Dual-Functional Ice/Water Interface Allows High-Yield Formation of Al$_{13}$ with Low Energy

Liang Kuang, Ning Li, William A. Jefferson, Yaohui Bai, Qinghua Ji, Huijuan Liu, and Jiuhui Qu

Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
University of Chinese Academy of Sciences, Beijing 100049, China

Supporting Information

ABSTRACT: Keggin Al$_{13}$(AlO$_4$Al$_{12}$(OH)$_{24}$(H$_2$O)$_{12}$)$^{7+}$ is a well-known efficient coagulant widely used in water purification and treatment. The production of high-content Al$_{13}$ is still costly, and it is therefore essential to develop new eco-efficient and low energy demand synthesis methods for practical application. Solid–water interfaces play a dominant role in heterogeneous reactions, which can be utilized in various processes through rationally designed interfaces. Here, we designed an Al$^{3+}$ and OH$^{-}$ interface by using NaOH-doped ice as a solid and AlCl$_3$ solution as liquid for Al$_{13}$ production. This system provides a natural and renewable solid–water interface through ice melting, while simultaneously minimizing external energy input and maintaining an effective heterogeneous interface reaction for production of high-quality Al$_{13}$ species. The dual-function of ice–water interface enables the formation of Al$_{13}$ with a high yield of up to 90% compared to initial total Al. Moreover, global areas with cold winter climate conditions may exploit this process reducing the need for external artificial energy. As AlCl$_3$ can be obtained with low cost, this method may have great potential for industrial mass production of Al$_{13}$.

KEYWORDS: Ice–water interface, Dual-functional, Keggin Al$_{13}$, Solid–water interface, Low energy, Water treatment

INTRODUCTION

Keggin Al$_{13}$(AlO$_4$Al$_{12}$(OH)$_{24}$(H$_2$O)$_{12}$)$^{7+}$ was discovered during the spontaneous hydrolysis of aluminum salts in solution and has characteristics of high positive charge and strong binding affinity to particles. Al$_{13}$ plays a key role in the chemistry of aluminous minerals and involves many sorption reactions at the solid–water interface. Its special properties have given rise to its widespread use as a coagulant during water treatment, and has been proven to be the most active species responsible for aluminum salt coagulation.

Researchers have long attempted to artificially reproduce the formation of aluminum hydrolysis to obtain higher yields. It has been considered that Al$_{13}$ is a polymer that has an AlO$_4$ center surrounded by 12 octahedral Al units. Many investigations suggest that the formation of Al$_{13}$ requires Al(OH)$_4$$^{-}$ as a key precursor (formed through reaction of Al$^{3+}$ with OH$^{-}$). However, the Al(OH)$_4$$^{-}$ usually exists at high pH whereas the 12 octahedral Al units rely on an acidic pH environment. Bersh et al. found microinjection of NaOH solution into AlCl$_3$ solution helpful in formation of Al$_{13}$. The process involved “acid–base-like” reactions between AlCl$_3$ and NaOH droplets, Al(OH)$_4$$^{-}$ formation and subsequent Al–OH$_4$$^{-}$ reaction with the octahedral Al units in AlCl$_3$ solution. This represents a typical synthesis method of Al$_{13}$, which although beneficial, the microinjection method may become prohibitive due to time consumption if applied to larger scale preparation of Al$_{13}$. Furrer et al. developed an Al$_{13}$ synthesis method by allowing Al(III) solutions to flow over granulated marble at designated flow velocities. They obtained a high content of Al$_{13}$ solution, but there was some loss of aluminum due to adsorption by the marble granulate or through precipitation of amorphous Al(OH)$_3$. This led final total concentrations of aluminum to be smaller than the initial concentrations. Researchers thus considered rapid Al(OH)$_4$$^{-}$
generation via a solid–water interface that could be equivalent to acid–base interface formed by the NaOH droplets and AlCl₃ solution. 

