

DETERMINATION OF THE VOLUMETRIC PROPERTIES OF DILUTE D-GLUCOSE SOLUTIONS TO 50.0 MPa AND 433.15K. J. C. Seitz¹, M. D. Schulte², A. S. Hall¹, and G. W. Rhett¹; ¹Department of Earth & Environmental Sciences, California State University, East Bay, 25800 Carlos Bee Blvd., Hayward, CA 94542, jeff.seitz@csueastbay.edu; ²Department of Geological Sciences, 101 Geology Building, University of Missouri, Columbia, MO 65211, schultemd@missouri.edu.

Introduction: The need to model and understand reactions among aqueous organic compounds and biomolecules has led to a number of experimental studies to determine the thermodynamic properties of these compounds. Unfortunately, there is a paucity of data for important compounds at elevated temperatures and pressures (including the current known temperature limits for biological activity, 122°C [1]). The immediate goal of this research is to develop an experimentally-determined database of the thermodynamic properties of important organic molecules and biomolecules. Experimentally determined volumetric properties of aqueous solutions at elevated conditions will provide direct tests of current estimation methods and aid in the refinement of these methods. The ultimate goal of this research is to develop a thermodynamic database of aqueous organic mixtures at high temperature and pressure in order to understand the metabolic processes of thermophilic organisms and aid development of more accurate geochemical models for the origin of life in aqueous environments.

Glucose is a monosaccharide important in biology as an energy source (product of photosynthesis), metabolic intermediary, and important step in cellular respiration (in prokaryotes and eukaryotes).

Experimental Methods: The volumetric properties of aqueous solutions of D-glucose were obtained using Anton Paar DMA 5000 and DMA HP densimeters. The DMA 5000 can measure fluid densities at conditions up to 363.150 K and 1.00 MPa and the DMA HP external cell is capable of achieving conditions as high as 473.15 K and 70.0 MPa. An isothermal *stepped-flow* method was employed in all of our experiments; the vibrating tube was evacuated and dried between fluids. The fundamental equation for calculating densities of fluids by vibrating-tube densimetry is

$$\rho - \rho_0 = K(\tau^2 - \tau_0^2)$$

where ρ is the density of the *unknown* solution, ρ_0 is the density of a *known* (standard) fluid, K is a proportionality constant parameter that depends on the physical properties of the vibrating tube, τ is the period of vibration for the *unknown* solution and τ_0 is the period of vibration for the *known* (standard) fluid. The value of K was evaluated at each P-T point using three standard fluids. Standard fluids were measured at the beginning and end of a run to check for instrumental drift; the periods of the vibrating tubes were remarkably stable. Standard fluids used in this study included

pure water, methanol (for $T \leq 333.15$ K), and 1.5 m and 3.0 m ($\text{mol}\cdot\text{kg}^{-1}$) NaCl aqueous solutions. The densities of water and methanol were calculated using the NIST REFPROP (version 8.0) program [2] and the densities of the NaCl solutions were obtained from the equation and program of Archer [3]. Water and methanol were research grade purity (Fisher Optima); the water was degassed by boiling and then drawing a vacuum for at least 24 hours. Solutions of D-glucose (Sigma, 99.5% pure) and NaCl (Fisher, 99.7% pure) were prepared by mass and stored in 50 ml glass bottles equipped with PTFE butyl septa. Solutions were extracted with a syringe to prevent solvent loss.

The fluid pressure in the densimeters was controlled using a piston screw pump. Pressure was monitored with Stellar Technology pressure transducers with a maximum uncertainty of ± 0.07 bars. Temperature was measured with integrated platinum thermometers with accuracies (as determined by the manufacturer) of ± 0.001 K and ± 0.05 K in the DMA 500 and DMA HP, respectively. Scatter on density measurements was generally ± 0.00005 $\text{g}\cdot\text{cm}^{-3}$ for the DMA 5000 and ± 0.0001 $\text{g}\cdot\text{cm}^{-3}$ for the DMA HP. As the major source of random error during analyses, these values for density reproducibility/repeatability exceed propagated errors associated with uncertainty in the measurement of temperature, pressure and fluid concentration.

Data and Comparison of Results with Previous Studies: Previous studies report experimentally determined volumetric parameters for glucose solutions up to 368.15 K and 0.35 MPa; this study extends the database up to 433.15 K and 50.00 MPa.

