

Investigation on the Stability of Aluminosilicate Colloids by Various Analytical Tools

Kirana Y. Putri*, D. H. Lee, J.-I. Yun

Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701 Korea

*Corresponding author: pui87@kaist.ac.kr

1. Introduction

Colloids are ubiquitous in natural aquatic systems. Aquatic colloids may play a significant carrier role for radionuclide migration in aquifer systems. Being omnipresent in natural aquatic systems, aluminosilicate colloids are considered as a kernel for various aquatic colloids [1]. Characterization of aluminosilicate colloids formed under various geochemical conditions is of importance to understand their chemical behavior in natural aquatic systems. In this work, a preliminary study on the formation of aluminosilicate colloids with a help of colorimetry and other colloid detection techniques is presented.

2. Experimental

2.1. Colorimetry

Sample preparation. For the purpose of calibration, six Si samples in various concentrations are prepared by dilution of Si ICP standard solution (Merck). 10 ml of sample is adjusted to pH 1.1 by 5% w/v ammonium molybdate (Merck) and 1 M hydrochloric acid (Merck). At this pH, β -yellow silicomolybdic acid is the only existing isomer. After 10 minutes of reaction, 1 ml of 50% v/v sulfuric acid (Merck) and 0.4 ml of 10% w/v oxalic acid (Merck) are added. 5 minutes are needed for the masking reaction. 0.2 ml of 0.05 N stannous chloride (Aldrich) is added subsequently to reduce the β -silicomolybdic acid within 20-40 minutes. The reduced substance has a blue color which is stable for 15 minutes [2, 3].

In addition, Si is determined in the presence of Al. Mixed Al-Si samples are freshly prepared with concentration ratios of 1:1, 10:1, and 100:1 for Al and Si, respectively. The samples are treated by the same procedure as mentioned above.

Calibration for Al colorimetry is carried out with ten samples of various Al concentrations with a commercial test kit (Spectroquant, Merck). The samples are prepared by dilution of ICP Al standard solution (Aldrich).

Instrument. Colorimetric measurements of prepared samples are performed in 10 mm cuvette using UV-Vis absorptiometer (Scinco S-4100 PDA).

2.2. Colloids measurement

Sample preparation. Samples of aluminosilicate are prepared with the following combinations: (1) pH 4-10;

(2) equal Al and Si concentrations of 10^{-3} M and 10^{-5} M; (3) in 0.1 M, 0.01 M, and 0.001 M NaCl. A 50 ml sample is prepared in a plastic bottle for each combination. 8 ml is then separated for the purpose of equilibrium monitoring.

Instrument. Equilibrium monitoring involves pH and particle size measurements. pHs are measured continuously to follow the changes toward stability. Laser induced breakdown detection (LIBD) and photon correlation spectroscopy (PCS) are used for confirmation of colloid formation. Information on colloidal size and concentration is obtained by plotting the effective focal length and breakdown probability according to the calibration curves for well-defined, monodisperse polystyrene nanoparticles. For the colloid detection, 60% of the threshold energy for ultrapure water ($18.2 \text{ M}\Omega \cdot \text{cm}$, Milli-Q Synthesis) was applied.

3. Results and discussions

3.1. Colorimetric determination of silicon and aluminum concentration

For the determination of Si, ICP-MS and ICP-AES suffer from spectral interferences due to matrix effects and from the formation of molecular ions with oxygen or carrier gas. ICP-MS is not sensitive for the determination of low mass elements like silicon. Furthermore, the sensitivity of these methods is relatively poor, compared with that of colorimetric method [4]. Thus, colorimetry is proposed as the analytical tool in determining the dissolved ions concentration.

Maximum absorbance of silicomolybdenum blue is observed at 812 nm. Concentration of Si correlates linearly with the absorbance. The molar extinction coefficient (ϵ) is determined to be $19754 \text{ M}^{-1} \text{ cm}^{-1}$ and detection limit is as low as 5×10^{-8} M. These values are in good agreement with those of commercial test kit. Increase of light path length, e.g. 1 m, will enhance the sensitivity of measurement.

Aluminum reacts with chromazurol S (CAS) in weakly acid (pH 5.5) to form a blue violet compound. Al-CAS complex has a maximum absorbance at 548 nm. The calibration curve indicates that Al colorimetry has tendency toward saturation near the detection limit.

The spectra obtained from measurements of mixed Al-Si in various concentration ratios show similar shape and absorbance, as shown in Fig. 2. Therefore, Al does not interfere with silicomolybdate complexes under the

experimental conditions, and the self-made reagents are applicable for the aluminosilicate study.