To our knowledge, there are at least four paths to synthesize high-content Al₁₃: (1) Microinjection method mentioned. (2) The method by Furrer et al. mentioned. (3) Preparation of Al₁₃ with electrolysis device, where an electrode–solution interface is used to an acid–base interface. (4) Preparation using membrane reactor, in which membrane was used to add NaOH solution rapidly and uniformly. Both methods 3 and 4 have enabled significant time savings compared to method 1, and obtain higher yields of Al₁₃ content. Nevertheless, these methods have drawbacks such as high electric energy consumption and prohibitive cost for special materials (electrode, membrane) and the electrolysis method also has a problem of residual as anode mud. Developing preparation methods with lower cost, lower energy, lower chemical reagents and even shorter reaction time still remains a largely unanswered challenge.

Previous investigations have repeatedly shown that the acid–base interface is of chief value in the synthesis of Al₁₃. Borrowing from naturally occurring environmental processes, i.e., “ice-melting”, we considered a new way to tackle an old problem for a more energy-efficient and renewable solid–liquid interface. During the ice-melting process, the solid–water interface exists freely in a state of flux, e.g., refresh and dissolving from beginning to end. The ice–water interface involves at least two special characteristics. In the first place, the ice–water interface could act as a heterogeneous solid–liquid in its simplest form, because ice and water are of the same chemical nature but differ only in physical form. At the same time, the melting of ice is autonomous. Meaning, there is no need for external energy input to maintain the interface reaction. Moreover, after the ice has melted over there is no other residue except water, implying that a heterogeneous interface like this seems to introduce no extra byproducts. We can derive a novel water–solid interface by freezing one main reactant solution into ice effectively changing an aqueous homogeneous reaction into a heterogeneous one.

To do so, we need to consider how to combine the ice-melting effect into the synthesis process of Al₁₃. The starting materials of Al₁₃ are usually NaOH solution and AlCl₃ solution at a molar ratio of 2−2.5. It is common sense that a direct mixing of these two solutions will lead to the formation of Al(OH)₃ hydroxides. We replaced the water of the ice balls with NaOH solution for subsequent addition to AlCl₃ solution.

## EXPERIMENTAL METHODS

**Synthesis Method.** The experimental scheme based on the ice-melting effect is illustrated in Figure 1. AlCl₃ solution was prepared as a source of Al for Al₁₃ synthesis and NaOH solution was frozen into ice balls. Even though we have used electric energy here, we could take advantage of cold weather in winter or in a cold area for practical production. The molar ratio of NaOH to AlCl₃ was set at an approximate range of 2.1–2.6 during different batches according to previous investigations. Each time, 10 mL of NaOH solution was added into a plastic retractable spherical shell with a copper core in the center. A thin wire was tied to the copper core. The shell with solution was then put in a frozen environment (−20 °C) in a refrigerator. After becoming frozen, the freshly formed NaOH ice balls were removed from the spherical shell and dropped into a beaker containing 90 mL AlCl₃ solution of 0.056 or 0.222 mol/L with magnetic stirring at 400 rpm (Figure 1). After the ice-melting process, the product was left standing for 12 h. A photograph of the NaOH ice-ball and normal water ice-ball comparison can be found in Figure S1.

**Characterization of Aluminum Speciation.** Both the raw AlCl₃ solution before the synthetic process and the synthetic product were detected by ESI-TOF-MS (2695XE micro, Waters). After that, the raw AlCl₃ solution and the product were characterized by 27Al nuclear magnetic resonance (NMR) spectroscopy obtained on a BRUKER AVANCE(III) (500 MHz) spectrometer with 130 MHz resonating frequency. The operation parameters were: repetition delay was 2 s, frequency was 130 MHz, scan width was 39680 Hz, and number of scans was 128. The total aluminum concentration was determined by an ICP-AES (PerkinElmer, Optima 2000, U.K.). The percentage of Al₁₃ was calculated by the results of 27Al NMR spectroscopy and ICP-AES. Determination of aluminum species (Al₉, Al₆, and Al₃) using the Ferron method can be found in Figure S2 of the Supporting Information.

