Influence of Aqueous Ionic Strength Upon Liquid:Liquid Interfacial Structure and Microsolvation

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Abstract

Ionic strength of an aqueous solution is often used to alter the efficacy of industrial processes that rely upon liquid:liquid phase boundaries (e.g. solvent extraction), however there is little understanding of how this condition may alter the properties of the phase boundary itself. The current work examines the interfacial structure and processes within the biphasic system $(\text{NaNO}_3)_{\text{aq}}:n\text{-hexane}$ from 0 – 10 M NaNO_3 at 298 K and 1 atm pressure. The extent of ion-pairing was quantified, alongside the primary solvation environments of both water and ions. Ion concentration was found to be depressed in the interfacial region relative to the bulk, and as such there is less likelihood of the formation of contact ion-pairs or ion-clusters at the interface. This in turn, leads to the interesting observation of more hydrogen bonds per water at the interface than in the bulk. At 10 M NaNO_3 enough ions are present at the interface to severely perturb the mesoscopic interfacial properties of width and tension (the latter doubling in size relative to the neat water interface with $n\text{-hexane}$). Chemical theories, like the Kelvin equation and its analogues for liquid:vapor interfaces, would intuit that such a large change in interfacial tension should influence the microsolvation processes of the immiscible solvents (microsolvation being the rare event where water can penetrate $n\text{-hexane}$ and $n\text{-hexane}$ may penetrate and be fully solvated by water). However, there is no statistical difference between the concentrations of water and $n\text{-hexane}$ in their respective co-solvents as a function of interfacial tension in these non-ideal solutions. Based upon these data, the ability of electrolyte concentration to alter transport across the interface does not appear to be related to the perturbation imparted by the electrolyte upon the interfacial properties themselves.

Keywords: liquid phase boundaries, microsolvation, interfacial tension, electrolyte

1. Introduction

The interfacial properties of aqueous electrolytes have been an active area of research for many years. The specific study of aqueous nitrate at the vapor interface has received much attention because it is abundant in the atmosphere and involved in a variety of reactions therein.[1, 2] Second harmonic generations (SHG) and vibrational sum frequency generation (VSFG) have been instrumental in developing an understanding of the relationship between ion concentration (between 1 M and 6.8 M)[3-9] and the meso-scale interfacial properties in the liquid:vapor system (e.g. surface tension, interfacial width) as well as the orientation of interfacial nitrate relative to the bulk liquid.[10]

Far less emphasis has been placed upon the study of nitrate concentration pertaining to liquid:liquid interfacial properties.[11] This has relevance to industrial processes, where ionic strength can alter the distribution of solutes across the aqueous:organic phase boundary. As an example, consider the Plutonium Uranium Redox Extraction (PUREX) process, which is used to recover uranium and plutonium from dissolved spent nuclear fuel.[12] There, changes in nitrate concentration in the aqueous phase can enhance the distribution of metal-ligand complexes through a variety of potential mechanisms.[13, 14] Nitrate can act as a metal complexant, however the ionic strength of an aqueous solution can also disrupt the hydrogen bond network properties of water, which presumably carries over to the interfacial organization of water and may lead to fundamental changes in both the mesoscopic and molecular-scale interfacial organization and dynamics.[10]

The first goal of this study is to understand whether the trends in the solvation environments of interfacial *n*-hexane, H₂O, Na⁺, and Cl⁻, as a function of [NaNO₃] coincide with the changes in the interfacial tension and width for the biphasic system NaNO₃(aq):*n*-hexane. Traditional post-processing analyses are used to investigate the orientational structure of water, *n*-hexane and the interfacial density as a function of proximity to the interface. However traditional spatial correlation functions present only average data and can mask essential rare events that may contribute to the interfacial transport properties. In particular, this work is interested in the distribution of different solvation environments at the interface, and also upon the rare microsolvation processes that are the thermochemical driving force for phase separation. Microsolvation is the process by which, during the dynamic motion of the interface, one solvent temporarily penetrates the phase of its immiscible co-solvent. Here, intermolecular network theory (INT) is used to create networks of all intermolecular interactions between the co-solvents as well as the ions so as to deconstruct what, if any, relationship may exist between the meso-scale interfacial properties (e.g. interfacial tension), the orientational order of the solvents, the solvation environments at the interface and microsolvation processes.[15-17] INT is well suited for this task as the topological properties of the intermolecular network have been well-demonstrated to not only yield the same average information as a spatial correlation function (e.g. a radial distribution function), but also all the sub-components (including rare events).[15] In prior work, INT has been used to study water:*n*-hexane interfaces in the presence of amphiphilic solutes, where significant changes in microsolvation, even far from the solute, were observed.[17] Further, in

liquid:air interfaces, the well-known Kelvin equation[18, 19] presents a clear relationship between vapor pressure and surface tension – and thus it is relevant to pursue whether at the liquid:liquid interface of a complex non-ideal solution, the change in solvation environments and concentration of co-solvents in each phase depend upon the interfacial tension of the phase boundary. In combination, these data help to develop a better understanding of the mesoscopic interfacial properties and molecular scale behavior of organic interfaces with aqueous electrolytes.

