

Temperature-Dependent Hydrophobic Crossover Length Scale and Water Tetrahedral Order

SUPPORTING INFORMATION

Xianguen Wu,[†] Wanjun Lu,[†] Louis M. Streacker,[‡] Henry S. Ashbaugh,[¶] and Dor Ben-Amotz^{*,‡}

[†]*State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, China*

[‡]*Purdue University, Department of Chemistry, West Lafayette, IN 47907, USA.*

[¶]*Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana 70118, USA.*

Materials and Methods. Our experiments were performed by dissolving alcohols (from Tianli Chemical Reagent Co., Ltd) in purified water with a resistivity of 18.24 M Ω -cm, to produce 0, 1, 2, and 5 wt% alcohol solutions. A capillary High-Pressure Optical Cell,¹ combined with a Linkam CAP500 heating-cooling stage, was used to control the pressure and temperature of the solution during the Raman measurements (see Figure 1), as previously described.²⁻⁴ More specifically, the samples were prepared as follows: (i) inject pure water (about 10 mm) into the closed end of the capillary cell (665 μ m OD, 300 μ m ID, 15 mm long); (ii) inject a plug of mercury (approximately 5 mm in length) into the cell with a small tube (200 μ m OD and 75 μ m ID); (iii) inject the alcohol solution into the cell, and then seal again with a plug of mercury; (iv) the capillary high-pressure optical cell is connected to a high pressure line (see Figure 1); (iv) the cell is mounted horizontally on the Linkam CAP500 temperature stage, and adjusted to maintain a constant pressure and temperature. The temperature of the cell was measured using a K-type thermocouple with an accuracy of ± 0.1 K. The pressure in the cell was maintained hydraulically using pressurized water, and read using a Seta 204D digital pressure transducer equipped with a Datum 2000TM manometer (69 MPa full scale; accurate to 0.14%).

Spectra were collected at temperatures ranging from 0°C to 374°C for pure water and ethanol solutions, and from 0°C to 300°C for the methanol and propanol solutions, at 30 MPa (or lower, see Additional Experimental and MD Results below), using a JY/Horiba LabRam HR800 Raman system with a frequency doubled Nd:YAG laser (532.06 nm, 10 mW at the sample), with a 50X long working distance Olympus objective with 0.5 N.A., and a 300 grooves/mm grating (with a spectral resolution of 3 cm^{-1}). Before reaching the spectrograph, the collected Raman scattered light was spatially filtered using a confocal pinhole of 200 μ m diameter (with magnification of 50X between the sample and the pinhole). Raman spectra were collected over a vibrational frequency shift range of 0 cm^{-1} to 4000 cm^{-1} , each with an acquisition time of 5 min. Two spectra were collected from pure water and the alcohol solution at each temperature. Neon (Ne) lamp reference peaks were obtained along with the Raman measurements at each temperature in order to calibrate the Raman frequency and confirm that no spectral drifts occurred during the experiment.

The MCR decomposition of the measured Raman spectra of water and aqueous ethanol solutions (measured at the

same temperature and pressure) was performed using Self Modeling Curve Resolution (SMCR).^{5,6} The Raman-MCR analysis was performed over the CH and OH stretch band region from 2433 cm^{-1} to 3914 cm^{-1} , and a linear baseline was subtracted from the resulting SC spectra. As part of the Raman-MCR analysis, the spectral weight of the pure water was adjusted to assure proper convergence to the minimum area SC spectrum. In other words, this assures that the resulting SC spectrum is equivalent to the spectrum obtained when subtracting the spectrum of pure water (times an adjustable weighting factor) from the measured solution spectrum, to yield a difference spectrum with the smallest non-negative area (above baseline) in the CH and OH stretch region. The resulting SC spectra were normalized to the CH area (by dividing each background-subtracted SC spectrum by the corresponding CH band area obtained between 2822 cm^{-1} and 3024 cm^{-1}). Spectra of the solutes and their full (or half) first hydration-shells were produced from a linear combination of the SMCR SC and pure water component spectra to form a spectrum whose OH/CH band area ratio, $A_{\text{OH}}/A_{\text{CH}}$, is consistent with the MD predictions for the ratio, $N_{\text{OH}}/N_{\text{CH}}$, of the number of OH groups in the non-polar hydration-shell to the number of CH groups in the alcohol. More specifically, $1.2 \times (A_{\text{OH}}/A_{\text{CH}}) = N_{\text{OH}}/N_{\text{CH}}$, as the average Raman cross section of an alcohol CH group is $\sim 1.2 \pm 0.1$ times greater than that of a water OH group (determined from quantitative comparisons of $A_{\text{OH}}/A_{\text{CH}}$ in aqueous alcohol solutions of various concentrations).⁶

