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Counting the Relative Number of Hydrogen Bonds in Several Alcohol Co-solvated Systems via GROMACS

Mongelli GF*

Department of Chemical Engineering, Case Western Reserve University, USA

Abstract

In order to better understand the solubility properties of polyalkane, polyether and polysilicone materials, which are critical to the foaming behavior of shampoo and shaving creams, GROMACS molecular dynamics NVT simulations were performed using the OPLS-AA force field to determine the time-average number of hydrogen bonds in solutions of water co-solvated with methanol, ethanol, isopropanol, dimethyl ketone and acetyl methyl carbinol.

Keywords: Surfactants; Polymer; Interactions; Molecular dynamics

Introduction

The specialty surfactants industry is expected to reach USD 29.2 billion globally in 2017 [1]. Surfactants are used as foaming agents in alcohol co-solvated systems. Such systems are very apparently significant, yet it is surprising that there is still a lack of understanding regarding which molecular properties make them so effective at foaming. The author suggests that their effectiveness comes from the combination of solubility properties and surface tension tuning. Regarding solubility properties, the critical aspect is that the polymer is insoluble in the alcohol co-solvated mixture and, therefore, present at the interface. The surface tension is reduced by the alcohol content and then further by the polymeric molecules, which results from a combination of dihedral interactions, LJ interactions and Coulombic interactions. This manuscript focuses on factors that affect polymer solubility based upon properties of the solvents.

Recent molecular simulations have shown that computational methods can offer significant insight into polyethoxy [2] and polysilicone [3] systems, hydrogen bonding [4], solvent-water interactions [5], and alkane properties [6]. Of particular interest in addressing surfactant materials are a study by Dalvi et al. discussing the source of the hydrophobic effect [7].

Several studies by van der Spoel have approached alcohol co-solvated systems with particular emphasis on evaluating hydrogen bonds in such mixtures. Another study sought to understand the thermodynamics and kinetics of hydrogen bond formation and breaking [8]. This manuscript bridges ideas from several studies and incorporates new details in quantifying hydrogen bonds in previously unexplored mixtures.

In order to ascertain what gives these surfactant polymers their solubility behavior in alcohol-water solutions, a critical examination of the properties of solvent systems via molecular simulation without polymers added is first necessary. This paper seeks to study and quantify the number of hydrogen bonds in a molecule number constrained system. This quantity is a key metric describing solvent interactions.

Model systems of interest include water mixed with methanol, ethanol, isopropanol, acetone and acetoin. In acetone and acetoin, there are noteworthy force field differences, those attributed to mixing a carbonyl and an alcohol moiety, which add to the complexity of the co-solvent series.

Methods

GROMACS molecular dynamics software was utilized to simulate the behavior of mixed solvent systems from classical principles. NVT simulations of solvents were analyzed to determine trends in hydrogen bond count. The key properties of the solvents reported are the number and types of hydrogen bonds as a function of alcohol structure and content. The hydrogen bonds were sub-characterized as between water and water, water and alcohol or alcohol and alcohol molecules. Counting the relative number of hydrogen bonds has implications in understanding relative free energies of solvation and, therefore, solubility and surfactantability of polymers solvated in these solutions.

A Berendsen thermostat was used with integration constant. Each chemical component had its own thermostat, with each thermostat having the same integration constant. The temperature for each unique molecular component is 298.13 K. The cut-off radius for long-range interactions is 1.2 nm. Bond constraints were enforced at 1 femtosecond intervals for 16 million steps. Periodic boundary conditions were used on the x, y and z ordinates. Particle Mesh Ewald type coulombic systems were used. The cut-off radius for Couloumbic and van der Walls interactions were set to 1.2 nm. The Fourier spacing was set to 0.22 nm. Since all of the reported were NVT simulations, pressure coupling was turned off.

The water model used in this work is the well-established Simple Point Charge Extended (SPCE) model [9]. Each individual mass fraction composition directly corresponds to a specific number of molecules that were incorporated into the simulation box; with a constrained total number of molecules implying the number of water and non-water molecules in each simulation. The total number of solvent molecules was arbitrarily chosen to be 2783. Computational power, simulation time rate and time to convergence of hydrogen bond counts dictated an optimum number of solvent molecules to choose.

The number of water-water solvent-water and solvent-solvent hydrogen bonds were counted. The existence of a hydrogen bond was

*Corresponding author: Mongelli GF, Department of Chemical Engineering, Case Western Reserve University, 10900 Euclid Ave., A.W. Smith 116, Clevland, OH 44120, USA; Tel: 12163682000; E-mail: Gfm12@case.edu

determined from the distances and angles between all acceptor oxygen and donor hydrogen atoms using the g_h bonds utility in GROMACS. This utility is fully described in the GROMACS manual and was applied by Luzar and Chandler [10] as well as Markovitch and Agmon [11].

