Supporting Information for: Interfacial heterogeneity is essential to water extraction into organic solvents

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Molecular Structure and Force Fields

The molecular structure of tri-*n*-butyl phosphate (TBP) is shown in Figure 1. The MD study of TBP is extensive, including the development of several different force fields with parameters empirically fit to various physicochemical properties and under a range of conditions, including pure TBP solutions,^{1–5} binary mixtures with organic solvents^{2–8} and interfacial TBP/alkane/aqueous systems.^{9–12} TBP is known to adsorb to at the interface with its dipole, aligned with the P=O bond of the phosphate head group, oriented towards the aqueous phase.¹³ It has further been predicted that TBP undergoes a significant conformational change in the interfacial region,¹⁴ and prior studies have described the dynamic process by which TBP extracts water molecules from the aqueous/organic interface into the bulk organic.⁹

Numerous studies have tested, optimized and compared classical non-polarizable TBP force fields for use in a variety of chemical environments.^{1–5} Khomami and coworkers optimized AMBER force field for various partial atomic charges sets and charge scaling¹ with the

alkyl tail carbon and hydrogen Lennard-Jones (L-J) parameters taking values from the OPLS force field for pure TBP and TBP/n-alkane solutions. For simulation of the water/(n-hexane TBP) system, Khomami and coworkers found that a 0.9 scaling factor to the atomic charges of a DFT-derived charge set for TBP accurately reproduced the experimentally determined concentration of water extracted by TBP into the organic phase.⁹

The charges for the TBP and *n*-hexane molecules, depicted in Figures 2 and 3 with the AMBER force field names for the different atoms types, are given in Table 1. The generalized AMBER Force Field (GAFF)¹⁵ with modification to the L-J potentials developed for linear alkanes by Vo *et al.*³ is implemented for *n*-hexane. The TBP force field is implemented from the modified AMBER potentials described by Cui *et al.*¹ where parameters for the L-J, bond, angle and torsion potentials are reported. Water is modeled with the TIP4P potential.¹⁶ Molecular dynamics simulations were conducted with the GROMACS 5.1 software package^{17,18} using periodic boundary conditions and a leap-frog Verlet integrator with a 2 fs time step. A 12 Å cutoff was used for Lennard-Jones (L-J) and short range electrostatic interactions with Particle-mesh Ewald summation implemented for long range electrostatics. The LINCS algorithm was used to constraining hydrogen-containing bonds for all molecules. Each system was equilibrated for 1 ns in the NPT ensemble with pressure set to 1 bar with a 2 ps coupling time constant with the Berendsen barostat and temperature to 300 K with a 0.4 ps coupling time constant using the velocity rescale thermostat. This was followed by 24 ns of further equilibration in the NPT ensemble with the Parinello-Rahman barostat and Nosé-Hoover thermostat to allow for migration of surfactant to the interface and equilibration of the interfacial TBP density. This was followed by 25 ns of simulation in the NVT ensemble with the Nosé-Hoover thermostat with the final 15 ns sampled for analysis at 20 ps intervals.



Figure 1: The molecular structure of tri-*n*-butyl phosphate.



Figure 2: The AMBER force field atom names for TBP.



Figure 3: The AMBER force field atom names for n-hexane.

Atom	Charge $[e]$
O2	-0.72747
Р	1.44864
OS	-0.55422
CT_1 (TBP)	0.32733
CT_2 (TBP)	0.02340
CT_3 (TBP)	0.10917
CT_4 (TBP)	-0.02934
HC_1 (TBP)	-0.02349
HC_2 (TBP)	0.00063
HC_3 (TBP)	-0.03483
HC_4 (TBP)	-0.00045
CT_1 (<i>n</i> -hexane)	-0.08890
CT_2 (<i>n</i> -hexane)	-0.07520
CT_3 (<i>n</i> -hexane)	-0.07580
HC_1 (<i>n</i> -hexane)	0.03150
HC_2 (<i>n</i> -hexane)	0.03620
HC_3 (<i>n</i> -hexane)	0.03650

Table 1: Charges for the TBP and *n*-hexane atoms.