MD simulations of water and 5 wt% alcohol solutions were performed using GROMACS⁷ over the temperature range 0°C to 374°C at 30 MPa, corresponding to the experimental conditions. Water was modeled using the TIP4P/2005 potential,⁸ while methanol, ethanol, and 1-propanol were modeled using the TraPPE-united atom potential.⁹ A total of 1000 molecules (waters + alcohols) were considered in each simulation. Following 5 ns of equilibration, simulations were conducted for 100 ns to evaluate equilibrium averages. Coordination numbers were evaluated by counting the number of waters in the first hydration shell of the alcohol. A water was assigned to be in the first hydration-shell of an alcohol's non-polar tail if it lies within 5.45 Å of a carbon, corresponding to the position of the first minimum in the corresponding water/alcohol correlation functions. The Errington-Debenedetti tetrahedral order param-

eter¹⁰ is evaluated as

$$q = 1 - \frac{3}{8} \sum_{i=1}^4 \left[\frac{1}{3} + \cos \theta_{ij} \right]^2$$

where θ_{ij} is the angle formed by the lines joining the oxygen of a given water and those of its four nearest neighbors i and j (≤ 4). A nearest neighbor is taken here to be another water oxygen or an alcohol hydroxyl group.

Additional Experimental and MD Results. The following figures contain additional Raman-MCR and MD results. The results in Figure S1 and S2 were obtained either by simultaneously analyzing spectra obtained from solutions with ethanol concentrations of 0, 1, 2, and 5 wt% (Figure S1), or ethanol concentrations of 0 and 2 wt% (Figure S2). The similarity of these results to those shown in Figure 1(B) demonstrate that the Raman-MCR SC spectra are essentially concentration independent up to 5 wt%.

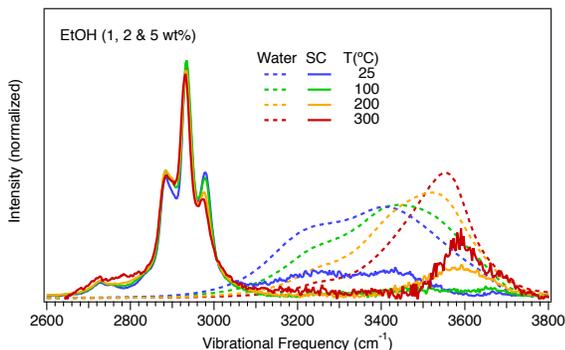


Figure S1. Raman-MCR (Raman-MCR spectra obtained from a simultaneous analysis of aqueous solutions with 0 wt%, 1 wt%, 2 wt% and 5 wt% ethanol, at a pressure of 20 MPa and temperature ranging from 25°C to 300°C. The solid curves are the ethanol SC spectra and the dashed curves are the corresponding pure water spectra.

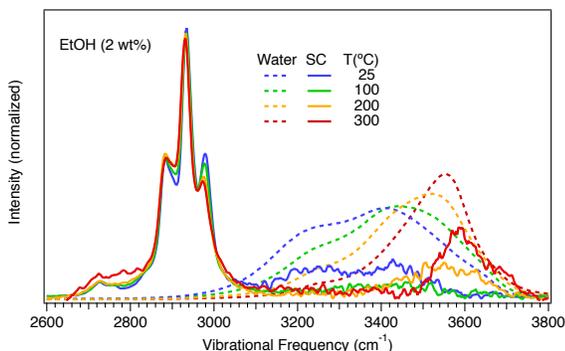


Figure S2. Raman-MCR spectra obtained from pure water (0 wt%) and 2 wt% aqueous ethanol solutions, at a pressure of 20 MPa and temperature ranging from 25°C to 300°C. The solid curves are the ethanol SC spectra and the dashed curves are the corresponding pure water spectra. Seven point Savitzky-Golay smoothing¹¹ of the input spectra was used to suppress the greater noise in the Raman-MCR results obtained at this concentration.

Figure S3 and Tables S1 and S2 contain MD results for the density of pure water and the number of water molecules in the first coordination-shell of the alkyl tails of methanol, ethanol, and n-propanol.

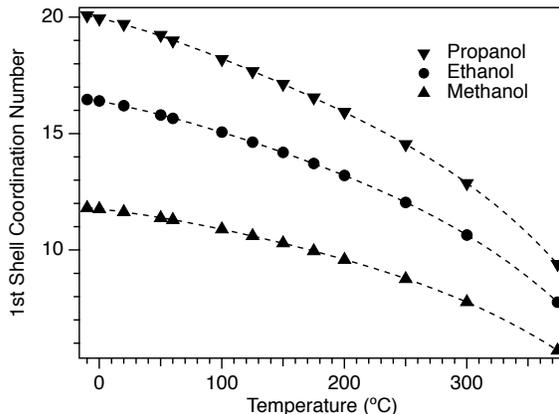


Figure S3. Coordination number in the first hydration-shell of the alkyl tails of methanol, ethanol, and n-propanol. The coordination numbers are obtained from MD radial distribution functions of the water oxygen atoms relative to the alcohol carbon atoms, integrated out to 5.45 Å, near the first minimum in the radial distribution function. The dashed curves are polynomial fits, whose coefficients are given in Table S2.