**Determination of the Temperature and pH of the Interface.** A microtemperature sensor was made using a platinum resistor, and the platinum resistance had been kept attached to the surface of the ice ball during the whole melt process. A microsyringe was used to take 100 μL solution samples near the surface of NaOH ice balls during the melting process to determine the pH. At the same time, the changes of temperature and pH of the bulk solution were determined, respectively.

**Jar Tests.** To test the performance of the raw AlCl₃ solution and the synthetic product, jar tests were performed by a Phipps and Bird six-paddle stirrer. The procedures include a 1 min rapid mix (200 rpm), 15 min slow mix (50 rpm), and a 30 min settling step. The samples were collected just after rapid mixing and determined immediately with a Zeta plus meter (Malvern, Zetasizer 2000, U.K.). After settling, the supernatants were used to determine the residual turbidity (HACH 2100N turbidimeter).

## RESULTS AND DISCUSSION

The ESI-TOF-MS spectra of raw AlCl₃ solution and the product are contrasted in Figure S3. Positive ion ESI-MS was used to detect the speciation of aluminum according to the procedure mentioned by Zhao et al. The most intense peaks of Figure S3b were at m/z 213, m/z 328 and m/z 337, showing that Al₁₃ was the typical dominant component in the product. The spectra proved that most aluminum oligomers had transformed into Al₁₃, which is a sufficiently stable polymer once formed. A full list of m/z calculated versus experimental values can be found in the Supporting Information (Table S1).
To quantify the content of Al\textsubscript{13} in the product, \textsuperscript{27}Al-NMR spectroscopy was used. Figure 2 shows the typical spectra of the raw material and the product, from which we can see the result having coherence with the spectra of ESI-TOF-MS (Figure S3). The product shows three signals in the spectra, the signal at 63 ppm resonance represented Al\textsubscript{13}. The signal at 0 ppm corresponds to monomeric Al, 80 ppm refers to Na aluminate solution as a reference material, and 63 ppm stands for Al\textsubscript{13}.\textsuperscript{13,22}

The concentration of Al\textsubscript{13} is calculated by using the 63 ppm signal multiplied by 13\textsuperscript{13,22} with total aluminum concentration determined by ICP-OES.

Considering that the AlCl\textsubscript{3} solution temperature might affect the efficiency of the ice-melting effect, and the molar ratio of NaOH to AlCl\textsubscript{3} has been proved to play an important role in Al\textsubscript{13} synthesis in previous studies. A series of products with varying molar ratios of NaOH to AlCl\textsubscript{3} were prepared, and the ice-melting process was kept under water bath at 15, 20 and 25 °C. The optimum molar ratio for Al\textsubscript{13} synthesis in the ice-melting process was 2.5 where the percentage content of Al\textsubscript{13} accounting for total Al reaches the highest at about 90% (Figure 3). Though the AlCl\textsubscript{3} solution temperature has little effect on the composition of product, under certain molar ratios of NaOH to AlCl\textsubscript{3} and the content of Al\textsubscript{13} exhibited small changes toward variation in AlCl\textsubscript{3} solution temperature. This reveals that the ice-melting process can be carried out under mild temperature conditions. The reaction time under a series of AlCl\textsubscript{3} solution temperature at 15, 20 and 25 °C was on average 85, 68 and 57 s, respectively. It signifies that the ice melting process was very fast at room temperature. Other methods usually take hours to accomplish the reactions at solid–water interface, indicating that the ice-melting effect has an enormous advantage in time-saving.

The ice–water interface divided the reaction area into two types of regions: a combination of alkaline region and acidic region, and at the same time a combination of relatively cold region and relatively hot region. The two combinations could account for the optimum conditions for synthesis, and this could be described chiefly as dual-function of the ice/water interface.

