Association constants of Fe(III)-As(V) complexes in solution and solubility product of scorodite up to 90 °C

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The solubility of Fe-As minerals has been intensively studied because of the environmental needs. But, the thermodynamic data for aqueous iron-arsenic species are inadequately characterized. The Gibbs free energy, enthalpy, entropy, and heat capacity and activity coefficients were refined in the Fe(II)-Fe(III)-As(V)-$HClO_4$ and Fe(II)-Fe(III)-As(V)-HCl systems using redox potential measurements from 5 to 90 °C. The association constants for $FeHAsO_4^+$ and $FeH_2AsO_4^{2+}$ at 25 °C are $10^{10.28}$ and $10^{4.02}$, and the corresponding association reaction enthalpies and heat capacities are 25.74 and 8.73 kJ mol^{-1} and 843.1 and -529.6 J K^{-1} mol^{-1}, respectively. Individual ion activity coefficients for H^+, ClO_4^-, Fe^{2+}, Fe^{3+}, $HAsO_4^{2-}$, and $H_2AsO_4^-$ at 25 °C in the form of the Hückel equation were derived for ionic strengths up to 1 mol^{-1} kg^{-1}. Newly derived activity coefficients and thermodynamic data were verified by calculating the Eh of laboratory solutions; the differences between calculated and measured Eh are all within 10 mV and relative differences are all lower than 1.5%. By incoporating the recently evaluated arsenic acid dissociation constants [1, 2] and solubility of scorodite ($FeAsO_4 \cdot 2H_2O$) in the congruent dissolution range together with our newly derived activity coefficients and thermodynamic data into PHREEQCI, the solubility product of scorodite was calculated as: $\log K_{sp} = -226.9 + 10872/T + 66.42 \times \log T$; (298.15 K $\leq T \leq$ 363.15 K). This study established an internally consistent thermodynamic data set which can be used for geochemical modeling of water-mineral interactions, speciation, and toxicity studies in Fe-As system.

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