2. Computational Details

2.1 Molecular Models

Pair-wise additive models represent the potential energy of the system, with intermolecular pair potentials being taken as the sum of all pair potentials between interaction sites within the molecules. The organic molecule *n*-hexane has been described by AMBER-99 potentials,[20-23] while water utilized a modified rigid TIP3P/Ew water potential.[24] In our prior work,[17] this combination of water and *n*-hexane potentials yields a calculated interfacial tension value for the pure water:*n*-hexane phase boundary that is in good agreement with prior theoretical studies and experimental values.[25-27] The sensitivity of the pair-wise interactions between the H-atom of water, H_w, and NO₃⁻ were tested using two nitrate force fields, that of Papoyan et al.[28] and Wipff and coworkers,[29] using the AMBER-99 potentials for Na⁺. [20] Subsequent analyses of the radial distribution functions (RDF's) of the equilibrated 1 M and 10 M NaNO₃ electrolytes indicated negligible dependence upon the ion force field (see Fig. S1 - S2 in

Supplementary Information). Hence in this work the Popayan et al. force field has been used for all ionic strengths. All simulations were performed using the LAMMPS software (version 13Sep 2013),[30] with the Verlet algorithm,[31] and a 1 fs time step. The long range electrostatic interactions were modeled by Ewald summation in K-space with a cutoff of 11 Å and an accuracy of 1×10^{-6} for determining the root mean squared (RMS) error when the forces are being evaluated. This reference value was chosen as representative of the magnitude of electrostatic forces in atomic systems and is the default in LAMMPS. Thus an accuracy value of 1×10^{-6} means that the RMS error will be a factor of 1,000,000 smaller than the reference force. The accuracy setting is used in conjunction with the pairwise cutoff of 11 Å to determine the number of K-space vectors. For further information regarding the estimation of the RMS force errors in real space for Ewald summation, we refer the reader to reference[32] and the LAMMPS documentation for the default parameters employed in this work.

2.2 Simulation Details

Four simulation boxes with different concentrations of aqueous sodium nitrate were constructed using the Packmol program,[33] that span 1 - 10 M NaNO₃ (Table 1). A water:*n*-hexane simulation box was initially constructed of dimension $L_x = L_y = 30$ Å and $L_z = 60$ Å that obeys periodic boundary conditions in all 3-dimensions, followed by the placement of NaNO₃ initially placed at random coordinates within the aqueous phase. In prior work, we have examined the impact of the simulation box configuration upon the quality of the equilibrated data and the resulting statistical analyses.[16] That work did not yield improvement if a configuration of the form organic:water:organic was used

relative to organic:water, and as such the configuration employed in Figure 1 has been used. The water component contained 902 molecules, while 123 *n*-hexanes were present. In order to understand the impact of the ionic strength upon the local organization of the bulk aqueous solution, four more cubic simulation boxes were constructed, 30 Å on a side containing the same number of NaNO₃ and water molecules (bulk solutions without an interface).

The systems were brought to mechanical and thermal equilibrium at 298 K using the NVT ensemble of No and Hoover,[34-36] followed by a series of NPT simulations until a pressure of 1 atm was reached.[35, 37] The systems were run in NPT for at least 1 ns followed by 1 ns of simulation in the NVE ensemble to verify the system temperature and pressure. The production run consisted of at least 10 consecutive 1 ns runs of NVE simulation to obtain reliable statistics for the network analysis.

Fig. 1. Initial configuration of the simulation box, wherein the NO_3^- and Na^+ are placed randomly within the aqueous phase, with layers B_{aq} and A_{aq} defined relative to the Gibbs dividing surface, $z_0 = 30 \text{ \AA}$, where $\rho_{\text{H}_2\text{O}} = 0.5 \text{ g/cm}^3$.

Table 1

The number of NaNO_3 within the simulation box and corresponding molarity; 902 H_2O were present in the simulations of the bulk liquid, while 902 H_2O and 123 C_6H_{14} were present in the biphasic system.

Molarity of NaNO_3 (mol/L)	Number of NaNO_3
1.0	16
3.0	48
5.0	81
10.0	162

2.3 Data Analysis and Intermolecular Network Theory

The data was analyzed using several methods so as to interrogate the role of the Na^+ and NO_3^- ions upon interfacial organization of water and *n*-hexane. Standard

analyses included the determination of the radial distribution functions (RDFs) between non-bonded O_w-O_w , O_w-H_w , O_w-N_n , O_w-Na , O_n-N_n , O_n-H_h , $Na-H_h$, O_w-H_h where O_w and H_w are the O- and H-atoms of H_2O and O_n and N_n are the O- and N-atom of NO_3^- , with H_h being the H-atom of *n*-hexane. The density profile, molecular orientation, interfacial tension and thickness have also been examined.

The orientation of water is defined as the cosine of the angle θ_i between the unit vector in the direction of the dipole (μ_i) and the unit vector normal to the interface (n_z),

$$S_z = \cos\theta_i = \mu_i \cdot n_z \quad (1)$$

The orientation order parameter of *n*-hexane is defined as:

$$S_z = \frac{1}{2}(3 \langle \cos^2\theta \rangle - 1) \quad (2)$$

where θ is the angle between the interface normal (the z -axis) and a vector that represents the local orientation and conformation of *n*-hexane.[38] For each *n*-hexane a vector is defined that bisects C-atoms that are two bond lengths apart, resulting in four vectors per *n*-hexane molecule. If an *n*-hexane is in the all *trans* conformation these vectors are all parallel, as in Fig. S3. Within Eq. 2, the average angle that each of the four vectors makes with the z -axis of the simulation box (the interface normal) over all molecules and all time is determined. The z -dependent profile of S_z is plotted in Fig. S3, wherein a value of 1 signifies an average orientation of the *n*-hexane parallel to the xy -plane (the interfacial plane). An S_z value of -0.5 denotes an average orientation of the *n*-hexane perpendicular to the xy -plane (the interfacial plane). A value of $S_z = 0$ indicates a completely random orientation.[27] The surface tension of water was calculated from the capillary wave

method using the procedure of Senapati and Berkowitz,[39] where the density profile of water (ρ_w) and is fitted to Eq. (3):

$$\rho_w(z) = 0.5\rho_w - 0.5\rho_w \operatorname{erf}\left(\frac{z - z_{0,w}}{\sqrt{2}w_c}\right) \quad (3)$$

