

AQUEOUS SOLUTION CHEMISTRY IN BINARY AND MULTI-COMPONENT SYSTEMS TO 700 MPa USING THE METHOD OF IMPULSIVE STIMULATED SCATTERING. S. D. Vance, J.M. Brown, E.H. Abramson, Earth and Space Sciences and Astrobiology, 351310, University of Washington, Seattle, WA 98195.

Introduction: Improved knowledge of material properties under the novel pressure-temperature conditions obtained inside icy satellites may point to phenomena not found on Earth [1]. On Earth, high hydrostatic pressures (~150 MPa) are obtained in subsurface aquifers extending up to four km into oceanic crust. In other planetary objects, fluid circulation depth may be orders of magnitude greater, and corresponding hydrostatic pressures in these extended environments may be up to fifty percent greater than those found in Earth's interior reservoirs [2,3]. Presently known icy satellites and outer solar system objects may have hosted liquid water for significant portions of their histories [4]. We present equation-of-state measurements for aqueous magnesium sulfate ($MgSO_4$) obtained by the method of impulsive stimulated scattering (ISS) and discuss a strategy for examining pressure's influence in multi-component systems.

Methods: Impulsive stimulated scattering is employed to measure sound velocities [5,6,7]. The method works as follows. An acoustic excitation is created in an optically-accessible sample by the convergence of picosecond infrared pulses from a NdYAG laser at a known angle. Sites of constructive interference form a grating in two dimensions. The heated regions impulsively expand, creating two counter-propagating sound waves. A subsequent diffracted pulse, delayed by time-of-flight, probes the interaction of these waves at a given time. The modulation of the probe pulse over the excitation's ~30 ns evolution gives the sound frequency in the material at the temperature, pressure, and solution composition of interest. Knowing frequency and wavelength – set by the condition for Bragg scattering – one infers the speed of sound.

At temperatures where the density and heat capacity of a fluid are known for at least one pressure, the equation of state at fixed composition is determined by recursive integration of the thermodynamic relations between speed of sound and density. Having calculated the density, all other thermodynamic properties may be obtained. Such measurements over a range of concentrations additionally allow calculation of partial molal volumes and chemical potentials.

A study of $MgSO_4$ (aq): Magnesium sulfate is expected to be the dominant constituent in volatile effluent from a chondritic differentiation [8]. Densities have been measured for $MgSO_4$ in the range of pressure and temperature shown in Figure 1. The majority of these

were made for concentrations less than one mol solute per kg of solvent (molality, m_B), with the exception of near-eutectic measurements by Hogenboom and co-workers [9]. The parameter space does not adequately address the region of simultaneously elevated pressure and temperature. Figure 2 compares available high-pressure density measurements [9,10] with predictions from the semi-empirical computational model FREZCHEM [11]. Deviation increases for elevated pressure and concentration. Non-standard temperature likely enhances this disagreement.

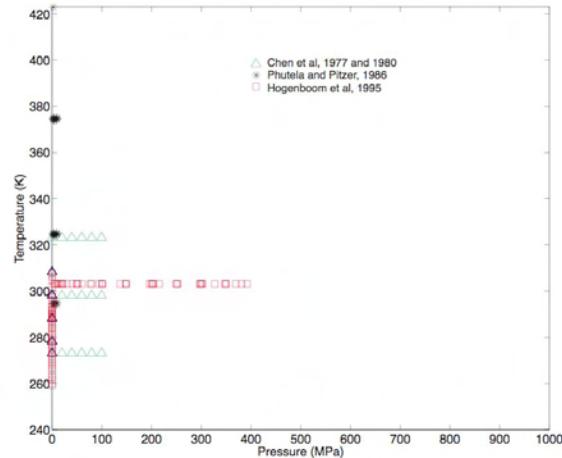


Figure 1. Pressures and temperatures at which densities in the $MgSO_4$ (aq) system have been measured [9,10,11,12].

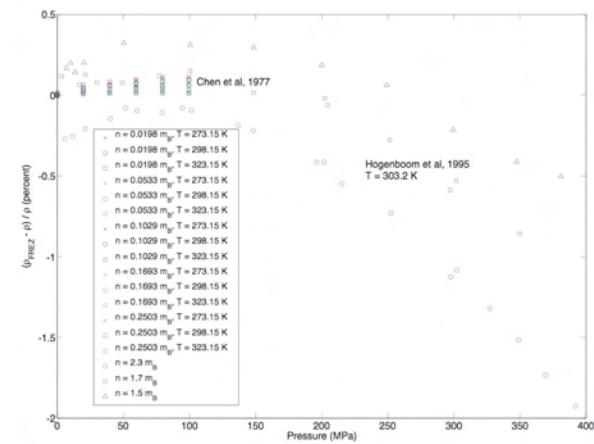


Figure 2. Percent deviation between FREZCHEM's predicted densities in the $MgSO_4$ (aq) system and available measurements at high pressures [9,10].

Discussion and Conclusions: The above analysis for MgSO₄ (aq) demonstrates the need for equation-of-state measurements in aqueous solutions at non-standard pressures and temperatures, and near-saturated concentrations. Future studies will examine other single-component aqueous systems relevant to icy satellites (*e.g.* Na₂SO₄, CaSO₄, NaCl). It is desirable to also examine multi-component systems, but the large parameter space limits the investigator to a targeted selection of such measurements. Available thermodynamic models for multi-component systems [13,14,15,16] are based on a self-consistent database of individual ion properties and the models extrapolate from the range of near-standard temperatures and pressures in which measurements are made. We can test the accuracy of such predictions for multi-component systems with a selection of equation-of-state measurements in multicomponent systems.

References: [1] Vance S. et al (2007) submitted to *Icarus*. [2] Vance S. et al (2006) submitted to *Astrobiology*. [3] Hussmann H. et al (2006) *Icarus*, 185, 258-273. [4] Vance S. and Brown J.M. (2005) *Icarus*, 177, 506-514. [5] Fayer M.D. *IEEE J. Quantum Electronics*, 22, 1437-1452. [6] Abramson E.H. (2001), *Int. J. Thermo-phys.*, 22, 405-414. [7] Abramson E. H. and Brown J. M. (2004) *Geochim. Cosmochim. Acta*, 68, 1827-1835. [8] Kargel J.S. (2000) *Icarus*, 148, 226-265. [9] Hogenboom H. et al (1995) *Icarus*, 115, 258-277. [10] Chen C.-T. et al (1977) *J. Chem. Eng. Data*, 22, 201-207. [11] Chen C.-T. et al (1980) *J. Chem. Eng. Data*, 25, 307-310. [12] Phutela R.C. and Pitzer K.S. (1986) *J. Chem. Eng. Data*, 31, 320-327. [13] Marion G. et al (2005) *Geochim. Cosmochim. Acta*, 69, 259-274. [14] Oelkers E.H. et al (1995), *J. Phys. Chem. Ref. Data*, 24, 1401-1560. [15] Krumgalz B. S. and Starinsky A. (2003), *J. Sol. Chem.*, 32, 853-854. [16] Denisov D.A. et al (2004), *Acoustical Physics*, 50, 518-522.