Results

The system equilibration was indicated by a time-steady hydrogen bond fluctuation. Adding alcohol as a co-solvent decreases the time-averaged number of HOH-HOH H bonds in all cases, as seen in the Table 1. There are on average 4861 HOH-HOH H bonds in pure water as seen in the Table 1. The Table 1 shows that the largest number of hydrogen bonds broken in transitioning to 50% mass of each of the alcohols at a constant number of molecules was in methanol. The next lowest number of hydrogen bonds at that content was in ethanol, then isopropanol, then acetoin and acetone, as inferred from consideration of the table. This ordering of change in hydrogen bonds follows in the higher alcohol contents also.

There is a hierarchy of the average number of alcohol-alcohol hydrogen bonds, denoted XOH-XOH H bonds. X-OH denotes an arbitrary alcohol, and XOH-XOH hydrogen bonds denotes the number of hydrogen bonds an alcohol forms with only the other alcohol molecules. In each of the model systems studied, the ranking of most self-hydrogen bonding alcohol to least self-hydrogen bonding alcohol in each alcohol content did not change ordering in 00%, 50%, 70%, and 100% cases, as shown in the table. The table also shows that the most self-hydrogen bonds in any alcohol is ethanol in all contents studied, then methanol, then isopropanol, then acetyl methyl carbinol, then acetone.

The number of HOH-XOH bonds increases from zero in the pure aqueous limit. The pattern in the hydrogen bonding is most complex for hydrogen bonds between alcohol and water. This is because the alcohol that has the most of this type of hydrogen bond changes with alcohol content: a change in ordering is not found in water-water nor alcohol-alcohol hydrogen bonds. In the 50% mass content, methanol has the largest number of HOH-XOH bonds. The next lowest at that content is isopropanol, then ethanol, then acetone and acetoin. In the 70% mass content, isopropanol overtakes methanol, and the rest of the ordering remains unchanged from the 50% content.

The total number of hydrogen bonds decreases with increasing alcohol content. Due to the nature of the change in ordering of the maximum XOH-HOH H bonds in each content, the total number of HOH bonds in each content does not have a rigid ordering structure with respect to alcohol content. The total number of hydrogen bonds is the sum of HOH-HOH, HOH-XOH and XOH-XOH H bonds. At 50% mass content, isopropanol has the largest number of hydrogen bonds, then ethanol, then methanol, then acetoin, then acetone. At 70% mass content, ethanol has the largest number of total hydrogen bonds, then isopropanol, then methanol, then acetoin, then acetone. At 100% mass content, ethanol has the largest number of total hydrogen bonds, then

Alcohol content	Simulation time-average HOH-EtOH Hydrogen bonds	Simulation time-average HOH-HOH Hydrogen bonds	Simulation time-average EtOH-EtOH Hydrogen bonds	Total
0	0	4861	0	4861
50	1282	2820	217	4319
70	1682	1585	551	3819
100	0	1585	2549	4134
Trend with increasing content	Increase	Decrease	Increase	Decrease
Alcohol content	Simulation time-average HOH-POH Hydrogen bonds	Simulation time-average HOH-HOH Hydrogen bonds	Simulation time-average POH-POH Hydrogen bonds	Total
0	0	4861	0	4861
50	1375	2851	97	4323
70	1863	1592	325	3780
100	0	0	2036	2036
Trend with increasing content	Increase	Decrease	Increase	Decrease
Alcohol content	Simulation time-average HOH-MeOH Hydrogen bonds	Simulation time-average HOH-HOH Hydrogen bonds	Simulation time-average MeOH-MeOH Hydrogen bonds	Total
0	0	4861	0	4861
50	1536	2283	306	4124
70	1769	1112	737	3618
100	0	0	2523	2523
Trend with increasing content	Increase	Decrease	Increase	Decrease
Alcohol content	Simulation time-average HOH-DMK Hydrogen bonds	Simulation time-average HOH-HOH Hydrogen bonds	Simulation time-average DMK-DMK Hydrogen bonds	Total
0	0	4861	0	4861
50	0	0	0	0
70	0	0	0	0
100	0	0	0	0
Alcohol content	Simulation time-average HOH-AMC Hydrogen bonds	Simulation time-average HOH-HOH Hydrogen bonds	Simulation time-average AMC-AMC Hydrogen bonds	Total
0	0	4861	0	4861
50	0	0	0	0
70	0	0	0	0
100	0	0	0	0

Table 1: The number of hydrogen bonds as determined by the GROMACS molecular dynamics package in several mixed solvent systems.

methanol, then isopropanol, then acetoin, then acetone. Note, again, that acetone has no hydrogen bonds at 100% alcohol content.