In Eq. 3, $z_{0,w}$ represents the Gibbs dividing surface for water. The width due to thermal fluctuations is w_c . After finding the value of w_c , one can find the value of γ_e due to the capillary wave and thermal fluctuations using Eq. (4):[40]

$$w_c^2 = \frac{k_B T}{2\rho g_e} \ln\left(\frac{L_x}{l_b}\right) \quad (4)$$

where L_x is the total length in the $x = y$ direction and l_b is the bulk correlation length (on the order of the molecular length). In this work we have estimated the value of l_b as the cut off distance of 11 Å. Our prior work has shown that this value of l_b reproduces the interfacial tension of pure water:*n*-hexane[17] and water:*n*-pentane,[16] however it is important to note that the interfacial tension is somewhat sensitive to l_b . For example, in reference [17], for water:*n*-hexane, a value of l_b of 10 Å yields γ_e of 49.7 dyne/cm, while $l_b = 11$ Å results in $\gamma_e = 46.3$ dyne/cm, and finally $l_b = 12$ Å yields a γ_e of 43.0 dyne/cm. Herein it is demonstrated that the interfacial tension nearly doubles when going from 1 M NaNO₃ to 10 M NaNO₃, and as such this primary observation will not be strongly sensitive to the choice of l_b chosen.

In comparison to analytic schemes that are fundamentally based upon the evolution of the position of atoms and molecules over time (e.g. pair correlation functions), the emphasis within Intermolecular Network Theory (INT) is to study the

organization and time-evolution of the intermolecular interactions between species. Networks have been constructed from each frame of data within the simulation trajectories that account for interactions between the following pairs of atoms: O_w-N_n , O_w-Na , O_w-H_w , O_n-H_w , O_n-H_h , O_n-N_n , O_n-Na , $Na-H_h$, and O_w-H_h using the aforementioned naming convention. The geometric criteria that define the distance threshold for the intermolecular interactions between non-bonded atom-A and atom-B are presented in Table 2, and are generally based upon the position of the first minima in the RDF between those centers. In the case of nitrate anion, the hydration about nitrate is highly varied in the literature. The water-nitrate interaction is rather weak, and as such the first peak in the radial distribution function obtained from simulations is often wide, and the minima is rather shallow (see for example the *ab-initio* MD studies in reference [41]). Experimentally challenges also exist due to the weaknesses of the nitrate-water interaction and the presence of multiple interaction points between the ion and solvent ($N_n \dots O_w$ vs. $O_n \dots H_w$). A variety of strategies, with various levels of success, have been developed to try to overcome these issues, for example using isotopic substitution to deconvolute contributions to experimentally determined RDFs.[42] However, the solvation of nitrate remains a significant challenge because it is difficult to cleanly delineate between first and 2nd shell water molecules about the anion. To focus upon the most salient aspects of the solvation structure, and maintain the emphasis of this work upon the role that nitrate has upon the structural organization of the water:*n*-hexane interface, only the closest interactions of water and nitrate will be studied. As illustrated by Ohtaki and Radnai, the reported literature hydration numbers for NO_3^- spans from 1.3

to 17.7.[43] If you assume that each O-atom of NO_3^- is in contact with 2 H_2O , then 6 H_2O molecules is a reasonable value, whereas the much larger hydration numbers must obviously include some 2nd shell H_2O . The value of the cutoff's employed in this work to define the first solvation shell as $\leq 3.5 \text{ \AA}$ for $\text{O}_w \dots \text{N}_n$ and $\leq 2.0 \text{ \AA}$ for $\text{H}_w \dots \text{O}_n$, which is somewhat conservative and emphasizes only those water molecules that are in closest contact with the anion.

While the distance criteria are between specific non-bonded atoms within a molecule, presented in Table 2, each molecule itself is converted into a single vertex, and if an intermolecular interaction is present, then an edge appears between molecular vertices in the network. Thus, multiple interactions between the same set of molecules is only considered as a single edge between molecular vertices. The INT approach benefits from the extensive analytic techniques employed by computer scientists and mathematicians for broadly analyzing networks of any type, specifically topological approaches like PageRank (employed by the Google search engine),[44-47] geodesic analysis (employed by Mapquest and other routing software), and network neighborhood analysis.[15, 48-50] The essential analyses discussed here are implemented in the *ChemNetworks* software package.[15]

The simplest analysis of the network consists of counting the number of edges to each vertex, so as to yield the distribution of intermolecular interactions for each molecule. The edge distribution is essentially a decomposition of the information that would be in an RDF between molecule/atom types. Consider that in the case of water, the RDF between non-bonded O- and H-atoms (see Fig. S4 in *Supplementary Information*)

yields the average H-bond environment about a given water, while the edge distribution provides the relative % of waters with 1 – 4 H-bonds that yield the overall H-bond number. The weighted average of the edge distribution is approximately that obtained by the integrated first peak of the RDF between the atom pairs of interest.

The emphasis of this work is to examine the properties of interfacial H₂O and *n*-hexane as well as the characteristics of the phase boundary itself as a function of concentration of aqueous NaNO₃. This includes examination of the solvation environment of the ionic solutes, the distribution of solvation environments about both Na⁺ and NO₃⁻ ions, and also the likelihood of ion-pair or cluster formation as a function of ion concentration. The ability of the cation and anion to alter the microsolvation reactions of both water and *n*-hexane was also studied. INT provides a facile framework to study microsolvation, which is defined as the rare event where one solvent molecule temporarily penetrates the respective co-solvent and is fully solvated therein.

