



## The Free Energy of Solvation for N-Decane in Ethanol-Water Solutions

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## Abstract

Within this work GROMACS computational molecular dynamics simulations were performed to determine the free energy of solvation of an n-decane molecule. The pull-code was utilized to draw the molecule across z-space to span from an initial gas state to a final solubilized state. The free energy was computed at each location of the molecule and this quantity is presented as a function of space for multiple alcohol contents. A single simulation of n-dodecane is considered for comparison in 100% water.

**Keywords:** Solutions; Molecule; Surface; Dynamics; Polymeric

## Introduction

Recent molecular simulations and force field development have indicated that computational methods can offer significant insight into the behavior of surfaces [1], polyethoxy [2] and polysilicone [3] systems, hydrogen bonding [4], solvent-water interactions [5], and alkane properties [6]. Of particular interest are several studies which treat mixing thermodynamically [7], as well as those discussing the source of the hydrophobic effect [8]. According to market evaluation firm Transparency Market Research, the “specialty surfactants industry is expected to reach USD 29.2 Billion Globally in 2017 [9]”. Furthermore, Transparency indicates that until at least that time non-ionic surfactants, which are solubilized in alcohol co-solvated systems, are expected to be the fastest growing of all surfactant classes. Such surfactants require solvation with water and alcohol for surface tension tuning. Although alcohol solvated systems are very apparently significant, it is surprising that there is still a lack of understanding regarding solvation free energy relationships in these systems. In order to ascertain what gives these polymers their surface presence in mixed solvent solutions, a critical examination of the free energy of solvation relationships is first necessary. That is what this work seeks to study. It is expected that this information might be useful in predicting solvophilicity of other materials. If the free energy of solvation of a new target molecule in a future study is simulated in any of the solutions studied in this paper and its free energy of solvation is determined, then the relative free energy of solvation for all of the other alcohol contents in this study is readily determinable. This is the concept of a free energy landscape. The free energy landscape as an abstraction can be a function of space, conformation or mass content. Model systems of interest for this study are composed of ethanol. Ethanol is a very common solvent in commercial products such as shampoos and shaving creams.

## Methods

GROMACS molecular dynamics (MD) software was utilized to simulate the macroscopic properties of polymeric materials from classical principles in simple binary mixtures. This molecular dynamics package creates an ensemble of interacting particles and simulates molecular motions by solving Newton’s equation of motion for incrementally small time steps on the order of a femtosecond. GROMACS accounts for bond stretching, hybridization changes, 1,4-diaxial, Lennard-Jones, and Coulombic interactions by parameterizing the relative strength of these forces for a molecular structure. Then it determines how the atoms in the system move under the action of those forces.

The water model used in this work is the well-established Simple Point Charge Extended (SPCE) model. Each individual mass fraction

composition directly corresponds to a specific number of molecules incorporated into the simulation box with a constrained total number of molecules implying the number of water and non-water molecules.

Within this manuscript, NVT simulations of solvents with polymer are analyzed to determine key properties and trends. The pull code creates a harmonic potential along the z-axis that interacts only with the N-decane molecule. The spring constant of the system is tuned to be stronger than the intermolecular repulsions of the solvent molecules and N-decane. For a molecule which is insoluble in a specific solvent system, there are increased repulsions the deeper into the bulk the molecule travels. In order to determine the free energy of solvation, the solute material must travel at least as far into the solvent as the cut-off radius for non-bonded interactions. The temperature of these simulations is 293.15 K. For the pull code constrained ensemble the equation which governs the key relationship between n-decane density and Gibb’s free energy is as follows:

$$\frac{\Delta G(z)}{k_b T} \propto \text{Log}_e(\rho(z)) \quad (1)$$

$$\text{Log}_e(\rho(z)) = \text{Log}(\text{Prob}(z)) \quad (2)$$

The simulation time average N-decane density as a function of z is supplied by the GROMACS density utility and is non-symmetrized. The density is convoluted into the free energy as a function of z by equation 1 given that equation 2 relates the density to the probability of finding the target molecule at position z. These results could be viewed as an indirect route to the same information that would come from the partition function of the system. The software does not readily report the ensemble properties of individual or sub-groups of molecules with the energy command, so this method was necessary. It is possible that looking at the free energy of the system as the molecule was pulled from the vacuum state to the solvated state would not be helpful since the free energy of solvation may be on the order of magnitude of the fluctuations in the ensemble properties of the system, though this

