1 Computational Analysis

Classical molecular dynamics simulations were performed to analyze the interface formed between various aqueous salt solutions and carbontetrachloride. Three salt solutions were simulated, as well as a reference system consisting of neat water for comparison to previous computational efforts.[1-6] The salts used in the simulations were NaCl, NaNO$_3$, and Na$_2$SO$_4$. These were chosen to compare to the experimental SFG results, and to supplement those experiments with additional molecular-level information. Analyses were performed on the simulation data to extract ionic and molecular density data, information about water coordination near to the interface, and water orientation data from order parameter analysis. The analyses are similar to, and logical extensions of previous computational work done on aqueous salt systems.

1.1 Density Profiles

Density histograms of simulated interfaces have been used in previous publications to show ionic and molecular distribution behavior in various systems.[2,4,6-11] In this work the density profile of water through the interface is fitted to a hyperbolic tangent function[8,12] as shown below:

$$\rho(z) = \frac{1}{2}(\rho_1 + \rho_2) - \frac{1}{2}(\rho_1 - \rho_2)\tanh\left(\frac{z - z_0}{d}\right) \tag{1}$$

Equation (1) relates the interfacial density, ρ, to the bulk densities of the two phases, ρ_1 and ρ_2, the location of the Gibb's dividing surface, z_0, and the interfacial width, d. The "90-10" thickness of the interface is related to the fitting parameter d by:

$$t = 2.197d \tag{2}$$

These measures of interfacial thickness provide a means of comparing the depths to which the water phase is affected by ions located at the interface. The density distributions of the salts depict concentration and depletion phenomena throughout the interfacial region, and also serve to illustrate ionic affinity within this region. Previous work has been performed on the air-water interface with various ions introduced, and each shows a particular level of interfacial affinity, with the more polar ions being the most interfacially active. We present the density distribution results below for the H$_2$O-CCl$_4$ interfaces studied. The density profiles of the different anionic species are fitted using a modified tanh() function that includes a gaussian function to more closely fit the concentration near the interface. The anion fitting function allows for a more direct comparison of location and peak width between the different systems.

$$\rho(z) = \frac{1}{2}(\rho_1 + \rho_2) - \frac{1}{2}(\rho_1 - \rho_2)\tanh\left(\frac{z - z_0}{d}\right) + ae^{-\frac{(x-b)^2}{2c^2}} \tag{3}$$

The gaussian function allows one to locate the anion peak height a, centered at an offset location b, with a width c.

1.2 Water Coordination

The coordination of water and distribution of the various coordination types was determined for each intefacial system. Water coordination refers to the hydrogen-bonding structure of water molecules, and is a measure of the number and type of bonds made. A simple naming scheme used to describe each type of water coordination have been developed previously,[4] and so that nomenclature will be used in this work. It has been established that certain bonding structures dominate in different regions of the interface, thus each of the water density profiles will be broken down further into component coordination types to show the areas in which the various types are most prevalent. The parameters used to define a hydrogen-bond are taken from a previous work by this group.[4] Analysis of water coordination profiles is valuable for comparison to experimental VSF results within the OH-bond stretching region of the vibrational spectrum. These give a molecular-level description of the composition of an interface, and show the various water bonding types that will contribute most to the VSF signal. Additionally, the results of this work are compared to previous studies on the air and salt water interfaces to establish differences due to the addition of an organic phase.

1.3 Order Parameters

One means of describing molecular orientation relative to a surface is by use of order parameters.[13] This technique has been applied to biaxial molecules such as water at organic interfaces,[2] and organic molecules to elucidate structuring within the interfacial region.[1] The results of this work show the two order parameters, S_1 and S_2, as functions of distance from the interface Gibbs dividing surface.

$$S_1 = \frac{1}{2} \left\langle 3\cos^2(\theta) - 1 \right\rangle \tag{4}$$

$$S_2 = \frac{\langle \sin(\theta)\cos(2\phi) \rangle}{\langle \sin(\theta) \rangle} \tag{5}$$

The order parameters are calculated from the euler angle values of the molecular "tilt" θ, and the "twist" ϕ. The order parameter distributions are further broken down to show the values for individual water coordination types for determination of orientational behavior of each.

2   Computational Methods

The molecular dynamics methods used in this work reproduce those from our previous computational efforts with some modifications described below.[1,2,4] All molecular dynamics simulations were carried out using the Amber 9 software package. The polarizable molecular model parameters are taken from previous works on similar systems.[11,14–17] The polarizable POL3 model was used for water molecules.[18] Fully polarizable models have been used in previous interface simulation studies because they are known to more accurately reproduce interfacial structure and free energy profiles.[19–22]

A total of 4 systems were simulated consisting of aqueous salt and CCl_4 phases. A slab geometry was used to produce two interface regions, the analyses of which were averaged.[1] The organic region was formed in a box 30-Å on a side with 169 CCl_4 molecules to reproduce standard temperature density of 1.59-$\frac{g}{mL}$. The aqueous region was formed in a box 30x30x60-Å, with the long axis labeled the z-axis. The number of water molecules and ions varied for each system in order to reproduce a density of 1.2-M. The specific populations of each molecule are listed in table 2. The organic and aqueous boxes were then joined to form a system 90-Å long with interface areas of 30x30-Å.