Simulation Systems

System compositions and simulation periodic box sizes in Table 2. The total number of TBP in the simulation per interface is half of the total value as the periodic system contains two interfaces. The largest TBP concentration, after migration of TBP to the interface, results in a bulk TBP concentration of roughly 30%, a typical concentration implemented in the Plutonium and Uranium Reduction EXtraction (PUREX) process. A water/n-hexane interfacial system without TBP is also simulated for reference. Initial configurations were generated with Packmol¹⁹ and energy minimized with a steepest descent algorithm. Simulations boxes were generated as adjacent water and oil phases with the water phase centered along the z-dimension and the n-hexane/TBP phase wraps through the z-dimension periodic boundary. For systems with TBP, the TBP molecules were initially randomly dispersed within the n-hexane phase before migration to the interface during equilibration.

Water	<i>n</i> -Hexane	TBP	Dimensions
			$\mathbf{X} \times \mathbf{Y} \times \mathbf{Z} \ [\text{\AA}]$
3205	586	0	$41.40 \times 41.40 \times 132.49$
3205	586	2	$40.96 \times 40.96 \times 136.55$
3205	586	10	$41.11 \times 41.11 \times 137.04$
3205	586	20	$41.36 \times 41.36 \times 137.88$
3205	586	42	$42.42 \times 42.42 \times 136.09$
3205	586	56	$42.20 \times 42.20 \times 140.66$
3205	586	84	$42.72 \times 42.72 \times 142.41$
3205	381	186	$43.40 \times 43.40 \times 138.88$

Table 2: The compositions and simulation periodic unit cell box sizes for the systems studied are provided here.

Hydrogen Bonding

The ChemNetworks software package²⁰ was used to identify hydrogen bonds between water and TBP molecules. Using a graph theoretic approach, water and TBP molecules are treated as vertices with an edge connecting any two vertices if there exists a hydrogen bond between those molecules. Hydrogen bonds were defined by an oxygen-oxygen distance and an H-O...O angle cutoff. For water-water hydrogen bonds, an oxygen-oxygen distance of 3.5 Å was employed with a 30° angle cutoff. For TBP-water hydrogen bonds, a 3.5 Å distance cutoff was used with 45° angle cutoff.

ITIM Implementation

In the ITIM algorithm,²¹ a probe sphere scans the interfacial surface and records exposed molecules from each point in a grid in the xy plane. Subsequent water layers were similarly determined after removing the previous interfacial molecules and rerunning the ITIM algorithm on the newly exposed water surface. Herein, the probe sphere radius was set to 1.5 Å with a grid spacing of 0.2 Å. To avoid counting water hydrogen bonded to TBP in the bulk organic phase, water molecules with z-positions outside of the 35-105 Årange were omitted from the ITIM search. That range was chosen from the density profiles of water and TBP, as

shown in Figure 6. For consistency with the the way in which water molecules were chosen to be included in the interfacial water identification, TBP were counted as interfacial if their phosphoryl oxygen atom fell within the that z-position range. The interfacial widths for each system were computed from the the full width at half maximum of a Gaussian function fit to the time average density profile of the interfacial water layer. The interfacial layer distributions were well described by the Gaussian fit, as shown in Figure 4 for the 42 total TBP system.



Figure 4: The Gaussian fit to the interfacial water density profile for the 42 TBP system which is used to compute the interfacial width.

Comparison of TBP Force Fields

To demonstrate that the conclusions of this study are independent of the choice of TBP force field, we compare the force field used in this study⁹ (AMBER 90% charge scaling) to two others developed in the literature with higher⁵ (GAFF) and lower¹ (AMBER 70% charge scaling) hydrophilicity. While the interfacial width and number of TBP adsorbed at the interface are, as expected, affected by the force field hydrophilicity, the trend with adsorbed TBP concentration in the interfacial width and connectivity of the water in the water

bridged TBP dimer are consistent between force fields, as shown in Figure 5. The significant underprediction of induced interfacial roughness by the 70% charge scaled AMBER force field is consistent with the reported lack of water extracted for this reduced hydrophilicity model.⁹ These data indicate that the mechanism of water extraction by TBP, through creating interfacial roughness and separating directly interfacial water from the bulk through the the water bridged TBP dimer structure, is not dependent on the force field, although the degree of its effectiveness at doing so is directly affected by the hydrophilicity of the surfactant.



