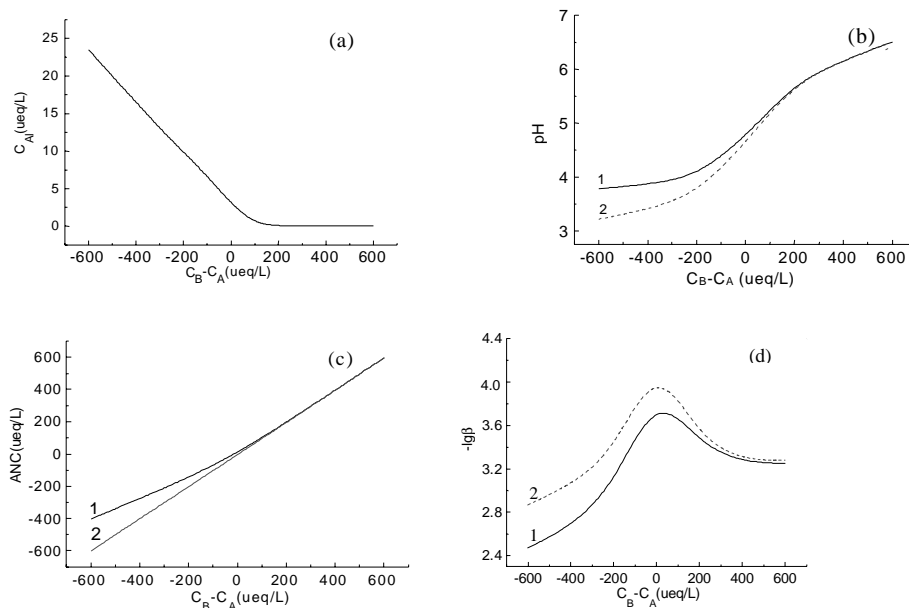
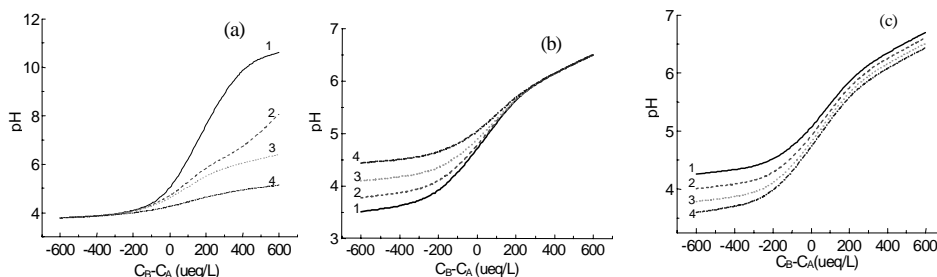


Figure 2 Influence of factors on the pH calculated.(Other parameters are the same as **Figure 1**)



- (a) DIC($\mu\text{mol/L}$): 1—100, 2—500, 3—1000, 4—10000
 (b) $\text{H}_4\text{SiO}_4^\circ$ ($\mu\text{mol/L}$): 1—1000, 2—100, 3—10, 4—1
 (c) Temperature: 1—268K, 2—283K, 3—298K, 4—313K

and so does the buffering function of Al. It's mainly buffered by the $\text{H}^+ - \text{HCO}_3^-$ equilibrium. The bigger the concentration of DIC, the larger the buffering capacity of $\text{H}^+ - \text{HCO}_3^-$, and the less the pH changes as is shown that the slope of line 4 is smallest among the four lines. When $C_B - C_A > 200 \mu\text{eq/L}$, the concentration of soluble Al is extremely low and the water is simply buffered by the $\text{HCO}_3^- - \text{H}_2\text{CO}_3$ equilibrium. The pH values remain at different values due to the different concentrations of DIC. At a fixed $C_B - C_A$, the bigger the concentration of DIC, the lower the pH calculated.

Equation 1 states a reciprocal solubility relationship between Al^{3+} and dissolved silica. When the $\text{H}_4\text{SiO}_4^\circ$ activity is high, the activity of Al^{3+} is depressed due to the increased stability of the aluminosilicate, so the changes of activities of $\text{H}_4\text{SiO}_4^\circ$ have the same effect as that caused by the changes of the solubility product K_{sp} of kaolinite. As the changes of K_{sp} of gibbsite have a remarkable effect on the aluminum's buffering function³, it suggests that the concentration of dissolved silica also affects pH apparently. **Figure 2(b)** demonstrates that in the region of $C_B - C_A < -200 \mu\text{eq/L}$, if the concentration of dissolved silica is high, the correspondent pH is low because of the depressed buffering function of Al. When $C_B - C_A > -200 \mu\text{eq/L}$, the water is buffered mainly by inorganic carbon equilibrium and the concentration of dissolved silica has no effect on the pH calculated.

We employed the Van't Hoff equation to adjust the effect of the temperature. **Figure 2(c)** shows that temperature has a considerable effect on the pH in the acidic region of $C_B - C_A < -200 \mu\text{eq/L}$. Raising the temperature will reduce the pH to a noticeable extent.

2. Prediction of pH in acidic natural waters equilibria with kaolinite

We apply the calculation to the practical analysis of natural sampling waters⁸⁻¹². The systems are all equilibria with kaolinite. The calculated pH values are compared with those from experiments. The linear regression equation is : $\text{pH}_{\text{cal}} = 0.934\text{pH}_{\text{mea}} + 0.431$, ($r=0.946$, $n=13$). The results are agreeable.

Acknowledgments

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