**MODELING THE VISCOSITY OF POTENTIAL CRYOVOLCANIC LIQUIDS.**  A. A. Morrison[1], A. G. Whittington[1], F. Zhong[2], K. L. Mitchell[2], and E. M. Carey[2], [1]The University of Texas at San Antonio, San Antonio, TX (aaron.morrison@utsa.edu), [2]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA.

**Introduction:** Cryovolcanism has been implicated on many icy bodies in the outer solar system to explain many of the observable surface features. Rheological properties of potential cryovolcanic products are fundamental in determining how features are emplaced and the morphologies that result. The few experimental studies [1,2] that have been conducted provide supporting data for only a narrow range of compositions. We conduct liquid viscosity measurements of aqueous brines to expand the compositional range where experimental data exist to be more relevant to the variety of material that may be erupted on icy bodies.
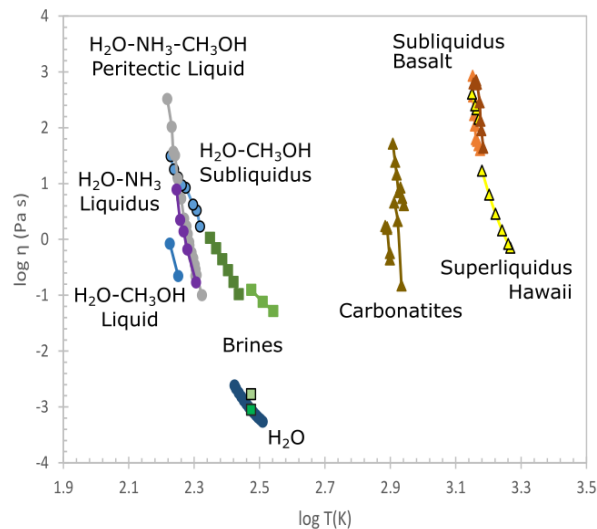


***Figure 1.*** *Viscosity data for water [3], brines [4,5], ammonia-water [1], methanol-water [1,2], ammonia-methanol-water [1], carbonatites [6], East African Rift basalts [7], Hawaiian basalt [8].*

Generation of briny compositions can result from hydrothermal alteration in the interior or by partial melting of an ammonia-water/ice source, modified by crystal fractionation [1]. Figure 1 shows that cryogenic compositions span a similar viscosity range as silicate lavas allowing a range of morphologies to occur (e.g., domes or flows). Many icy bodies exhibit flow features/constructs and having a defined rheology allows inferences about possible compositions based on the observed morphology. This would be particularly useful on bodies, like Titan, Triton, or Pluto, that have atmospheres or erupted deposits that may cover or otherwise obscure other features in (e.g., methane) frost or ejecta complicating spectral analysis of the feature itself.

The rheological data will allow comparisons to terrestrial silicates and determinations of how similarly the two kinds of materials behave. If they are, in fact, analogous to silicate systems, are they formed and emplaced by the same mechanisms and processes? And if not, what factors are contributing to the differences? Determining rheological properties of these cryogenic materials should allow us to answer these questions.

**Methods:** The $H_2O$-$XCl$ (X = Na,K,$NH_4$) and $H_2O$-$YSO_4$ (Y = $K_2$,Mg,$(NH_4)_2$), $H_2O$-$NH_3$, and $H_2O$-$CH_3OH$ binary systems were chosen to cover a wide compositional space and for their relevance to species detected on various icy bodies. Solutions of different concentrations between pure water and the eutectic were synthesized from reagent grade powders and deionized water for each composition. An Anton Paar MCR302 rheometer was used to measure liquid viscosity with a cone-and-plate configuration, utilizing a Peltier plate temperature control system. Isothermal measurements were made at intervals between room temperature and the freezing point and at shear rates of 1 – 600 s$^{-1}$.

**Results:** Liquid viscosity ($\eta$) data for each composition at each concentration were fit using a Vogel-Fulcher-Tammann (VFT) equation [9]

$$\log \eta = A + B_i / (T - C_i)$$

where $A$, $B_i$, and $C_i$ are adjustable terms. The root mean squared deviation (RMSD) is minimized by adjusting these parameters to reduce the difference between the measured data and the model curve. To incorporate a concentration dependence to this model, the adjustable terms need to be parameterized for each compositions. Since the $A$ term represents a represents a limiting viscosity (y-intercept in viscosity temperature space), we defined this value for all investigated compositions as the $A$ value fit to the pure $H_2O$ data (-4.29). This reduces the degrees of freedom and allows the values for water to be recovered when the concentration of solute reduces to 0 wt%.

The $B_i$ and $C_i$ terms can be parameterized using a line or a quadratic requiring one or two empirical fitting terms (degrees of freedom) respectively. We argue that a linear $B_i$ and quadratic $C_i$ parameterization (Figure 2) offers the best compromise between lowest RMSD (i.e., best fit) and fewest degrees of freedom (i.e., simplest). This parameterization requires three degrees of freedom and has the second lowest RMSD

of the different combinations of linear and quadratic parameterizations.