The O_w-N_n, O_w-Na, H_w-O_n, O_n-H_n, Na-H_n, O_w-H_n, O_n-Na, O_n-N_n and O_w-H_w interactions were studied in different layers, or distances, relative to the interface. Two layers, each 10 Å wide, were constructed (Fig. 1). The point of origin within the interface itself is defined by the Gibbs dividing surface in the water density profile (Fig. 2). The Gibbs dividing surface z_0 is the position in the *z*-axis where the density is half the bulk density; in the case of water, z_0 is where the density of water is equal 0.5 g/cm³.^[51] The Gibbs dividing surface for each system was determined from the density profile of water, with the average value being found to be 30 ± 2 Å. The position at 30 Å was then used as the reference point for analysis of the 10 Å wide layers, labeled layer A_{aq} and B_{aq} for the

two 10 Å regions closest to the aqueous phase (Fig. 1). Thus, layer A_{aq} exists between 30 and 20 Å and layer B_{aq} is between 20 and 10 Å. The molecular simulation data of each layer in the biphasic system was then converted into a network based upon the intermolecular interactions of interest.

Fig. 2. Density profile of water, *n*-hexane, NO₃⁻ and Na⁺ in the aqueous 0[17] and 10M NaNO₃ solutions. See Fig. S7 in *Supplementary Information* for the density profiles of the intermediate concentrations studied.

Table 2

Distance criteria employed to define the intermolecular interactions. N_n and O_n are N-atom and O-atom of nitrate ion, O_w and H_w are O-atom and H-atom of water and H_h is *n*-hexane H-atom (note that the definition of a hydrogen bond in water also employed an angle criterion for θ_{HOH} of 145 - 180°).

Atom-A	Atom-B	r_{AB} (Å)
O _w	H _h	4.3
O _n	H _h	4.3
Na	H _h	4.5
O _w	Na	3.5
O _w	N _n	3.5
H _w	O _n	2.0
N _n	O _n	2.5
O _n	Na	2.5
O _w	H _w	2.5

The formation of ion-pairs, as well as clusters of ions, was examined using geodesic analysis of the network whose edges were ion-ion interactions. Networks were first made that accounted for all potential cation-anion, and anion-anion interactions, using the distance criterion provided in Table 2. No cation-cation interactions were observed and have thus been ignored within the discussion. A modified geodesic analysis was then employed to quantify the number of vertices (ions) within the network, and thus the size of the cluster that was formed. Geodesics (gd) are the shortest pathways in the network that connect every pair of vertices. In this case, the paths of ion-ion interactions in an ion-pair or cluster. The N×N geodesic distance matrix has entries that are the lengths of gd's that connect every pair of ions in the system. For each gd that is calculated, *ChemNetworks* maintains a connectivity list such that all ions that are part of the geodesic pathway are known. Inspection of the connectivity lists reveals that many of the gd's in the geodesic distance matrix are redundant (e.g., a geodesic that connects

vertices 1-2-3 also contains the 1-2 geodesic), and thus these “sub-geodesics” have been removed to create what is termed the isolated geodesic distance matrix. Based upon the connectivity information of each isolated geodesic distance matrix, the number of different ions was determined in each network associated with an individual ion cluster. The size distributions of the ion-pairs and clusters as well as their concentrations were then examined as a function of ionic strength of the aqueous solution and in different layers relative to the interface in the biphasic system. This approach is only a small portion of the capabilities of INT in understanding ion-pairing. Though not the focus of the current work, the use of intermolecular networks can be used to complement our conventional understanding of the degree of association between ions by creating networks that illustrate ion-pairs, poly-ionic clusters, contact ion-pairs, or ions that interact with one another through second or higher order solvation shells. In this manner the explicit concentration of different ion-pairs, as well as the mapping of specific reactants to product transformations of ion association can be elucidated which can improve upon our mechanistic understanding of ion pairing and the assumptions made within traditional ion-association theories[52-54] that generally ignore poly-ionic species.

3. Results and Discussion

The results first consider the bulk aqueous NaNO_3 solutions, the respective solvation environments, and nature of any paired ion species or ion-clusters. The biphasic system is then examined with a particular emphasis upon the change in solvation environments of water and ions within the aqueous interfacial layer A_{aq} and the bulk layer B_{aq} , as well as the orientation of both water and *n*-hexane. The influence of the ions

at the interface upon the microsolvation events, or ability of water to penetrate *n*-hexane and *vice versa*, was then studied.

3.1 (NaNO₃)_{aq} Solutions

While the focus of the current work is to understand how ionic strength influences the aqueous:organic interfacial structure, the bulk behavior must first be elucidated. We focus solely upon understanding the primary solvation environments about water, Na⁺, and NO₃⁻, and upon the likelihood of ion-pair and ion-cluster formation as a function of NaNO₃ concentration.

