Goldschmidt 2022 Abstract
https://doi.org/10.46427/gold2022.10410

Raman Spectroscopy and AC Conductivity: Complementary Tools for Quantitative Aqueous Speciation Studies under Hydrothermal Conditions

PETER TREMAINE

University of Guelph

Presenting Author: tremaine@uoguelph.ca

The unique flow AC conductivity instrument developed by RH Wood and his co-workers [1] provides thermodynamic and transport property data at temperatures up to ~350 ^{o}C at concentrations from ~10^{-4} to 0.1 molal. Frequency-dependent impedance measurements determine molar conductivities whose concentration dependence can be analyzed with the Turq-Blum-Bernard-Kunz (TBBK) or Frölich-Hsa-Fernandez-Prini (FHFP) theoretical models. These yield limiting conductivities ($\lambda°$), ionization constants, and ion-pair formation constants consistent with the Debye-Hückel limiting law. The method is very accurate but is restricted to dilute solutions and relatively simple speciation conditions.

Confocal Raman spectrometers provide spectra and *in situ* visual observation of complex speciation and phase equilibria that take place at higher concentrations, typically ~0.1 to 20 molal. Modern lasers are so stable that polarized spectra of sample solutions and solvent can be measured over the course of a day, from which quantitative, solvent-subtracted reduced isotropic spectra can be determined. Hydrothermal studies are carried out in quartz capillary cells [2,3] and/or sapphire flow cells [4] at temperatures up to 350 and 425 ^{o}C, respectively, and pressures up to 25 MPa. The temperature-independent scattering coefficients required to calculate the equilibrium concentrations are determined by selecting conditions at which only one predominant equilibrium species is present. Density functional theory is employed to predict the structures, relative stability, and Raman scattering coefficient of species for comparison with the experimental results.

Examples presented in this talk illustrate the power of using both conductivity and Raman techniques as complementary tools to determine equilibrium constants and speciation. These include direct measurements of the ionization constants of SO_4^{2-} and PO_4^{3-}; and the step-wise complexation constants of La^{3+} and Sb^{3+} with chloride at temperatures up to and above 300 ^{o}C at 25 MPa.

[1] H. Arcis *et al., Phys. Chem. Chem. Phys.* **18**, 24081-24094 (2016)

[2] C. Alcorn *et al.*, *J. Phys. Chem. B* **123**, 7385-7409 (2019).

[3] I-M. Chou and A. Wang, *J. Asian Earth Sci.* **145**, 309-333 (2017)

[4] S. Sasidharanpillai *et al*. *J. Phys. Chem. B*, **123**, 5147-5149 (2019).