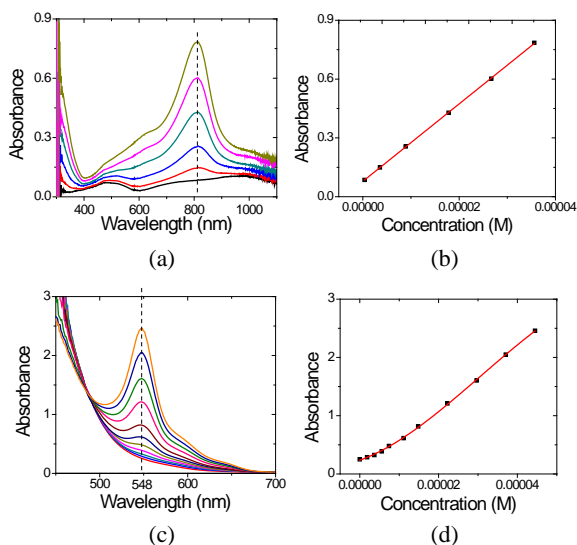


Fig. 1. Spectra of silicomolybdenum blue (a) and its calibration curve (b) (top), and spectra (c) and calibration curve (d) of aluminum colorimetry (bottom).

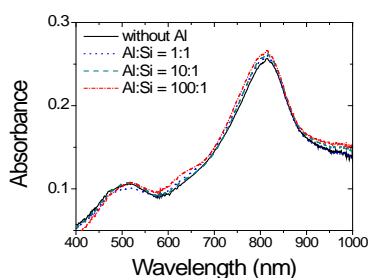


Fig. 2. Silicomolybdenum blue in absence and presence of Al.

3.2. Stability of aluminosilicate colloids

Hitherto, measurements with PCS are unable to give any significant data. Thus, the particle size can be estimated smaller below the detection limit. Nevertheless, tendencies are observed from the LIBD results. At the same ionic strength, samples with 10^{-3} M of Al and Si formed more colloids than 10^{-5} M Al and Si. On the other hand, at the same Al and Si concentration, the breakdown probability increases as ionic strength decreases, i.e. more colloids are formed.

Most aluminosilicate colloids are observed at near neutral pH. It asserts the lowest solubility of aluminosilicate at pH 6. The solubility curve of some known aluminosilicates is given somewhere else [1]. Contrarily, very low amount of colloids are observed at pH 4, probably due to the oxygen bridge breaking caused by acidic pH effect [1].

Sample of 10^{-3} M of Al and Si in 0.1 M NaCl has the highest breakdown probability at pH 4.5. The breakdown probability is around 30% with effective focal length of 493 μm . The measurement is performed

in the same condition with that of polystyrene calibration. Aluminosilicate colloid size is estimated to be 20 nm with concentration of 104 ppt according to the calibration curve of polystyrene nanoparticles.

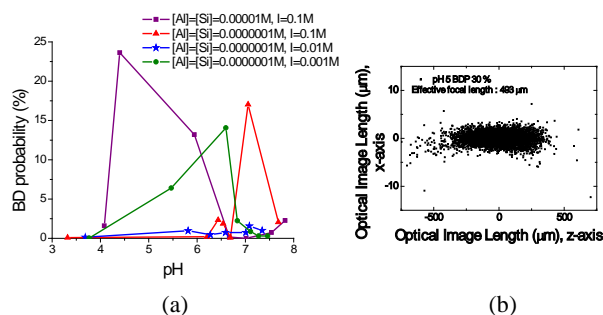


Fig. 3. (a) Breakdown probability as a function of pH showing the relative particle size distribution at various pHs, concentrations, and ionic strengths in NaCl solutions. (b) Distribution of breakdown events on the beam axis for sample of $[\text{Al}] = [\text{Si}] = 10^{-3}$ M in 0.1 M NaCl and at pH 4.5.

4. Conclusions

Investigation on the formation of aluminosilicate colloids as a function of pH and ionic strength has been performed. Various analytical tools are used for the investigation. Sensitivity of colorimetric method makes it able to be applied for the determination of dissolved Al and Si ion concentration. LIBD and PCS are also employed for the colloid characterization. LIBD provides information on colloidal size and concentration, whereas PCS is heretofore unable to give any considerable data. For the purpose of characterization, filtration will be carried out using 450 nm and 10 kDa filter to separate each phase of interests: precipitate, colloid, and dissolved ions. It will be conducted once the equilibrium is reached. For the time being, equilibrium has not yet been reached. Furthermore, the formation of aluminosilicate colloids under more various geochemical conditions, e.g. in various salt concentrations, is to be investigated.

REFERENCES

- [1] M.A. Kim, P. J. Panak, J.I. Yun, J.I. Kim, R. Klenze, K. Köhler, Interaction of Actinides with Aluminosilicate Colloids in Statu Nascendi Part I: generation and characterization of actinide(III)-pseudocolloids, Colloids and Surfaces A: Physicochem Eng. Aspects, No. 26, p. 97, 2003.
- [2] F.A.J. Armstrong, The Determination of Silicate in Sea Water, Journal of the Marine Biological Association of the United Kingdom, Vol. 30 No. 1, p. 149, 1951.
- [3] J.B. Mullin, J.P. Riley, The Colorimetric Determination of Silicate with Special Reference to Sea and Natural Waters. Analytica Chimica Acta, Vol. 12, p. 162, 1955.
- [4] J. Isoe, K. Morita, E. Kaneko, Determination of Trace Silica in Highly Purified Water Based on Delayed Quenching Of Rhodamine B Through Nanoparticle Formation with Molybdate, Analyst, Vol. 130, p. 872, 2005.