System	H_2O	Cation	Anion
Neat Water	1800	0	0
NaCl	1759	40	40
$NaNO_3$	1732	40	40
Na_2SO_4	1740	86	43

Table 1 — Aqueous molecule and ion numbers. Listed are the populations of each component for the 4 simulated aqueous phases. All systems were simulated at near 1.2-M salt concentrations.

The water, salts, and CCl_4 were each randomly packed into their respective boxes with a minimum packing distance of 2.4-Å. After joining the aqueous and organic phases and forming the two interfaces, the total system was energy minimized using a conjugate gradient method. Following minimization, the system was equilibrated at a constant temperature of 298-K with weak coupling to a heat bath for a period of 10-ns, using a simulation timestep of 1.0-fs. A non-bonded potential cutoff of 9.0-Å was used. Following equilibration the system was simulated with the same parameters for a further 10-ns with atomic position data recorded every 50-fs. This resulted in a total of 200,000 snapshots which were used in the data analysis.

3 Component Densities

Each of the simulated system's density profiles were calculated to quantify lineshapes and deviations from the neat-water system. The water density profile of each system was fitted to a hyperbolic tangent (Eq. 1) with the fitting parameters listed in table 2. The resulting data was shifted such that the location of the Gibb's dividing surface (z_0) was used as the origin for distance calculations.

System	ρ_I	d	t_{90-10}
Neat Water	1.613	3.545	
NaCl	1.732	3.806	
NaNO$_3$	3.264	7.171	
Na$_2$SO$_4$	1.271	2.793	

Table 2 — Water density profile fitting parameters. The system origin was shifted for analysis such that z_0 corresponds to a long-axis location of 0.0. Equation 2 relates the interfacial width to the "90-10" thickness of the water profile. ρ_I is the bulk density value in the aqueous phase.

The fluctuations in the surface density profiles of water have been noted previously and attributed to thermal capillary waves on a larger length-scale than the system size.[23] The same work also made note that the interfacial thickness is size-dependent on the interfacial surface area. Increasing the surface area dimensions should cause an increase in the interfacial width. Two works on the water-CCl$_4$ surface offer direct comparison of this.[2,23] In comparing the interfacial widths, there is an increase in width as the system cross-sectional area is increased. This phenomenon implies that care must be taken when making quantitative comparisons between simulation studies.

Ionic density profiles were fitted by adding a gaussian function to the hyperbolic tangent function (Eq. 3) to more closely capture the concentration enhancement excess near or within the interfacial region. The lineshape parameters for each salt system are shown in table 3.

System	Anion					Cation				
	a	b	c	z_0	d	a	b	c	z_0	d
NaCl	0.464	-1.726	1.361	-3.190	1.928	-0.257	-8.252	2.154	-2.278	1.666
NaNO$_3$	0.732	0.655	1.520	-0.962	0.407	0.335	-1.614	1.982	-2.769	1.384
Na$_2$SO$_4$	0.474	-3.551	1.162	-5.594	2.307	-0.707	-8.648	3.439	-3.203	1.791

Table 3 — Lineshape fitting parameters for the ion density profiles. The data for each density profile is fit to a convolution of a hyperbolic tangent and gaussian peak functions (Eq. 3). The parameters a, b, and c are used for fitting the gaussian peak to model the concentration of ion near to the interfacial region. z_0 and d are the two parameters used to model the hyperbolic tangent lineshape for the bulk concentration and the decrease of density within the H$_2$O-CCl$_4$ interface.

Most of the recent studies on ion concentration near water interfaces have noted that large and polarizable ions will concentrate at the surface,[10,21,24,25] while small non-polarizable ion tend to be repelled. The

surface enhancement calculated from molecular dynamics, however, portrays the lower bound of the actual effect because of the reduced polarizability values used in simulations to avoid the so-called "polarization catastrophe." The enhancement of surface anions is also believed to be the cause of the subsurface cation density increase. The counterions are attracted to the concentrations of anions at the surface, which are in turn stabilized by the increased polarization of the water due to the distorted interfacial electric field. The affinity for the surface follows the trend of surface tension increments, $\frac{d\gamma}{dm_2}$, where $Na_2SO_4 > NaCl > NaNO_3$.[24] This also follows the hoffmeister series trend for anions found to be the most "structure-making", and they are found to be enhanced further into the interface.

4 Water Orientation

5 Water Orientational Order Parameters

6   Calculated Sum-Frequency Spectra

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