Figure 5: Left panel: The interfacial width, as a function of the number of TBP adsorbed at the interface, is plotted for three TBP force fields—the one implemented in the this study (AMBER 90% charge scaling⁹) and two others which are expected to over- (GAFF⁵) and under-predict (AMBER 70% charge scaling¹) the impact of adsorption on interfacial roughness due to varying hydrophilicity. Right panel: The change to the water-water connectivity of the water in the water bridged TBP dimer within the directly interfacial layer (solid lines) and with the subsequent subsurface layer (dashed line) are plotted for each TBP force field.

Density Profiles and Interfacial TBP RDFs

The density profiles of each of the ternary simulation systems in this study are plotted are plotted in Figure 6. The water Gibbs dividing surface for each system is calculated as the time averaged z-position of the water density profile at half of the bulk density. The surfactant character of TBP is apparent from the high density in the interfacial region, with some degree of excess TBP in the bulk *n*-hexane phase, often forming hydrogen bonded clusters with extracted water molecules. For the lowest TBP concentration, panel A, the peak in *n*-hexane density near the interface results from the parallel orientation of the alkane combined with the center of mass determination of molecule position for the density profile. At higher concentrations, sufficient TBP is present at the interface to instead reduce the *n*-hexane density near the interfacial regions. Variations to the *n*-hexane and TBP densities in the organic phase regions of the z-position, noticeable in panels E and F, result from transient organic phase clusters of TBP with extracted water rather than variation of the actual equilibrium distribution of molecular species.

Two-dimensional RDFs plotted in the main text are generated for interfacial TBP with their positions defined by the coordinates of the phosphoryl oxygen projected onto the x-y plane. Distances between each pair of TBP are evaluated with a 0.2 Å bin size. The number of counts in each bin are then time averaged and normalized by the bin area and $(N_t - 1)/N_t$, where N_t is the number of interfacial TBP at time t, to account for the finite size effects of the simulation on the effective interfacial TBP concentration. It should be noted that the non-zero value of g(r) when r is close to 0 Å is not direct spatial overlap of the TBP phosphoryl oxygens. Rather, it results form overlap of the oxygen positions as projected onto the x-y plane for the high interfacial TBP concentrations which produce significant surface roughness such that two TBP molecules are able to occupy the same position in the x-y plane at different z-positions.

Interfacial Tension

Surface and interfacial tensions are often calculated from simulation using one of two methods: with the diagonal elements of the pressure tensor or by fitting the capillary wave



Figure 6: The TBP (green), water (red) and *n*-hexane (black) density profiles as a function of z-position are plotted for the 2, 10, 20, 42, 56, 84 and 186 total TBP systems in that order in panels A-G.

fluctuations to the density profile.²² In the pressure method, the interfacial tension, γ , is defined as the integral over the z dimension with a box length of L_z

$$\gamma = \frac{1}{N_{int}} \int_0^{L_z} \left\langle P_{ZZ} - \frac{P_{XX} + P_{YY}}{2} \right\rangle dz \tag{1}$$

where P_{ZZ} , P_{XX} and P_{YY} are the diagonal components of the pressure tensor where the interfacial normal is in the z direction and N_{int} is the number of interfaces in the periodic box. The interfacial tensions calculated in this study are done so with this method.