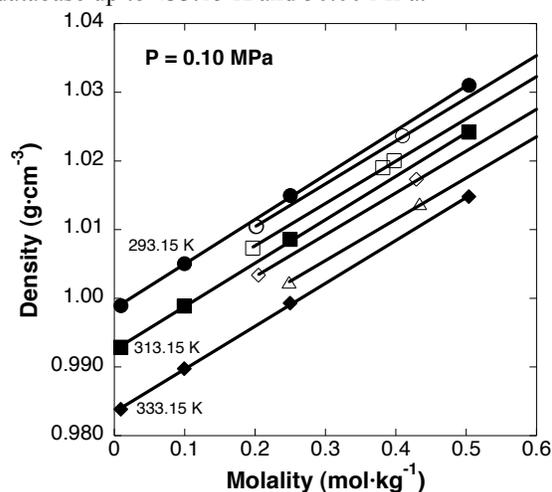


Figure 1 shows a comparison of measured densities at 0.10 MPa from this study at three different temperatures (filled symbols) with those of Kishore *et al.* [4] at 298.15 K (\circ), 307.30 K (\square), 318.71 K (\diamond), and 327.01 K (\triangle). The lines represent simple linear regression fits to the data. Direct comparison and interpolation of fluid densities indicates good agreement between these two different data sets.

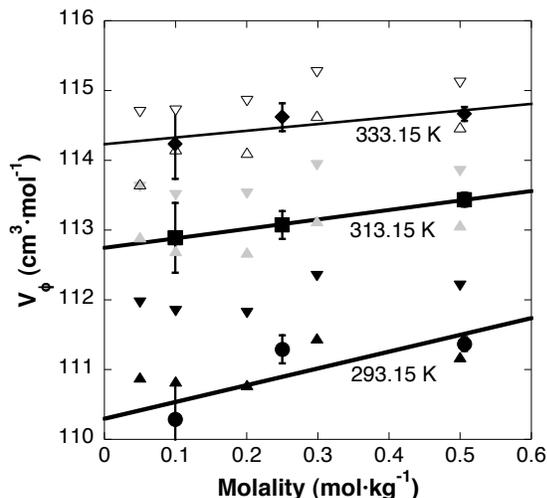


Figure 2 shows the apparent molar volumes of glucose (V_ϕ) determined from experimentally measured fluid densities (data in figure 1) at three temperatures and 0.10 MPa as a function of molality (filled symbols). In addition, the data of Origlia *et al.* [5] at 0.35 MPa and 288.15 K (\blacktriangle), 298.15 K (\blacktriangledown), 308.15 K (\blacktriangle), 318.15 K (\blacktriangledown), 328.15 K (\triangle), and 348.15 K (∇) are plotted for comparison. The determination of the partial molar volumes at infinite dilution are calculated from the linear extrapolation of these data to zero molality. Comparisons of V_ϕ 's from this study and [5] indicate good agreement.

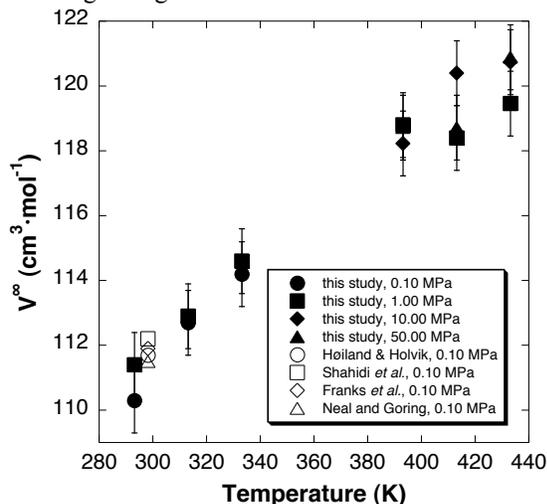


Figure 3 shows partial molar volumes at infinite dilution (V^∞) for glucose at 0.10-50.00 MPa and 293.15-

433.15 K determined in this study. Error bars represent an approximate uncertainty in the determination of V^∞ of $\pm 1.0 \text{ cm}^3 \cdot \text{mol}^{-1}$. In addition, the data from previously published studies [6, 7, 8, 9] at 298.15 K and 0.10 MPa are plotted for comparison. Comparisons of these data indicate a high degree of agreement between the different studies. The data from this study significantly extend the available volumetric data for dilute glucose solutions to elevated pressures and temperatures.

References: [1] Takai *et al.* (2008) PNAS, 105, 10949-10954. [2] Lemmon, E.W. *et al.* (2007) NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 8.0. [3] Archer, D. G. (1992) *J. Phys. Chem. Ref. Data*, 21, 793-826. [4] Kishore *et al.* (1993) *J. Chem. Thermodynamics*, 25, 847-859. [5] Origlia M. L. *et al.* (2000) *J. Chem. Thermodynamics*, 32, 847-856. [6] Høiland H. and Holvik H. (1978) *J. Solution Chem.*, 7, 587-596. [7] Shahidi F. *et al.* (1976) *J. Solution Chem.*, 5, 807-816. [8] Franks F. *et al.* (1972) *J. Solution Chem.*, 1, 3-16. [9] Neal J. L. and Goring D. A. I. (1970) *Can. J. Chem.*, 48, 3745-3747.