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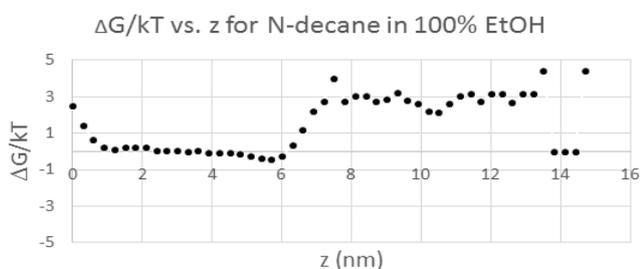
was not exclusively checked. Simulation equilibration was observed by increasing the simulation time until the density profile decreased by less than 5% with increased simulation time at 1 ns intervals. The simulation time was greater than 15 ns in all cases (Figures 1-7).

## Results

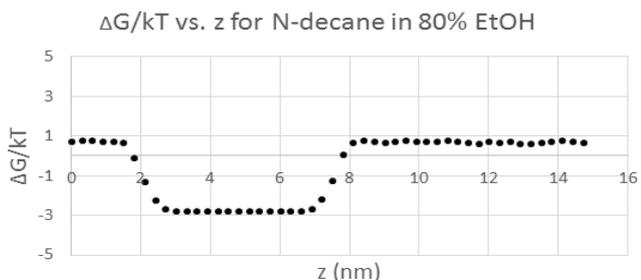
The free energy of the simulation is plotted versus the center of mass of the molecule of interest as it is pulled throughout the system. The solvents occupy approximately 2 to 8 nm. The solvent thickness varies in each alcohol content as is fixed by the constrained total number of molecules. The negative free energy arbitrarily corresponds to system instability. The free energy scale is relative and can be shifted to be completely positive.

## Discussion

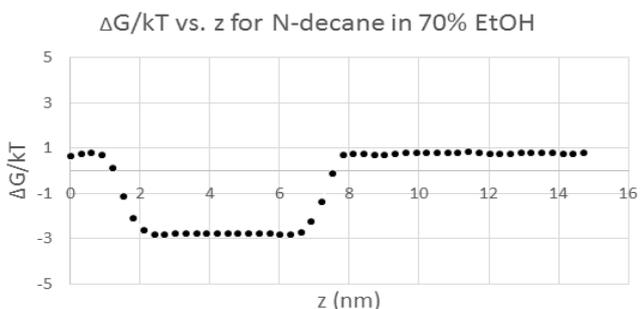
The free energy of solvation is determined by taking the maximum



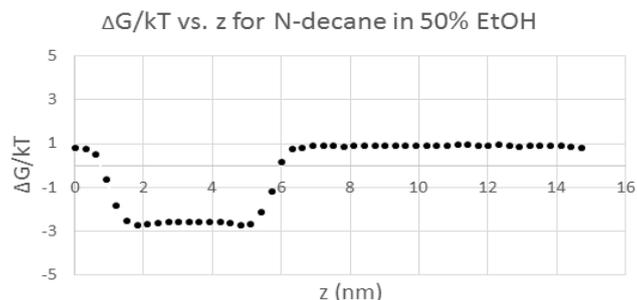
**Figure 1:** This figure depicts the free energy increasing as the polymer enters into the bulk. The polymer prefers to be in the surface state. The free energy of solvation is  $4.87 \cdot kT$  or  $2.00 \cdot 10^{-20}$  J.



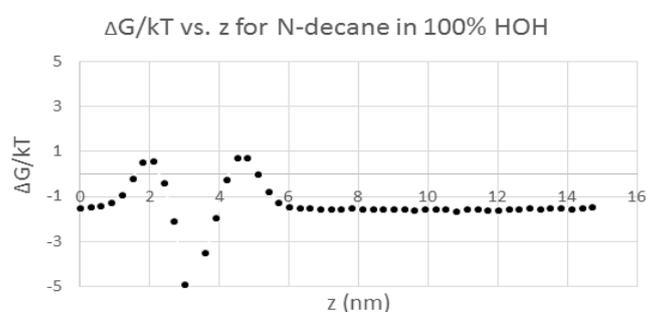
**Figure 2:** This figure depicts the free energy decreasing as the polymer enters the bulk. The solubilized state is preferred over the surface state. The free energy of solvation is  $3.87 \cdot kT$  or  $1.88 \cdot 10^{-20}$  J.