Previous investigations\textsuperscript{10,13} suggest Al(OH)\textsubscript{4} acting as a key precursor in the formation of Al\textsubscript{13}, for that the center of keggin Al\textsubscript{13} is a AlO\textsubscript{4} structure. The formation of Al\textsubscript{13} could be concluded in two main steps:

\[
\text{Al}^{3+} + 4\text{OH}^{-} \rightarrow \text{Al(OH)}_4^- \\
\text{Al(OH)}_4^- + \text{Al}_4 (\text{octahedral Al units}) \rightarrow \text{Al}_{13} 
\]

The precursor Al(OH)\textsubscript{4} is generated in the former step under alkaline pH condition. The benefit of the ice–water interface is that it offers an alkaline region conveniently, without need of external energy input or long reaction times for Al\textsubscript{13} aggregation. The ice–solution interface involves two special regions: The alkaline interfacial region closest to the ice ball to form the precursor Al(OH)\textsubscript{4}–, and the bulk solution region containing “acidic” AlCl\textsubscript{3} octahedral Al units to accomplish step 2. The pH of the samples near the surface of the ice balls is shown in Figure 4, providing direct evidence of the alkaline region near the surface of the ice balls.

In addition, the ice–water interface provides a cold zone for the reaction. In general, the low temperature near the interface allows the hydrolysis process of Al\textsuperscript{3+} to occur at a relatively slow speed, and makes polymerization of the hydrolysis products more favorable. Step 1 mentioned is an exothermic reaction, therefore it requires a relatively low temperature to produce...
Al(OH)$_4^-$ though step 2 is an endothermic step, it is favorable for a relatively high temperature. Thus, the optimum conditions for the synthesis is to divide the whole system into two regions: a relatively cold region for step 1 and a relatively hot region for step 2. The temperature of the interface during the melting process is shown in Figure 5. It shows that the temperature at the surface of the ice ball was kept below $-15\,^\circ C$ during the reaction. The melting of ice would uptake the heat of step 1 and maintain a low temperature at the ice–water interface, meaning the interface kept a relatively low temperature for step 1 to form the precursor Al(OH)$_4^-$ though the bulk solution maintained a relatively high temperature region for step 2, where the Al(OH)$_4^-$ will enter to finish step 2.

For a comparison of coagulation behavior of synthetic product, the raw AlCl$_3$ solution and commercial PACl is shown in Figure S4 and Figure S5. The pH of suspension was 7.3 with a dosage of $10^{-5}$ mol. Obviously, the zero point of charge of synthetic product is much lower than the raw AlCl$_3$ solution, and it is even lower than commercial PACl. The higher charge neutralization ability is due to the high percentage of Al$_{13}$. Figure S4 shows the lower dosage for optimum coagulation and removal of turbidity indicate the high efficiency of synthetic inorganic polymer flocculants. Figure S5 compares the efficiency of synthetic product with raw AlCl$_3$ solution and commercial PACl solution under a series of initial pH conditions, the results show that the synthetic product has a higher performance in each case, whether acidic or alkaline.

The comparison of this method toward other methods is shown in Table S2.

**CONCLUSIONS**

In summary, it has been verified that the ice-melting effect was successfully used in the synthesis of Al$_{13}$. It provides a novel form of the solid–water interface with characteristics of low energy cost, short reaction time, high yield and no hazardous residual chemical reagents. Reactions at the solid–water interface are of great importance across many scientific disciplines including biochemistry, electrochemistry and catalytic chemistry. However, such reactions in artificial systems almost always require highly specialized conditions to provide a suitable reactive interface while simultaneously keeping undesirable effects low. Because the nature of the ice-melting effect is to create an interface by change of phase without change of chemical composition, this investigation may represent a typical case of the ice-melting effect applied in an acid–base interface reaction. It also offers an applicable framework to reactions associated with solid–water interfaces. The main associated energy cost of the ice-melting process comes from the freezing step. For future application, it would be interesting to see if the process could be applied in cold global regions or during the winter for a cost-effective way to freeze solutions and further reduce energy costs.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b01630.

Additional experimental details, figures of ice balls, Ferron and ESI-TOF-MS studies, result of jar tests and comparison of various synthetic methods (PDF)
Corresponding Author

J. Qu. Telephone/Fax: +86-10-62849160. E-mail: jhqu@rcees.ac.cn.

ORCID
Ning Li: 0000-0001-8963-8550
William A. Jefferson: 0000-0001-9250-9434
Huijuan Liu: 0000-0003-0855-0202
Jiuhui Qu: 0000-0001-9717-093X

Acknowledgments

The authors thank Junfeng Xiang in the Analysis and Testing Center, Institute of Chemistry, Chinese Academy of Sciences for NMR detection and analysis. This work was financially supported by the National Natural Science Foundation of China (51422813).

