Evaluating Temperature and Pressure Dependencies of Hydrophobic Interactions of Methanol, Ethane, and Ethanol in Water

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Introduction

From a macroscopic perspective, the lack of affinity of oil for water is a readily apparent observation. The insolubility of oils in water is utilized to great effect in the assembly of amphiphilic molecules, like surfactants and proteins, to form large scale structures in aqueous solution. The existence of stable clathrates, ice structures encasing hydrophobic gases, however, serves as one example of a challenge to the traditional perceptions of hydrophobicity. On a molecular scale the details of the interactions between small hydrophobic molecules and water molecules remain a topic of continued debate. The intricacies of the temperature and pressure dependencies of entropy and enthalpy domination of the hydrophobic effect remain an important area of interest in current research due to the significant applications of the hydrophobic effect as observed in cold denaturation of proteins and micelle formation.[1] Here we evaluate the osmotic second virial coefficient for several solutes with varying degrees of hydrophobicity and size in water in an effort to obtain a greater understanding of the temperature and pressure dependencies of the hydrophobic effect. The solutes investigated included methanol, ethane, and ethanol.

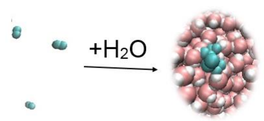


Fig.1 Representation of the hydrophobic effect with the tendency for nonpolar molecules to associate in water minimizing contact with water molecules.

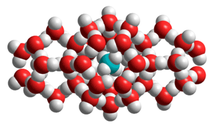
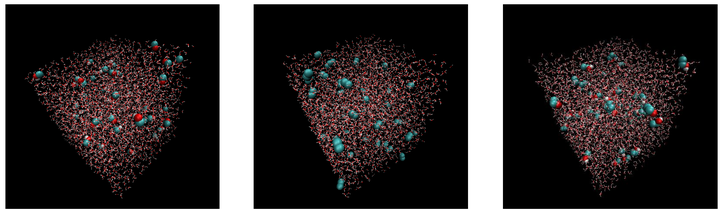


Fig. 2 Structure of a methane clathrate.[4]

Simulation Methods

Molecular Dynamics simulations of methanol, ethanol, and ethane in water were conducted using the Gromacs 5.1.3 package. Previously analyzed simulations of methane conducted by Ashbaugh et al were included in this data analysis.[2] The TIP4P/2005 model was used for water, and the TraPPE-United Atom model was used for methanol, ethanol, and ethane. Each simulation consisted of two minimizations, two equilibrations, and a production run with 40 molecules of the specified solute in a box containing 4000 water molecules. Temperatures tested at a pressure of 1 bar included the range 275K to 370K in increments of 5K. Pressures tested for methanol at a temperature of 300K included the range 1 bar to 5000 bar in increments of 500 bar.

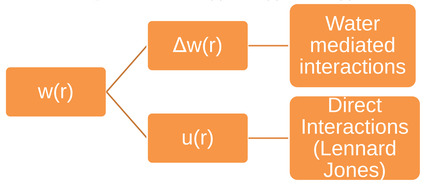


(a) (b) (c)

Fig. 3 (a) Methanol in water at 280K and 1 bar. (b) Ethane in water at 280K and 1 bar. (c) Ethanol in water at 280K and 1 bar.

Potential of Mean Force

The potential of mean force, w(r), serves as an indication of the energy involved in bringing together nonpolar molecules, and can be calculated according to the following formula: $w(r) = u(r) + \Delta w(r)$.[1]



The potential of mean force can also be calculated from the radial distribution function of the solute, g (r): $w(r) = -kT\ln g(r)$ where k is the Boltzmann constant and T is the temperature (K). The role of the solvent as an impetus for assembly of the nonpolar solutes can be observed by subtracting the direct interactions from the potential of mean force. While the radial distribution function can be determined experimentally through x-ray diffraction, molecular simulations provide a more efficient and accurate method for purely hydrophobic solutes.[3] X-ray diffraction techniques require high solute concentration which is difficult to obtain with purely hydrophobic solutes.