Table S1. Comparison of experimental¹² and MD (TIP4P-2005) densities of pure water as a function of temperature, at a pressure of 30 MPa.

T (°C)	ρ_{Expt} (gm/cm ³)	ρ_{MD} (gm/cm ³)
-10	...	1.014 ± 0.008
0	1.015	1.014 ± 0.008
20	1.012	1.012 ± 0.008
50	1.001	1.001 ± 0.008
60	0.996	0.995 ± 0.008
100	0.972	0.970 ± 0.009
125	0.954	0.951 ± 0.009
150	0.933	0.929 ± 0.010
175	0.910	0.905 ± 0.011
200	0.885	0.879 ± 0.011
250	0.826	0.818 ± 0.013
300	0.751	0.743 ± 0.015
374	0.563	0.574 ± 0.022

Table S2. Polynomial fits to the 1st shell coordination numbers of alcohols in water.

A(i)	Methanol	Ethanol	n-Propanol
A(0)	11.764	16.394	19.961
A(1)	-0.005688	-0.009485	-0.012177
A(2)	-3.9356e-05	-5.14347e-05	-7.35199e-05
A(3)	1.1209e-07	1.5887e-07	2.64684e-07
A(4)	2.2002e-10	-3.1669e-10	-4.8933e-10

References

- (1) Lu, W. J.; Chou, I. M.; Burruss, R. C. Determination of methane concentrations in water in equilibrium with sl methane hydrate in the absence of a vapor phase by in situ Raman spectroscopy. *Geochim. Cosmochim. Acta* **2008**, *72*, 412–422.
- (2) Guo, H. R.; Chen, Y.; Hu, Q. C.; Lu, W. J.; Ou, W. J.; Geng, L. T. Quantitative Raman spectroscopic investigation of geo-fluids high-pressure phase equilibria: Part I. Accurate calibration and determination of CO₂ solubility in water from 273.15 to 573.15 K and from 10 to 120 MPa. *Fluid Phase Equilib.* **2014**, *382*, 70–79.
- (3) Ou, W. J.; Guo, H. R.; Lu, W. J.; Wu, X. E.; Chou, I. M. A re-evaluation of the effects of temperature and NaCl concentration on quantitative Raman spectroscopic measurements of dissolved CH₄ in NaCl aqueous solutions: Application to fluid inclusion

- analysis. *Chem. Geol.* **2015**, *417*, 1–10.
- (4) Wu, X. E.; Lu, W. J.; Ou, W. J.; Caumon, M. C.; Dubessy, J. Temperature and salinity effects on the Raman scattering cross section of the water OH-stretching vibration band in NaCl aqueous solutions from 0 to 300 °C. *J. Raman Spectrosc.* **2017**, *48*, 314–322.
 - (5) Lawton, W. H.; Sylvestre, E. A. Self Modeling Curve Resolution. *Technometrics* **1971**, *13*, 617–633.
 - (6) Davis, J. G.; Gierszal, K. P.; Wang, P.; Ben-Amotz, D. Water structural transformation at molecular hydrophobic interfaces. *Nature* **2012**, *491*, 582–585.
 - (7) Hess, B.; Kutzner, C.; van der Spoel, D.; Lindahl, E. GROMACS 4: Algorithms for highly efficient, load-balanced, and scalable molecular simulation. *J. Chem. Theory Comput.* **2008**, *4*, 435–447.
 - (8) Abascal, J. L. F.; Vega, C. A general purpose model for the condensed phases of water: TIP4P/2005. *J. Chem. Phys.* **2005**, *123*, 234505.
 - (9) Chen, B.; Potoff, J. J.; Siepmann, J. I. Monte Carlo calculations for alcohols and their mixtures with alkanes. Transferable potentials for phase equilibria. 5. United-atom description of primary, secondary, and tertiary alcohols. *J. of Phys. Chem. B* **2001**, *105*, 3093–3104.
 - (10) Errington, J. R.; Debenedetti, P. G. Relationship between structural order and the anomalies of liquid water. *Nature* **2001**, *409*, 318–321.
 - (11) Savitzky, A.; Golay, M. J. E. Smoothing + differentiation of data by simplified least squares procedures. *Anal. Chem.* **1964**, *36*, 1627–1639.
 - (12) Lemmon, E. W.; Huber, M. L.; McLinden, M. O. NIST Standard Reference Database 23, Version 8.0. 2007.