References

(1) Johansson, G. On the crystal structures of some basic aluminium salts. Acta Chem. Scand. 1960, 14 (3), 771–773.
(2) Reussler, D.; Casey, W. H.; Naveotsky, A. Energetic Insight into the Formation of Solids from Aluminum Polyoxocations. Angew. Chem., Int. Ed. 2015, 54 (32), 9253–9256.
(3) Phillips, B. L.; Casey, W. H.; Karlsson, M. Bonding and reactivity at oxide mineral surfaces from model aqueous complexes. Nature 2000, 404, 379–382.
(4) Casey, W. H. Large aqueous aluminum hydroxide molecules. Chem. Rev. 2006, 106 (1), 1–16.
(5) Stumm, W.; O’Melia, C. R. Stoichiometry of coagulation. J. Am. Water Works Assoc. 1986, 60 (5), 514–539.
(6) Wang, W. Z.; Hsu, P. H. The Nature of Polynuclear OH-Al Complexes in Laboratory-Hydroryzed and Commercial Hydrosylyaluminum Solutions. Clays Clay Miner. 1994, 42 (3), 356–368.
(7) He, Z.; Lan, H. C.; Gong, W. X.; Liu, R. P.; Gao, Y. P.; Liu, H. J.; Qu, J. H. Coagulation behaviors of aluminum salts towards fluoride: Significance of aluminum speciation and transformation. Sep. Purif. Technol. 2016, 165, 137–144.
(8) Hu, C. Z.; Liu, H. J.; Chen, G. X.; Jefferson, W. A.; Qu, J. H. Ar(III) oxidation by active chlorine and subsequent removal of As(V) by Al-13 polymer coagulation using a novel dual function reagent. Environ. Sci. Technol. 2012, 46 (12), 6776–6782.
(9) Parthasarathy, N.; Buffle, J. Study of polymeric aluminium (III) hydroxide solutions for application in waste water treatment. Properties of the polymer and optimal conditions of preparation. Water Res. 1985, 19 (1), 25–36.
(10) Akitt, J.; Farthing, A. Aluminium-27 nuclear magnetic resonance studies of the hydrolysis of aluminium (III). Part 4. Hydrolysis using sodium carbonate. J. Chem. Soc., Dalton Trans. 1981, 1617–1623.
(11) Akitt, J.; Farthing, A. Aluminium-27 nuclear magnetic resonance studies of the hydrolysis of aluminium (III). Part 5. Slow hydrolysis using aluminium metal. J. Chem. Soc., Dalton Trans. 1981, 1624–1628.
(12) Bottero, J. Y.; Axelos, M.; Tchoubar, D.; Cases, J. M.; Fripiat, J. J.; Fiesinger, F. Mechanism of formation of aluminum trihydroxide from kegg Al13 polymers. J. Colloid Interface Sci. 1987, 117 (1), 47–57.
(13) Bertsch, P. M.; Thomas, G. W.; Barnhisel, R. I. Characterization of hydroxy-aluminum solutions by aluminum-27 nuclear magnetic resonance spectroscopy. Soil Sci. Soc. Am. J. 1986, 50 (3), 825–830.
(14) Furrer, G.; Trusch, B.; Muller, C. The formation of polynuclear Al13 under simulated natural conditions. Geochim. Cosmochim. Acta 1992, 56 (10), 3831–3838.
(15) Pi, K. W.; Gao, L. X.; Li, Z.; Wang, M.; Huang, L. PAC with high content of Al-13 polymer prepared by electrolysis with periodical reversal of electrodes. Colloids Surf., A 2011, 387 (1–3), 113–117.

Notes

Huijuan Liu: 0000-0003-0855-0202

ORCID
Ning Li: 0000-0001-8963-8550
J. Qu. Telephone/Fax: +86-10-62849160. E-mail: jhqu@rcees.ac.cn.