Application of the Pitzer ion interaction model to the Fe₂(SO₄)₃-H₂SO₄-H₂O System

N. J. TOSCA, A. SMIRNOV AND S. M. MCLENNAN

Department of Geosciences, State University of New York at Stony Brook, Stony Brook, NY 11794-2100 USA

Ferric iron-bearing acid sulfate systems are important to a variety of industrial and surficial environments, specifically areas affected by acid mine drainage (AMD). Accurately describing the thermodynamic properties of such highly concentrated waters has been hindered mainly by the lack of experimental data for the $Fe_2(SO_4)_3$-H_2SO_4-H_2O system. However, with the recent availability of isopiestic measurements yielding solvent activities for $[Fe_2(SO_4)_3$-$H_2SO_4]$ mixtures [1,2], the Pitzer ion interaction model may be applied and used as an additional tool in describing the equilibrium state of many natural systems. Hydrolysis at low pH and the importance of sulfate-bisulfate equilibria present complications in applying the Pitzer approach to the $Fe_2(SO_4)_3$-H_2SO_4-H_2O system. Here, we describe the application of an extended Pitzer model based upon the Clegg *et al*. [3] model for H_2SO_4(aq). The model fits available isopiestic data for $[(1-y)Fe_2(SO_4)_3$-$yH_2SO_4]$ mixtures to 3.00 molal and $0.0435 \leq y \leq 0.9370$. A slightly less accurate representation of a more extended molality range to 5.47 molal extends over the same y values. A more limited isopiestic dataset at 323.15 K is also analyzed with the Pitzer model. Available solubility data are examined using a recent calorimetric study of ferricopiapite and rhomboclase. We also discuss some examples of model applications to geochemical problems in AMD environments. The resulting Pitzer model provides an important step toward a more detailed picture of Fe-sulfate mineral stability in AMD systems. In turn, controls on the cycling of acidity and toxic metals in AMD environments may be better predicted and identified.

References

[1] Rumyantsev, A. *et al*. (2004) *Z. Phys. Chem.*, **218**, 1089.
[2] Velazquez-Rivera, M. *et al*. (2006) *J. Sol. Chem.*, **35**, 1699.
[3] Clegg, S. *et al*. (1994) *J. Chem. Soc., Faraday Tans.*, **90**, 1875.

Calculating the stability, Raman and UV spectra and acidity of As sulfides in aqueous solution

J. A. TOSSELL, M. D. ZIMMERMANN AND G. R. HELZ

Dept. of Chemistry and Biochemistry, Univ. of Maryland, College Park, MD 20742 USA (tossell@umd.edu)

Since the chemical and biological reactivity of As sulfides depends strongly upon their speciation, it is important to determine exactly what species are present within a given environment. Spectral probes such as Raman and UV can give partial information about speciation, but uncertainties and ambiguities generally remain. We are engaged in a program to perform state-of-the-art quantum mechanical studies of the strucctures, stabilities, spectra (Raman and UV) and acidity of As sulfide species in aqueous solution. We typically use very high level methods, such as CCSD with triple zeta, doubly polarized basis sets for the gas phase part of the calculation, and a lower-level polarizable continuum or nanocluster approach to simulate the effect of hydration. Anharmonic vibrational effects are calculated using 2nd order perturbation theory within a HF – DFT hybrid nethod. Using this approach we can accurately reproduce the Raman spectra of thioarsenious acid, $As(SH)_3$ and its conjugate bases. The Raman spectra of $As(SH)_3$ is also reproduced with errors of less than 10 cm-1 and the As-O(H) distances with errors of only 0.02 Å Such calculations establish that the neutral species in arsenious acid solutions is indeed $As(SH)_3$ rather than $HAsO_2$. This assignment is also supported by our calculated UV spectra. However, accurate calculation of the Raman spectra of the conjugate bases of $As(SH)_3$ requires the inclusion of both explicit waters and counterions. Trends in the acidity of As acids with changing oxidation state, ligand and degree of protonation are well reproduced, but accurate absolute vaues for the oxidic species are elusive. Possible reasons for the overestimation of pKas for the oxidic species are presented. We have established computationally that the conjugate bases of $As(SH)_3$ are susceptible to sulfidation by H2S, while As(III) sulfides such as $AsS(SH)_2$-are susceptible to oxidation to As(V) by elemental sulfur or polysulfides. By contrast the addition of H_2S to $AsS(SH)_2$- to form $As(SH)_4$- is calculated to be unfavorable. We can thus generate a comprehensive picture of speciation based upon direct quantum mechanical calculation of a number of properties for possible candidate species.