Capillary wave theory density profile fitting is also implemented in the literature to calculate the interfacial tension from MD simulation. In contrast to the pressure tensor method, capillary wave fitting of the water interface relies upon fitting the density profile of water to an error function with the form

$$\rho(z) = \frac{1}{2}\rho - \frac{1}{2}\operatorname{erf}\left(\frac{z - z_0}{\sqrt{2}w_c}\right)$$
(2)

where $\rho(z)$ is the density of water as a function of z position, ρ is the bulk density of water, z₀ is the Gibbs dividing surface, located at the z position corresponding to a water density equal to half its bulk value, and w_c is the width due to capillary wave fluctuations. The w_c parameter is then related to the interfacial tension by

$$w_c^2 = \frac{k_B T}{2\pi\gamma} \ln \frac{L}{l_b}.$$
(3)

Here, k_B is the Boltzmann constant, T is the temperature, L is the x and y box length and l_b is the bulk correlation length. As the bulk correlation length is not known a priori, the slope of the linear relationship between w_c^2 and $\ln(\frac{L}{l_b})$ can be obtained by varying L which then allows for direct evaluation of γ .²³ The reported γ value is the average over both interfaces in the simulation. The assumptions underlying the density fitting for the surfactant-laden systems were found to prohibit calculation of reasonable and consistent interfacial tension

values and therefore we only report values form the pressure tensor method for intefaces with TBP.

Both methods have been demonstrated as effective for water/vapor and water/organic interfaces. However, the assumptions required by these different approaches and their potential utility in obtaining accurate values is affected differently by the presence of surfactant molecules. The pressure method relies on an accurate description of the forces between particles, which define the virial from which the pressure tensor is obtained. It is therefore affected by approximations to the pairwise potentials, including the L-J and Coulmobic cut-offs used in simulation.²² Capillary wave theory attributes all fluctuations of the density at the interface to the formation of capillary waves, which is not the case for systems where surfactant adsorption significantly affects the density profiles at the interfacial region, particularly for the protrusion features resulting form TBP which are visually apparent for the higher TBP concentrations. While the pressure tensor method will slightly underestimate the interfacial tension compared to density profile fitting (giving 47.7 mN/m versus 53.4 mN/m from capillary wave fitting for the water/n-hexane interface in this study, compared to 51.4 mN/m from experiment²⁴), it is commonly applied to simulation of surfactant systems²⁵⁻²⁸ and the reported interfacial tension values in this study are reported with this method. In contrast, we found that the capillary wave fitting method was not applicable for even the moderate TBP concentrations.

Interfacial Water Hydrogen Bonding and Orientation

As discussed in the main text, adsorption of TBP at the interface impacts the hydrogen bonding character of interfacial water through reorientation of water which TBP is directly hydrogen bonded to and through distortion of the nearby water-water hydrogen bonding network in response to TBP-induced surface roughness. Details and data concerning the nature and magnitudes of these effects are discussed here. The changes of the hydrogen bond distribution of interfacial water molecules are compared to the water/*n*-hexane interface for water-water hydrogen bonding both within in the interfacial layer and with all layers is plotted in Figure 10. The hydrogen bond distribution of the water/*n*-hexane interface for each layer plotted in Figure 9, showing that by the second layer the hydrogen bonding has nearly converged to its bulk-like behavior. Interfacial water edge distributions for the water/*n*-hexane simulation are consistent with results from Sega *et al.* for a variety of water potentials.^{29,30}

Within the interfacial water layer, water's tetrahedral structure limits its ability to form more than three hydrogen bonds.³⁰ On average, we find that in the absence of TBP interfacial water forms on average about two hydrogen bonds within the interfacial layer and a single hydrogen bond with the subsurface layer. Water reoriented to hydrogen bond with a TBP molecule is often able to maintain the remaining three hydrogen bonds, with the reorientation to hydrogen bond to TBP sometimes occurring at the expense of hydrogen bonding to the subsurface water layer.

Figure 7 shows the decrease in water-water hydrogen bonding between the interfacial and second layers with increasing TBP concentration. This is shown in Figure 7 where the total number of hydrogen bonds between the interfacial layer and the first subsurface layer is plotted as a function of interfacial TBP concentration. Over the range of concentrations, the total connectivity between layers is reduced by roughly 5%. For the lower TBP concentration, Figure 10A-C shows a reduction in the total water-water hydrogen bonding of interfacial water, primarily through a transition of the 4-hydrogen bond population to 3-hydrogen bond. However, this transition was not observed for the hydrogen bonding between interfacial water. The reduction in total water connectivity therefore comes from a loss in hydrogen bonding between the interfacial and subsequent subsurface layer. Therefore, when TBP occupies water hydrogen acceptor sites, the water restructures in a way that limits loss in connectivity within the interfacial water layer at the expense of connectivity between the surface layer and the bulk. As discussed in the main text, the roughness induced by TBP enables the tetrahedral hydrogen bonding water to more readily hydrogen bond with interfacial neighbors due to their offset in the z-dimension.