Pure aqueous systems have only one type of H bonding: HOH-HOH bonds. 50% mass ethanol has three types of H bonding, with HOH-HOH bonds being the largest number, then EtOH-HOH, then EtOH-EtOH. In 70% EtOH, the number of EtOH-HOH bonds overtakes the number of HOH-HOH bonds, with EtOH-EtOH bond number trailing. In 100% EtOH, there are approximately half as many hydrogen bonds as pure aqueous systems. There are trivially no H bonds between HOH molecules nor between HOH molecules and EtOH molecules in 100% mass alcohol simulations.

The number of HOH-HOH bonds decreases in all alcohol contents as the mass fraction of alcohol increases. There are 4861 hydrogen bonds on average the pure water system. The number of XOX-XOH hydrogen bonds increases in all cases as XOH mass content increases except for DMK, which cannot form XOH-XOH hydrogen bonds due to the weak nature of carbonyl oxygen non-bonded forces. The number of XOH-HOH hydrogen bonds increases in all alcohol contents.

The total number of hydrogen bonds decreases with increasing alcohol content in all cases. This makes placement of polyalkane and polysilicone polymers into the bulk less destabilizing than in pure aqueous systems, therefore decreasing the free energy of hydration and solvation.

Conclusions

The numbers and types of hydrogen bonds were quantified via molecular simulation with GROMACS. A evaluation of the simulated number of hydrogen bonds is critical in understanding how specific types of molecules approach the bulk solution or interface states as a function of alcohol content. Knowledge of the relative number of hydrogen bonds at a fixed number of molecules gave insight into the free energy of solvation. With additional simulations, relative free energy of solvation relationships will be confirmed.

Surprisingly, counting the hydrogen bonds in a constant molecule number system does not best describe how hydrogen bonding takes place in the system. Rather, hydrogen bonds per unit volume or per unit mass should be considered in future studies.

The results from this work can be combined with free energy of solvation computations to understand the contribution hydrogen bond breaking has relative to the attractive or repulsive interactions between a molecule and the solvent atoms.

For a non-polar molecule which does not form hydrogen bonds with either of the solvents, decreasing the number of hydrogen bonds will generally decrease the free energy of solvation; that is the barrier toward entry of the molecule in the bulk. An example of a category of molecules that fits into this category is a polyalkanes: polyethylenes, polypropylenes and polyisobutylenes.

Determining the number of hydrogen bonds formed between surfactant molecules and these solvents will give insight to the cause of free energy of solvation relationships. Such information is useful, when combined with free energy of solvation simulations, in predicting solvophilicity of organic and inorganic materials in arbitrary solvent mixtures, especially when the polarity or non-polarity of the solute material can be readily compared to that of the solvent but does not explain the solubility properties.

For a molecule which forms more hydrogen bonds with a certain solvent molecule than the cosolvent molecule does, there will be some easement of the free energy of solvation. For example, if a polyethyleneoxide (PEO) molecule formed more hydrogen bonds with either water or ethanol than water does with ethanol or ethanol does with water, then the free energy of solvation will favor PEO to enter the bulk. For molecules which form more hydrogen bonds with either solvent or both solvents, the free energy of solvation will favor bulk states over interface states. Molecules which are expected to fall into this category are the polyethers and polysilicone. More simulation studies are required to confirm this hypothesis.

A study of the interactions between solutes and solvents from a fundamental forces and free energies of solvation perspective is required to determine the theoretical underpinnings behind complex alcohol content dependent solubility relationships. Such guiding calculations will allow for new insight into which aspects of mixtures can be tuned to have desirable properties, such as surfactantability and foaming based upon careful selection of alcohol content and polymer concentration. With current known properties in the literature, the observed patterns in molecular solvophilicity are seemingly random. Such suggested studies will provide insight into the molecular characteristics which give these mixtures their properties.

Further studies should seek to determine the content at which the maximum average number of achievable XOH-HOH H bonds occurs. Selection of the alcohol content at which a specific material is insoluble, whether in pure water or a mixed solvent content, allows for the tuning of surface tension and foaming capability.

Furthermore, simulations should be performed to simulate the properties of non-ionic surfactants such as the polyether series (PMO, PEO, PPO, P3MO) in mixed solvent systems. The recently published surface parameter [12] should be evaluated and its value confirmed to match experiments.

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