In several prior studies, an increase in the concentration of ions within water has decreased the overall average number of hydrogen bonds about individual H₂O, with a specific decline in the concentration of waters with 3 - 4 H-bonds and increases in the number of waters with only 1 - 2 H-bonds.[55, 56] Similar changes to the primary solvation environment about every H₂O have been observed here within the concentration regime of 0 - 10 M NaNO₃. While the changes in H-bond distribution about each water (with associated error bars from 3 1ns runs of NVE) are presented in Table S3 in *Supplementary Information*, it is more effective to illustrate the differences in solvation environment by plotting them relative to those environments observed in pure bulk water. Specifically, the % observation of a specific number of interactions in the electrolyte is subtracted from those % observations in pure water. Thus positive values indicate an increase in that environment relative to the bulk water, while negative values present a decrease in observation. Pertaining to the primary solvation shell of individual H₂O, two aspects can be considered: the distribution of hydrogen bonds, and the total

number of species in the shell (edges to the central vertex). Fig. 3A presents the change in the H-bond distribution of water between 1 and 10 M NaNO₃ relative to pure TIP3P/Ew water. As the ionic strength increases the number of waters with 3 and 4 hydrogen bond decreases while at the same time the number of waters with 1 and 2 hydrogen bond increases. As observed in prior work, the H-bonds in the primary solvation shell become replaced with ion-dipole interactions involving Na⁺ and NO₃⁻. [1] The changes in the total number of interactions about an individual water, which accounts for both ion-dipole and H-bonding is much more interesting and generally not discussed. As presented in Fig. 3B, an average increase in the first solvation shell interactions is observed relative to pure water, with positive values for solvation environments with 4 - 5 edges to the central water vertex. To further investigate the nature of the solvation about water, the dominant composition of the first solvation shells was identified. More than 55 different solvation species were identified, however most only contribute a small percentage to the overall ensemble. Those that are observed more than 5% of the time during the course of the simulation are illustrated in Fig. 4.

The change in solvation environments about water is gradual and initially consists of the replacement of H₂O in the first solvation shell with either Na⁺ or NO₃⁻; no preference of the ion is observed (recall however that only the closest contacts between H₂O and NO₃⁻ are being monitored – see Computational Methods). At 1 M NaNO₃ these **H₂O(H₂O)₂₋₃(Na⁺)** and **H₂O(H₂O)₂₋₃(NO₃⁻)** exist only 1% of the time in the simulation. As the ionic strength is increased, the range of environments with varying numbers of Na⁺ and NO₃⁻ is also enhanced. The relative concentration of **H₂O(H₂O)₂₋₃(Na⁺)** and

$\mathbf{H_2O(H_2O)_{2-3}(NO_3^-)}$ increases and species where both the cation and anion are in the first solvation shell of water begin to be observed. The 10 M NaNO_3 solution exhibits the broadest range of solvation environments involving both cation and anion, including $\mathbf{(H_2O)(H_2O)(NO_3^-)(Na^+)_2}$ and $\mathbf{(H_2O)(H_2O)(NO_3^-)_2(Na^+)}$, which are observed ~10% of the time. Necessarily, the replacement of solvating waters with either cations or anions means an overall decrease in the average number H-bonds to H_2O . At 10 M NaNO_3 , the number of water molecules with 3 and 4 H-bonds is only 5%.

Fig. 3. (A) Change in the % observation of waters with different number of hydrogen bonds within the first solvation shell, n_{HB} , as a function of aqueous NaNO_3 concentration, from 1 – 10 M NaNO_3 . The average number of hydrogen bonds, $\langle n_{\text{HB}} \rangle$, is presented for each concentration. (B) Change in the percent observation of the total number of species in the first solvation shell of water, $n_{1\text{st-shell}}$, characterized by both hydrogen bond and ion-dipole interactions, within the same concentration regime. The average number of 1st shell coordination numbers, $\langle n_{1\text{st-shell}} \rangle$, is presented for each concentration.

Fig. 4. Distribution of the primary solvation environments about individual H_2O as a function of NaNO_3 concentration from 1 – 10 M. Only those environments observed more than 5% of the time are presented, using the convention $(\text{H}_2\text{O})(\text{H}_2\text{O})_n(\text{NO}_3^-)_x(\text{Na}^+)_y$, wherein the H_2O in bold is the central molecule.

These data are in good agreement with previous studies of the ultrafast optical Kerr effect and dielectric constant which have indicated that the static dielectric constant decreases by a factor of 2.9 as a function of MgCl_2 concentration (0 – 5 M).[57, 58] That result was attributed to the effective “removal” (or immobilization) of water molecules from the bulk due to cation solvation,[59] however we note that here species involving the anion in the first solvation shell are also observed and quantified.

Given that both cations and anions are observed, sometimes simultaneously, in the first solvation shell of water, the specific formation of contact ion-pairs (defined by the direct interaction of Na^+ and NO_3^-) and clusters of ions was also examined. As

observed in Fig. 5 at 1 M NaNO_3 only 2% of all ions within the simulation participate in a contact ion-pair. This agrees well with combined MD and neutron diffraction studies of CsNO_3 at approximately the same molarity.[60] As the concentration of ions increases so too the ion-pairs, with 21% of all ions participating in an ion-pair in the 10 M solution. Larger clusters of ions are also observed, however appreciable concentrations of these are only observed in the 10 M NaNO_3 . There, 8% of all ions present exist within a cluster consisting of three ions, with 4% and 2% of all ions participating in clusters of four and five ions, respectively. These results are comparable to previous combined diffraction and MD studies of aqueous NaNO_3 between 1.9 and 7.6 M,[61] which focused upon the RDF's between respective ions and H_2O , wherein a build-up of the ion-pairs was observed.

The contact ion-pair and cluster species are reflected in a detailed analysis of the primary solvation environments about individual ions (cation or anion) in solution, where more than 360 configurations have been distinguished. Those that are observed more than 5% of the time during the course of the simulation are illustrated in Fig. 6 for NO_3^- . As discussed in the Computational Methods, the current analysis of the solvation environment about NO_3^- focuses solely on the closest $\text{NO}_3^- \dots \text{H}_2\text{O}$ contacts. In this case, nitrates solvated by 7 - 8 waters are the most abundant species irrespective of ionic strength. The contact ion-pairs are evident in this first solvation shell analysis, as well as the growth of these ion-pairs and the clusters containing three total ions as the total ionic strength is increased.