The effect of TBP on water orientation is quantified with orientation profiles of the interfacial water layers are plotted in Figure 8 for each simulation system. The net orientation is defined as

$$\left\langle \sum_{i} \cos(n_z \cdot \mu_i) \right\rangle / V_{slab},$$
 (4)

where the dot product of the dipole vector of water molecule i, μ_i , is taken with the zdimension unit vector, n_z . The time averaged summation over of the dot products are divided by the slab volumes, V_{slab} , for 0.5 Å slabs in the z-dimension. Contributions to the net orientation are broken down into the opposing contribution from water hydrogen bonded to TBP and those which are not. The net orientations of this partitioning of the interfacial water population is compared to the total (not just interfacial) net orientation profile of the water/n-hexane system without TBP. The opposite orientations of water hydrogen bonded to TBP and those which are not remains consistent across the TBP concentrations.

The reason that the total hydrogen bonding of interfacial water is relatively constant despite a reduction in hydrogen bonding between layers and the significant occupation of hydrogen bond donor sites by TBP is an increase in hydrogen bonding within the interfacial layer for water which is not occupied by TBP. To investigate this, the interfacial water is partitioned into those hydrogen bonded to TBP and those which are not, as discussed above in the analysis of water orientation. Figure 11 shows the number of water per interfacial area as a function of interfacial TBP for all water (black) and water not hydrogen bonded to TBP (red). The number of water per interfacial area for the water/n-hexane interface is plotted for reference as a line. The increase in the total number of water per interfacial area as a function of TBP concentration increases significantly upon transition to the regime where interfacial roughness increases significantly. At that transition, the addition of interfacial water through creation of interfacial area outpaces the occupation of those interfacial water by TBP and the number of interfacial water not hydrogen bonded to TBP reaches a minimum value before beginning to increase. Changes to the hydrogen bond distribution for interfacial water not hydrogen bonded to TBP, compared to the reference water/n-hexane system, are plotted in Figure 12A. The addition of TBP increases the 3- and 4-hydrogen bond water populations, while depleting 1- and 2-hydrogen bond relative to the reference water/n-hexane interface. Figure 12B shows the corresponding total change in water-water hydrogen bonds per interfacial water not hydrogen bonded to TBP, which approaches a value of 0.2 for the highest TBP concentration (roughest interface) system.



Figure 7: The average number of water-water hydrogen bonds for interfacial water with water in the second layer is plotted as a function of interfacial TBP concentration.



Figure 8: The net orientation profiles of interfacial water for the 2, 10, 20, 42, 56, 84 and 186 total TBP systems are plotted in A-G. The orientation contributions are broken down into water hydrogen bonded to TBP (blue) and those that are not (red) and compared to the total net orientation of the water/n-hexane system (black dotted line).



Figure 9: The edge distributions of hydrogen bond numbers for water in the first (black squares), second (red triangles) and third (blue circles) interfacial layers for the no TBP water/n-hexane interface.

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Figure 10: The change in hydrogen bond edge distributions from the water/n-hexane interface for all hydrogen bonds of interfacial water (black squares) and hydrogen bonding within the interfacial layer (blue triangles) for 2, 10, 20, 42, 56, 84 and 186 total TBP is plotted in panels A-G.



Figure 11: The total number of water (black squares) and number of water not hydrogen bonded to TBP (red triangles), per interfacial area, is shown for different the numbers of interfacial TBP.



Figure 12: Change to the hydrogen bond distribution of (A) interfacial water not hydrogen bonded to TBP with increasing interfacial TBP concentration and (B) the change in the total number of hydrogen bonds per interfacial water not hydrogen bonded to TBP as a function of TBP concentration.

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