Additionally, preliminary measurements in the ternary system $H_2O$-$NH_3$-$CH_3OH$ and pseudo-ternary system $H_2O$-$NaCl$-$MgSO_4$. These measurements were used to test whether the model could be extended to more complicated systems. Due to the higher number of components involved, more degrees of freedom are required. We argue that quadratic $B_i$ and $C_i$ terms are the best compromise, where six degrees of freedom are required, and produce a RMSD of the same order as a ten-degree-of-freedom parameterization. Figure 2 shows these data can be fit well, to within 5% relative uncertainty.
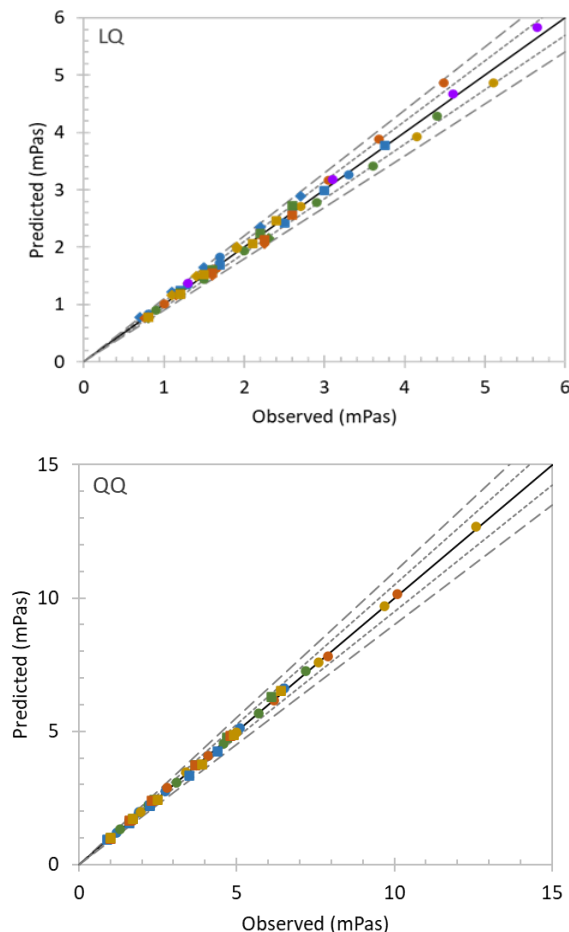


**Figure 2.** *Comparison of modeled viscosity from the VFT equation to the experimental data. Long-dashed lines represents 10% relative uncertainty and short-dashed lines represent 5% relative uncertainty. (top) Chloride data as a representative sample of binary system data. LQ indicates results for $B_i$ fit with a line and $C_i$ fit with a quadratic with three degrees of freedom. (bottom) All data from ternary systems. QQ indicates results for both $B_i$ and $C_i$ fit with a quadratic with six degrees of freedom.*

**Conclusions:** Experimental viscosity measurements for aqueous chloride, sulfate, ammonia, and methanol solutions at sub-ambient conditions were used to produce a viscosity model for aqueous solutions. The VFT equation, commonly used in the silicate rheology literature, works well to describe the viscosity of water and aqueous solutions. While the form of this equation is semiempirical and strictly temperature dependent, the fitting terms were parameterized to allow a concentration dependence to be included for a given composition. The resulting model reproduced the experimental dataset to within 10% relative uncertainty (typically within 5%). The model is capable of extrapolating down to sub-ambient temperatures relevant to cryovolcanism without any singularities. This, and the coupled temperature and concentration dependence, are the key improvements over previous models. Preliminary investigation of ternary systems suggests this model can be scaled up to successfully reproduce experimental datasets of more complicated systems than just binary systems.

This model was not intended for use on concentrations on the non-water side of the eutectic, as extrapolations to those concentrations are not adequately represented. Special caution should be taken when using the model for $K_2SO_4$, as the water-rich side of the phase diagram spans only 6 wt%. Additionally, we did not study concentrations as ammonia-rich as the eutectic for the $H_2O$-$NH_3$ system, resulting in a narrower calibration range for this composition.

Constraining the rheology of potentially cryovolcanic compositions will facilitate better modeling of the formation of observable morphological features and allow comparisons to more familiar silicate systems. Additionally, expanding this model to ternary and more complicated systems (e.g., $H_2O$-$NaCl$-$MgSO_4$) relevant to subsurface oceans would improve model applicability but may require further refinement.

**References:** [1] Kargel J. S. et al. (1991) *Icarus, 89*, 93–112. [2] Zhong F. et al. (2009) *Icarus, 202*, 607–619. [3] Kestin J. et al. (1978) *J. Phys. Chem. Ref. Data, 7*, 941–948. [4] Ozbek H. et al. (1977) *Am. Chem. Soc.* 29th Southeast Reg. Meet. [5] Zhang H. L. et al. (1997) *J. Chem. Eng. Data, 42*, 526–530. [6] Norton, G. & Pinkerton, H. (1997) *Eur. J. Mineral. 9*, 351–364. [7] Morrison A. A. et al. (2020) *Volcanica, 3*, 1–28. [8] Sehlke A. et al. (2014) *Bull. Volc., 76*, 876. [9] Vogel H. (1921) *Phys. Z., 22*, 645–646.