Fig. 5. Out of all ions present in each system, the percent that participate in ion-cluster formation associated with different cluster sizes, as a function of total concentration of NaNO_3 . A contact ion-pair is defined by a cluster consisting of only 2 ions.

Fig. 6. Distribution of the primary solvation environments $(\text{NO}_3^-)(\text{H}_2\text{O})_n(\text{NO}_3^-)_x(\text{Na}^+)_y$ about individual NO_3^- observed more than 5% of the time as a function of NaNO_3 concentration, wherein the NO_3^- in bold is the central molecule.

3.2 $(\text{NaNO}_3)_{\text{aq}}:n\text{-hexane}$ Systems

The analogous series of analyses have been performed for the same ionic strengths in the biphasic $\text{NaNO}_3(\text{aq}):n\text{-hexane}$ system, however “mesoscopic” interfacial properties that include the orientational profile of both water and $n\text{-hexane}$, as well as interfacial tension and width have also been determined. In prior work, vibrational sum frequency generation has suggested that mole fractions of NaNO_3 between 0.01 and 0.2 modifies the first layer of surface water molecules compared to neat water.[7] However, the detailed structure (e.g., location and orientational distribution) of interfacial water molecules and ions has not been examined in liquid:liquid systems. In order to quantify the role of NaNO_3 ions upon interfacial properties, the average number of ions within the two layers, B_{aq} and A_{aq} , were first determined. Recall that A_{aq} is the 10 Å wide layer immediately at the interface (starting at the Gibbs dividing surface of water, $z_0 = 30$ Å), while B_{aq} is defined by the 10 Å layer adjacent to A_{aq} but in the bulk (see Computational Methods and Fig. 1). Interestingly, the relative concentration of ions in the interfacial layer, A_{aq} , is approximately half that of the bulk layer B_{aq} in the 1 - 5 M solutions. In the 10 M solution the concentration of interfacial ions is still lower than in the bulk layer, however by only ~20%. While initial studies produced conflicting reports regarding the propensity of nitrate ions at the water:vapor interface,[62-64] the most recent work agrees that the majority of nitrate ions exist below the vapor surface of solution over a wide range of ion concentrations.[10, 65, 66]

Table 3

Average number of anions and cations present in the layers A_{aq} and B_{aq} (see Fig. 1), along with the total molarity of aqueous NaNO_3 in biphasic $(\text{NaNO}_3)_{aq}:n\text{-hexane}$.

$[\text{NaNO}_3]$	$\langle \text{NO}_3^- \rangle_{B_{aq}}$	$\langle \text{Na}^+ \rangle_{B_{aq}}$	$\langle \text{NO}_3^- \rangle_{A_{aq}}$	$\langle \text{Na}^+ \rangle_{A_{aq}}$
1M	7.29 ± 1.04	7.29 ± 0.42	4.03 ± 0.31	4.19 ± 0.18
3M	18.34 ± 0.25	18.39 ± 0.75	11.99 ± 0.51	12.16 ± 1.03
5M	29.22 ± 0.17	29.19 ± 0.25	23.10 ± 0.92	23.24 ± 1.10
10M	51.56 ± 0.64	52.63 ± 0.19	49.45 ± 0.45	48.92 ± 0.40

Despite the depressed ion concentration at the interface relative to the bulk, the affect of the interfacial ions upon the “mesoscale” interfacial properties of interfacial tension and width is substantial when a high enough bulk molarity is reached. As indicated in Table 4, the calculated surface tension of the neat water:*n*-hexane interface, taken from our recent study in reference 17, is in good agreement with prior experimental and theoretical work.[25-27] As the $[\text{NaNO}_3]$ increases, the calculated interfacial tension increases slowly up to 5M NaNO_3 , then nearly doubles between the 5 M to 10 M. This is the same trend, but less pronounced, than that in the measured surface tension at the $\text{NaNO}_{3(aq)}:\text{vapor}$ interface as a function of NaNO_3 molarity.[10] In that work, the surface tension increased from 1.8 dyne/cm at 1.5 M to 8.8 dyne/cm at 8.5 M NaNO_3 . [10] These observations also follow trends observed at the vapor interface with other ionic solutions.[67, 68] Interestingly, chemical intuition would imply that increased interfacial tension would inhibit transport of a solute across the phase boundary, yet this is the opposite of how ionic strength is generally employed in solvent extraction strategies. There, ionic strength typically increases the migration of a solute across the phase boundary,[12-14] though it may do so through a variety of mechanisms (including complexation of the metal solute).

Table 4

Interfacial tension, γ_e , and thickness, w_e , of the pure water:*n*-hexane system as well as $\text{NaNO}_3(\text{aq})$:*n*-hexane from 1 – 10 M NaNO_3 . The 0 M data is taken from our recent work,[17] using the same force fields and simulation protocol.

