

A kinetic study of the formation of iron (hydr)oxides at pH 2-4 and at 5-55 °C

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Iron (hydr)oxides are widely distributed in the earth's surface environment. The formation process and adsorption characteristic of iron (hydr)oxides and the material transport mediated by iron colloids are receiving attention. In the present study, we evaluated (i) the rate at which iron (hydr)oxides are formed from dissolved Fe^{3+} at pH 2-4 and (ii) the effect of the difference of anions on the reaction behavior.

First, a solution of Fe^{3+} 100 ppm was prepared by dissolving FeCl_3 into pure water (chloride system). This solution was reacted at 15, 25, 35, 45, and 55 °C. At 25 °C pH of the solution was ~ 2.7 at the start of the reaction and decreased to ~ 2.2 as reaction time passed. Such change in pH is known to occur as a result of the following reactions: hydration of Fe^{3+} (release of H^+) \rightarrow formation of dissolved $\text{Fe}(\text{OH})_3 \rightarrow$ formation of solid $\text{Fe}(\text{OH})_3$ (Grundl and Delwiche, 1993). Therefore, information of the formation rate of iron (hydr)oxides can be obtained by monitoring the pH of the solution. After the initial stage of the reaction in which the concentration of dissolved $\text{Fe}(\text{OH})_3$ decreased slowly presumably due to nucleation, first-order-like decrease of $\text{Fe}(\text{OH})_3$ concentration proceeded in the intermediate stage, and the reaction behavior deviated from the first-order reaction at the later stage. By focusing on the intermediate stage, rate constants of $3.3\text{E-}5 - 1.1\text{E-}2 \text{ s}^{-1}$ were obtained at 15-55 °C. Good linearity was confirmed in an Arrhenius plot of these rate constants, and an activation energy (E_a) of $118 \pm 5 \text{ kJ/mol}$ was obtained.

Secondly, solutions of Fe^{3+} 100 ppm were prepared by dissolving $\text{Fe}(\text{NO}_3)_3$ nonahydrate and $\text{Fe}_2(\text{SO}_4)_3$ n-hydrate into pure water to compare the reaction behavior between chloride, nitrate, and sulfate systems. Temperatures for the reactions were 15, 25, 35, and 45 °C in the nitrate system, and 25, 35, 45, and 55 °C in the sulfate system. At 25 °C, initial pH were ~ 2.9 for the nitrate solution and ~ 2.7 for the sulfate solution, and pH for both the solutions decreased to ~ 2.5 as time passed. Rate constants obtained in the same way as the chloride system were $2.7\text{E-}5 - 3.6\text{E-}3 \text{ s}^{-1}$ in the nitrate system and $6.7\text{E-}5 - 5.9\text{E-}3 \text{ s}^{-1}$ in the sulfate system, again showed good linearity in Arrhenius plots. $E_a = 122 \pm 4 \text{ kJ/mol}$ for the nitrate system and $E_a = 119 \pm 4 \text{ kJ/mol}$ for the sulfate system were obtained. These results showed that the activation energies agree within the margins of error regardless of the difference of the kind of anions.

Finally, a solution of Fe^{3+} 10 ppm was prepared by dissolving FeCl_3 into pure water to evaluate the reaction rate at pH 3-4. Temperatures for the reactions were 5, 15, 35, and 25 °C. At 25 °C, pH of the solution decreased from ~ 3.8 to ~ 3.3 as reaction time passed. The rate constants obtained was $2.7\text{E-}5 - 2.9\text{E-}3 \text{ s}^{-1}$, which was about 16 times faster than that of Fe^{3+} 100 ppm at pH 2.2-2.7. The activation energy obtained was $E_a = 162 \pm 3 \text{ kJ/mol}$ and higher than that at pH 2.2-2.7.

Keywords: kinetics, iron (hydr)oxide, activation energy