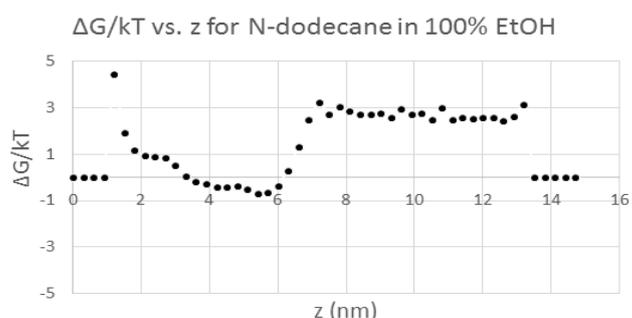
**Figure 3:** This figure depicts the free energy as a function of z for a ten carbon alkane material in 70% by mass ethanol. The solubilized state is preferred over the surface state. The free energy of solvation is  $3.63 \cdot kT$  or  $1.76 \cdot 10^{-20}$  J.



**Figure 4:** This figure depicts the free energy as a function of z for a ten carbon alkane material in 50% by mass ethanol. The solubilized state is preferred over the surface state. The free energy of solvation is  $3.69 \cdot kT$  or  $1.808 \cdot 10^{-20}$  J.

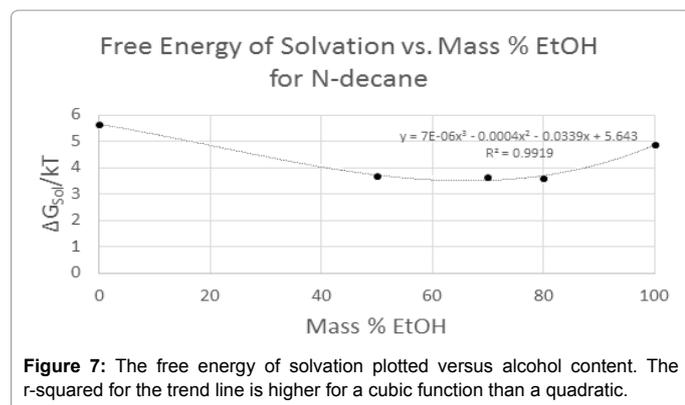


**Figure 5:** This figure depicts the free energy as a function of z for a ten carbon alkane in 100% by mass ethanol. The interface state is preferred over the solubilized state. The free energy of solvation is  $5.64 \cdot kT$  or  $2.74 \cdot 10^{-20}$  J.



**Figure 6:** This figure depicts the free energy as a function of z for a twelve carbon alkane in 100% by mass ethanol. The interface state is preferred over the solubilized state. The free energy of solvation is  $5.1 \cdot kT$  or  $2.48 \cdot 10^{-20}$  J.

free energy and subtracting the minimum value. Each of those values corresponds to either the gas state or the solubilized state. The free energy of solvation decreases with increasing alcohol content then decreases after a certain point. That point represents the content at which solvent-solvent attraction interactions overtake the solvent A-solvent B repulsion interactions modified by the solvent A or solvent B attraction to the alkane. An N-decane molecule was simulated in 100% ethanol and the free energy of solvation of this system is greater than n-decane in the same content. The trend is expected to continue at higher and lower contents. Meaning that the free energy of solvation of n-novae in 100% EtOH is expected to be less than that of N-decane



and that the free energy of solvation of simple  $n\text{-C}_{13}\text{H}_{28}$  in 100% Et OH is expected to be larger than that of N-dodecane in the same solvent.

## Conclusions

This manuscript details the free energy as a function of z-space for a small alkane in several alcohol contents. It is determined from an inversion of the time-averaged alkane density profile and allows for the calculation of the free energy of solvation. A longer alkane free energy of solvation was presented for single alcohol content and a trend that is expected to hold as a function of molecular weight is asserted. Though there are entropic considerations associated with the configurations of the backbone carbons rotating in solubilized versus bulk states. In small molecule alkanes, the end carbons LJ and Coulombics could impact free energy of solvation more than in high molecular weight Polk alkanes where such forces would have a much smaller contribution to the free energy of solvation. Future work should seek to determine the alcohol content at which free energy of solvation begins to increase. Furthermore, to determine the order of the best fit polynomial for the

free energy of solvation as a function of alcohol content for different alkanes. Additionally to determine to what extent dihedral interactions contribute to the entropy of solvation and whether LJ or Coulombics contribute more to the mass content dependent, molecular weight dependent free energy of solvation relationships for various target molecules.

## Acknowledgements

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