NaNO_3	γ_e (dyne/cm)	w_e (Å)
0 M	46.3 (43.9[27], 50.0[25, 26])	1.37
1 M	42.05 ± 1.99	1.25 ± 0.03
3 M	45.37 ± 0.32	1.20 ± 0.004
5 M	49.63 ± 0.88	1.15 ± 0.01
10 M	83.55 ± 0.19	0.89 ± 0.001

The changes in ion concentration at the interface also have a marked impact upon the orientation of water. It has been shown previously that water exhibits a bimodal orientational profile[69, 70] at the aqueous interface with hydrocarbon solvents. While this behavior is observed in 1 M sodium nitrate, as the concentration increases the number of alternating orientational layers of water increases (Fig. 7A). This agrees with prior observations at the $(\text{NaNO}_3)_{\text{aq}}$:vapor interface,[10] though the multimodal behavior is more pronounced. The changes in orientational profile are likely related to the oscillations or layering of the ions that is observed in the density profile (Figure 2, and S7), however this is beyond the scope of the current work. Interestingly, the orientational profile of the *n*-hexane is also perturbed in the presence of the electrolyte at high NaNO_3 concentration. As observed in Fig. 7B, at the neat water interface, interfacial *n*-hexane immediately in contact with water at $z = 30$ Å preferentially adopts an orientation perpendicular to the interface ($S_z = -0.43$). However, the depth of the peak of the orientational order parameter of *n*-hexane at $z = 30$ Å decreases from -0.43 in the neat water interface to -0.35 in the 10 M NaNO_3 binary solution. This indicates a decrease in population of *n*-hexane molecules that are oriented perpendicular to the interface, or an

enhancement of parallel oriented *n*-hexane molecules. Such an orientational change may be related to the increase in the interfacial tension, which almost doubles in the 10 M NaNO_3 solution relative to the neat water:*n*-hexane binary system.

Fig. 7. (A) The orientational order parameter of H_2O and (B) the orientational order parameter of C_6H_{14} as a function of NaNO_3 concentration. The 0 M data is taken from reference 17.

In addition to the orientational features of the two solvents, it is useful to examine the local intermolecular interactions. Recall that in the bulk electrolyte, as the concentration of ions increased, the number of H-bonds per H_2O decreased but the overall connectivity number of intermolecular interactions per H_2O increased as the ions replaced water in the first solvation shell of individual water molecules. In the biphasic systems, similar behavior is observed, however because of the decreased ion concentration at the interface a scenario develops wherein the interfacial water actually has more hydrogen bonds than in the bulk. This is demonstrated in Fig. 8, where the hydrogen bond distribution is compared between the A_{aq} and B_{aq} layers. The B_{aq} layer has the same H-bond distribution as the bulk solution and thus the change in hydrogen bonding is demonstrated by subtracting the B_{aq} H-bond distribution from the A_{aq} distribution. Negative numbers then indicate a decrease in that particular H-bond number in A_{aq} , while a positive number indicates an increase in that H-bond coordination environment. Clearly, in Fig. 8 there is a higher concentration of waters with 3 – 4 H-bonds in the interfacial A_{aq} layer relative to the bulk as $[\text{NaNO}_3]$ is increased.

Fig. 8. Change in the % observation of H₂O with different number of hydrogen bonds, n_{HB} , within the first solvation shell of water in the A_{aq} interfacial layer relative to the B_{aq} layer, which has the bulk hydrogen bond distribution, as a function of aqueous NaNO₃ concentration, from 1 – 10 M. Negative numbers indicate a decrease in that particular H-bond number in A_{aq} relative to B_{aq} while a positive number indicates an increase in that H-bond coordination environment.

From the perspective of the primary solvation environments about individual water molecules in solution, more than 81 configurations were distinguished. Those that are observed more than 5% of the time during the course of the simulation are plotted in Fig. S5 and Table S4 in *Supplementary Information*. The solvation species of water in A_{aq} are very similar to those of the bulk solution at the same effective molarity of NaNO₃ (i.e. there is a depressed ion concentration in the interfacial region and thus you must compare to a comparable molarity in the bulk solutions). Because of the lower interfacial ion concentration, the only solvation environments about water observed in significant

quantity are those with a single cation or anion present (e.g. $\text{H}_2\text{O}(\text{H}_2\text{O})_3(\text{NO}_3^-)$, and $\text{H}_2\text{O}(\text{H}_2\text{O})_3(\text{Na}^+)$). Of course, for the waters immediately in contact with *n*-hexane, solvation environments with the C_6H_{14} in the first solvation shell are also observed (Fig. S5 and Table S4 in *Supplementary Information*), however the total number of H_2O in direct contact with *n*-hexane is much smaller than the number of H_2O in the A_{aq} layer and thus the concentration of the solvation environments with hexane in the first solvation shell is negligibly small.

The information about ion-concentration, hydrogen bonding and the solvation environments of water necessarily imply that the extent of the Na-NO_3 ion pairing will be decreased at the interface relative to the bulk. This is demonstrated in Fig. 9, which plots the ion-pair/cluster size distribution of the A_{aq} layer minus that observed in the B_{aq} layer. At all molarities there is a decrease in ion-pairing and ion-cluster formation in the A_{aq} region.

Fig. 9. Change in the % observation of ion-pairs and ion clusters of different sizes observed in the interfacial layer A_{aq} relative to the bulk layer B_{aq} , obtained by subtracting the cluster size distribution of B_{aq} from A_{aq} . A contact ion-pair is defined by a cluster consisting of only 2 ions.