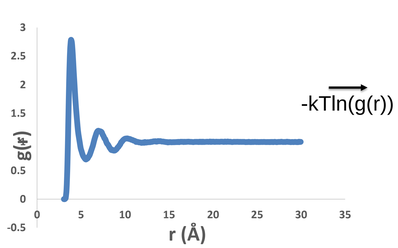


Fig. 4 Radial distribution function of methane in water at 1 bar and 300K

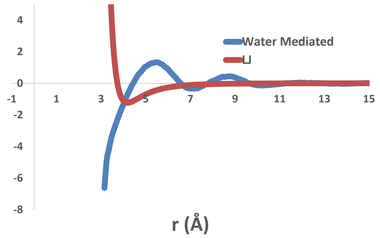
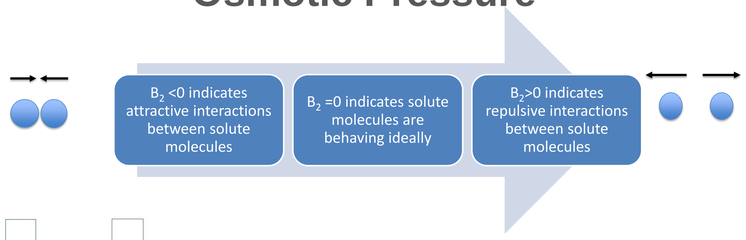


Fig. 5 Lennard Jones (LJ) and water mediated contributions to the potential of mean force of methane in water at 1 bar and 300K

Osmotic Pressure



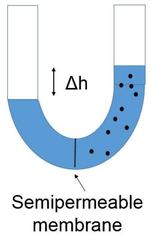
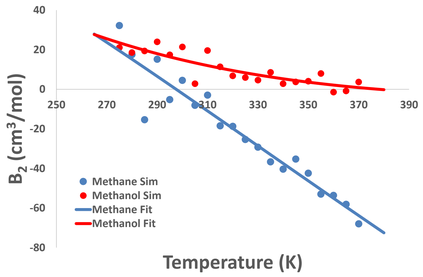


Fig. 6 Apparatus for osmotic pressure experiment.

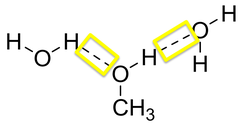
The osmotic pressure of a solute, π, is calculated as: $\pi = \rho g \Delta h = RTc + RTB_2c^2$ where ρ is the density, g is the gravitational constant, Δh is the difference in height indicated in Fig.6, R is the ideal gas constant, T is the temperature (K), c is concentration, and B_2 is the second osmotic virial coefficient. The osmotic second virial coefficient of a solute can be calculated experimentally through the osmotic pressure using an apparatus as the one displayed in Fig. 6. The osmotic second virial coefficient can also be calculated using g(r) as: $B_2 = \frac{1}{2}\int(1-g(r))dr$. For an ideal gas, π= RTc, and B_2 is used to describe deviations from ideal behavior.

Methane and Methanol

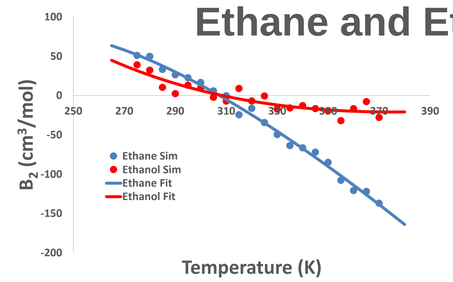


Comparison of the methane and methanol data for the osmotic second virial coefficient reveals the hydroxyl group reduces the attractive forces between molecules at higher temperatures. This is expected due to the noted increased solubility of methanol in water as compared to methane. The additional hydroxyl group allows for hydrogen bonding between the water and solute molecules.

Fig. 7 Osmotic second virial coefficient of methanol and methane in water at 1 bar as a function of temperature. Points represent data points obtained through molecular simulations. Data has also been fitted to a curve as displayed.



Ethane and Ethanol



As compared to methane and methanol, ethane and ethanol present the characteristic decrease in B_2 with increasing temperature in a markedly more dramatic manner. The larger size of ethane and ethanol is likely the cause of this trend.

Fig. 8 Osmotic second virial coefficient of ethanol and ethane in water at 1 bar as a function of temperature. Points represent data points obtained through molecular simulations. Data has also been fitted to a curve as displayed.

Methane Ethane

Conclusions

Molecular dynamics simulations of methanol, ethane, and ethanol in water confirmed the previously observed trend of decreasing B_2 with increasing temperature and provided further insight into the role of solute size and water mediated interactions in hydrophobic solute assembly.

References

1. Ben-Amotz, D. Hydrophobic Ambivalence: Teetering on the Edge of Randomness. *J. Phys. Chem. Lett.* 2015, 6, 1696-1701.
2. Ashbaugh, H. S., Weiss, K., Williams, S. M., Meng, B., Surampudi, L. N. Temperature and Pressure Dependence of Methane Correlations and Osmotic Second Virial Coefficients in Water. *J. Phys. Chem. B* 2015, 119, 6280-6294
3. Chandler, D. *Introduction to Modern Statistical Mechanics*. Oxford University Press: Oxford, 1987.
4. Chaplin, M. "Clathrate Hydrates." *Water Structure and Science*, 2017. Web. 26 July 2017.

Acknowledgements

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