3.3 Microsolvation Processes at the $(NaNO_3)_{aq}:n\text{-hexane}$ Interface

Solvent molecules at the interface with an immiscible co-solvent can experience a variety of solvation environments. Partial solvation by the co-solvent is a common occurrence as the individual molecules come into direct contact with the co-solvent and partially diffuse through the interfacial region. Based upon prior density functional theory calculations and also the distribution of solvation environments observed, partial solvation of water by *n*-hexane occurs when there are between 1 and 5 *n*-hexane molecules. More than this number of *n*-hexane constitutes a completely microsolvated structure, wherein water is temporarily embedded within the *n*-hexane solvent. Partial

solvation of *n*-hexane by water occurs when there are < 20 water molecules, with more than 20 H₂O necessary to form a completely microsolvated *n*-hexane.[17, 71] Unlike partial solvation, microsolvation is a rare event, however our prior work has demonstrated that solutes at the interface can alter microsolvation processes and thus presumably influence interfacial permeability. Certain amphiphilic molecules (e.g. tributyl phosphate) have been shown to increase microsolvation of *n*-hexane in water,[17] which in turn increases the concentration of *n*-hexane in its immiscible co-solvent. The relationship between interfacial tension and phase dependent concentrations has been extensively studied at liquid:air interfaces (in this case the concentration is the vapor pressure above the interface). Examples include the Kelvin equation and its variants.[18, 19] Yet to our knowledge, no rigorous theory has explored the equilibrium concentrations of immiscible co-solvents at liquid:liquid phase boundaries as it pertains to the interfacial tension. Given the high non-ideality of these solutions, such a theory may never exist, however there is utility in empirical studies of this behavior. The concentrations of each co-solvent in their respective immiscible phase partners will be dictated by the microsolvation reactions at the phase boundary. In our prior work it was presumed that the enhanced microsolvation of *n*-hexane in the presence of amphiphilic solutes was related to two concurrent observations: 1) a change in conformation of the solute as it traversed the phase boundary, 2) an increase in the concentration of perpendicularly arranged *n*-hexane molecules in subsequent solvation shells about the solute as a result of the conformational change.[17] In this work we probe whether ionic strength influences the microsolvation processes of water and *n*-hexane through a similar mechanism.

Let us first consider the microsolvation of water and *n*-hexane in the neat biphasic interface, 0 M NaNO₃.^[17] As observed in Fig. 7, *n*-hexane has high concentrations of molecules that are oriented with a perpendicular alignment to the interface which leads to an S_z close to -0.5 and as the ionic strength increases a decrease in the population of perpendicularly oriented *n*-hexane is observed (S_z becomes less negative). Yet the orientational change does not appear to alter the probability of microsolvation of *n*-hexane, which is predicted constant as a function of aqueous ionic strength. Fig. S6 in *Supplementary Information*, plots the extent of partial solvation of *n*-hexane by water at 10 M NaNO₃ relative to the neat water interface. There, less than a 0.05% change in the microsolvation probability of *n*-hexane by water as a function of [NaNO₃] is observed. Equivalent results are obtained for the change in the microsolvation of H₂O by *n*-hexane. One would anticipate that the change in orientation of *n*-hexane, in combination with the increase in interfacial tension, would decrease the concentration of the co-solvents in their immiscible phase partner by decreasing the probability of microsolvation reactions. While this does not appear to be the case, it is important to keep in mind that microsolvation is already an incredibly rare event and as such it may be that significantly longer simulation times are required in order to accumulate statistics that show any decrease in microsolvation probability. Nevertheless, if any such correlation exists it is thus very low and cannot be the sole source of altered transport properties within solvent extraction systems.

A complementary discussion is to enquire about the ability of Na⁺ and NO₃⁻ to interact with *n*-hexane and potentially migrates into the organic phase. As observed in

Table S5 in *Supplementary Information*, the actual concentration of these ions on the organic side of the phase boundary is on average zero. Further, if the total number of instances that nitrate penetrates the organic phase are counted, and normalized according to the number of nitrate in the A_{aq} layer it is apparent that the probability of nitrate temporarily entering *n*-hexane is indeed much smaller than the probability of water that migrates into *n*-hexane.

4. Conclusions

The study of sodium nitrate concentration, or electrolyte strength broadly, upon liquid:liquid interfacial properties is relatively obscure. However, it is highly relevant to a number of industrial processes, where ionic strength can enhance the distribution of solutes across the aqueous:organic phase boundary. In the case of the PUREX process changes in nitrate concentration in the aqueous phase can alter the distribution of metal-ligand complexes through a variety of potential mechanisms that span everything from nitrate binding as a complexant to the metal to the impact of the electrolyte upon the hydrogen bond network properties of water at the interface and perturbation of interfacial structure and dynamics. The current work examines the interfacial structure and microsolvation process of the biphasic system $(\text{NaNO}_3)_{aq}:n\text{-hexane}$ from 0 – 10 M NaNO_3 .

The extent of ion-pairing was quantified, alongside the primary solvation environments of both water and ions. Ion concentration was found to be depressed in the interfacial region relative to the bulk, and as such there is less likelihood of the formation

of contact ion-pairs or ion-clusters at the interface. The ion concentration causes enhanced multimodal orientation of water in successive layers from the interface. At 10 M NaNO_3 enough ions are present at the interface to severely perturb the average mesoscopic interfacial properties of interfacial width and tension. In the neat water:*n*-hexane interface the interfacial tension is 46.3 dyne/cm with an interfacial width of 1.37 Å. However large ion concentrations at the interface can double the interfacial tension (83.55 dyne/cm at 10 M NaNO_3) and dramatically contract the interfacial width (going to 0.89 Å at 10 M NaNO_3). The sharp change in the average mesoscopic scale properties of the interface does appear to correlate with the change in orientation of *n*-hexane, where the population of *n*-hexanes that are perpendicular to the interface decreases. Yet, the combined orientational changes and enhancement of interfacial tension do not yield a statistical decrease in the probability of microsolvation of water or *n*-hexane. While there may indeed be no relationship between the microsolvation processes and interfacial tension, the need for longer simulation times to yield more accurate statistics cannot be ruled out due to the rarity of the microsolvation reactions. Based upon these data, the influence of electrolyte concentration upon the transport properties across the interface do not appear to be related to the perturbation imparted by the electrolyte upon the interfacial properties themselves.

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